



## **D4.9.2: Testing report of the new equipment for off-line aerosol speciation at INFN Genova**



<b>Deliverable number:</b>	D4.9.2
<b>Work package:</b>	WP4 – Atmosphere
<b>Intermediate Objective:</b>	IO4.5
<b>Deliverable type:</b>	<input checked="" type="checkbox"/> Document, report
	<input type="checkbox"/> Websites, patent filings, videos, etc.
	<input type="checkbox"/> Other: please specify .....
<b>Dissemination level:</b>	<input checked="" type="checkbox"/> Public
	<input type="checkbox"/> Restricted
<b>Estimated delivery (bimester):</b>	B10
<b>Actual delivery date:</b>	21/06/2024
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IR0000032 – ITINERIS, Italian Integrated Environmental Research Infrastructures System - CUP B53C22002150006 (D.D. n. 130/2022)  
 Funded by EU - Next Generation EU  
 Mission 4 “Education and Research” - Component 2: “From research to business” -  
 Investment 3.1: “Fund for the realization of an integrated system of research and innovation infrastructures”

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## LIST OF ACRONYMS

**FAIR:** Findable, Accessible, Interoperable and Reusable

**ED-XRF:** Energy Dispersive X-ray Fluorescence

**SDD:** Silicon Drift Detector

**PM10:** Concentration of Particulate Matter with aerodynamic diameter up to 10  $\mu\text{m}$

## INTRODUCTION

This deliverable is prepared in the context of the ITINERIS project, within Work Package 4 that deals with the integration of Research infrastructures working in the atmospheric domain through synergistic approaches and cross boundaries developments. This deliverable reports the implementation plan of Task 4.9.2. The main objective of this task is the empowerment of ChAMBRE facility, addressing the capability of off-line typing of particulate matter with different origin and composition. In this view, the INFN-Genova unit has purchased two state-of-art instruments for off-line analyses of Particulate Matter (PM) samples (e.g: provided by PM sampling on filters and/or multi-stage impactors): an ED-XRD spectrometer (for elemental speciation of atmospheric aerosol) and a thermal-optical analyzer to measure the concentration of carbonaceous aerosols. Both the instruments have been installed and fully tested and are now completely operative at the ChAMBRE facility.

The document is structured in five different chapters.

## 1. TECHNIQUES

### 1.1 ED-XRF

The ED-XRF is a widespread and versatile technique for quantifying the elements present in a sample, and even traces thereof but with atomic number  $Z > 10$ . ED-XRF is based on the ionization of the inner atomic shells obtained by irradiating the samples with electromagnetic radiation: inner shell vacancies get promptly filled by outer shell electrons, releasing radiant energy within characteristic lines carrying a signature of the emitting atom. The ED-XRF has several advantages: it does not destroy the sample being analyzed, so the same sample can be analyzed with other techniques. It has a broad detection range, able to measure a wide range of elements (from Na to U). It requires little to no sample preparation, which saves time and reduces the potential for sample contamination. It can be used for both qualitative and quantitative analysis, offering flexibility in different types of investigations. For all these reasons, ED-XRF is one of the powerful techniques used to speciate aerosol collected on filters.

### 1.2 EC/OC THERMAL-OPTICAL ANALYSIS

The OC/EC thermal-optical analysis is a method used to determine concentrations of particulate organic carbon (OC) and elemental carbon (EC) collected on quartz fiber filters. First, the system is closed and pressurized, and then the oven is purged with helium to remove ambient air. A stepped temperature ramp is used to increase the oven temperature to 650°C, which thermally desorbs the organic compounds. The OC fraction is oxidized to CO<sub>2</sub> gas in a manganese dioxide (MnO<sub>2</sub>) oxidizing oven, and the CO<sub>2</sub> is measured using non-dispersive infrared (NDIR). The oven temperature is then reduced to 500 °C, at which point all the carbon measured represents the original OC compounds on the filter sample. What remains on the filter is the original EC as well as EC produced from thermal pyrolysis (charring) of organic compounds such as high molecular weight OC's and polymeric materials, especially from natural products. The carrier gas is then replaced by a mixture of helium and 2% oxygen. A second temperature ramp is initiated to oxidize the remaining

EC from the filter, which will be detected by NDIR. The measured total carbon (TC) of the sample is the sum of organic and elemental carbon ( $OC+EC=TC$ ).

## 2. SCIENTIFIC OBJECTIVES

The ED-XRF instrument helps determine the elements concentrations from Na to U in particulate matter. This has dual benefits. On one hand, it allows quantifying the concentration of metals reported in the new EU Directive (P9 TA-2024 0319) for ambient air quality and cleaner air for Europe, especially Pb, As, Cd, and Ni. On the other hand, certain elements in particulate matter are specific tracers of aerosol sources (such as Na and Cl from marine aerosol, Al, Si, and Ti from resuspended soil, Cu and Pb from traffic, etc.). Measuring their concentrations and studying their temporal trends on an hourly or daily basis enables retrieving the contributions of aerosol sources using receptor models. This knowledge is crucial for reducing particulate matter in the atmosphere by understanding the contribution of each aerosol source.

The EC/OC thermal-optical instrument measures the concentration of OC and EC in particulate matter collected on a quartz filter. OC and EC play a crucial role in air quality, climate change, and human health. OC is a significant component of atmospheric particles, and it is emitted from natural and anthropogenic sources, such as biomass burning, fossil fuel combustion, and biogenic emission and can be formed in the atmosphere also through chemical reactions (i.e. oxidation of VOCs). EC originates from combustion processes, such as vehicle emissions, industrial activities, and biomass burning. The EC strongly absorbs sunlight, contributing to atmospheric warming. When deposited on snow and ice, it reduces albedo, accelerating melting. Both OC and EC have a health impact; in addition, the EC is mainly concentrated in the fine particulate matter and the inhalation of fine particles can lead to respiratory issues, cardiovascular diseases, and other health problems. Thermo-optic analysis is one of the methods to measure OC and EC and an accurate measurement and analysis of them are essential for understanding its sources, impacts, and mitigating strategies.

## 3. INSTRUMENTS

### 3.1 ED-XRF INSTRUMENT

The instrument is an Epsilon 4 Air Quality manufactured by Malvern Panalytical (figure 1). It is an ED-XRF instrument with an X-ray tube with Ag anode and a maximum voltage, current and power of 50 kV 3 mA and 15 W, respectively. It mounts an SDD with a Peltier cooling and a resolution of 145 eV @ 5.9 keV. The particulate matter filters of 47 mm are allocated on an autosampler with 10 positions. Four measuring conditions (table 1) have been set to optimize the sensitivity for groups of elements. The analysis is performed in helium and air path: the helium path is used for light elements to avoid soft X-ray attenuation by air. Finally, the samples are rotated during the analysis to average the signal over a larger surface.

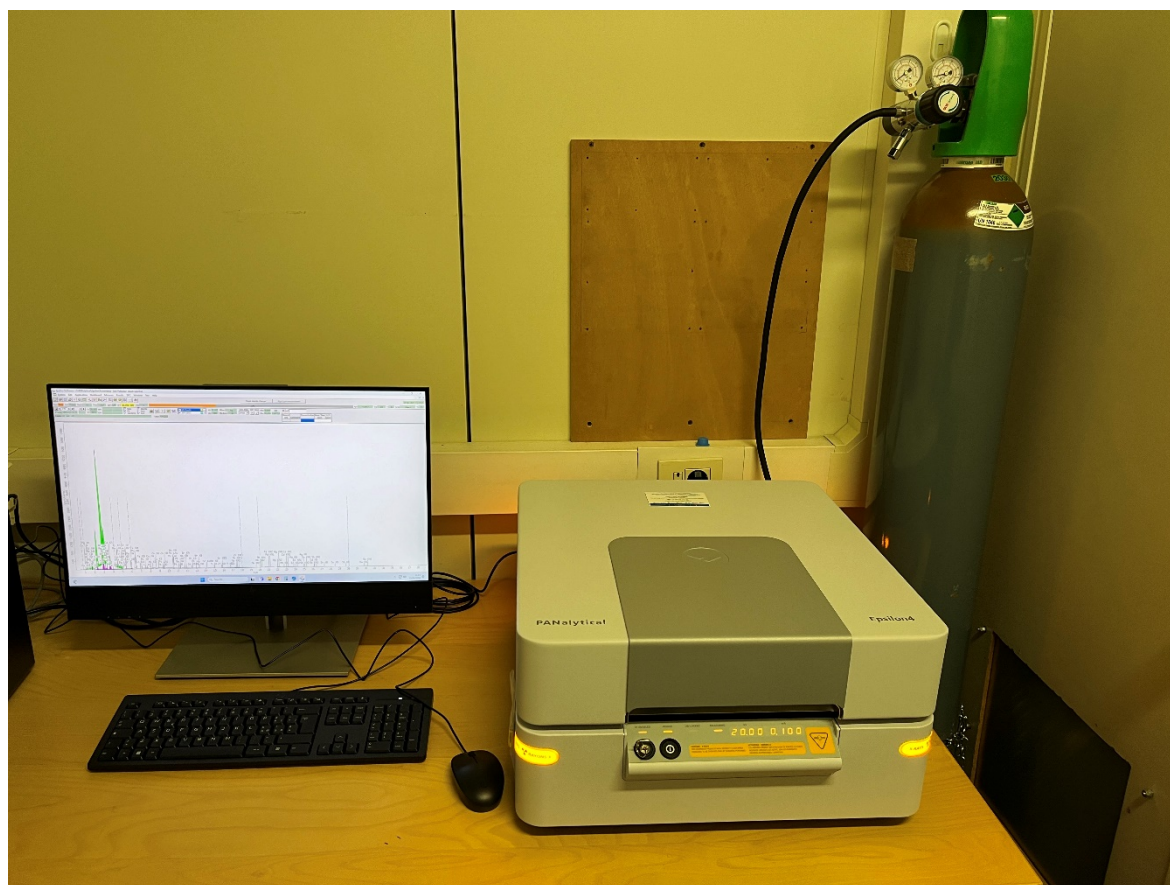


Figure 1: The Epsilon 4 spectrometer installed at the ChAMBRé facility.

Table 1: Operating conditions used on the Epsilon 4 spectrometer.

	Cond. 1	Cond. 2	Cond. 3	Cond. 4
Anode voltage (kV)	9	30	50	50
Anode current (mA)	1660	500	300	300
Primary filter	Ti	Al-50	Ag	Cu-300
Path	Helium	Helium	Air	Air
Measurement time (s.)	450	450	450	450
Elements	Na → Si	P → V; Ba, La	Cr → Mo; Pt, Pb	Rh, Pd, Cd, In, Sn, Sb

The minimum detection limits (MDL) of all elements, defined as  $2 \cdot (N_b)^{0.5}$  where  $N_b$  is the number of background counts observed at a specific energy of X-ray fluorescence, are reported in Figure 2.

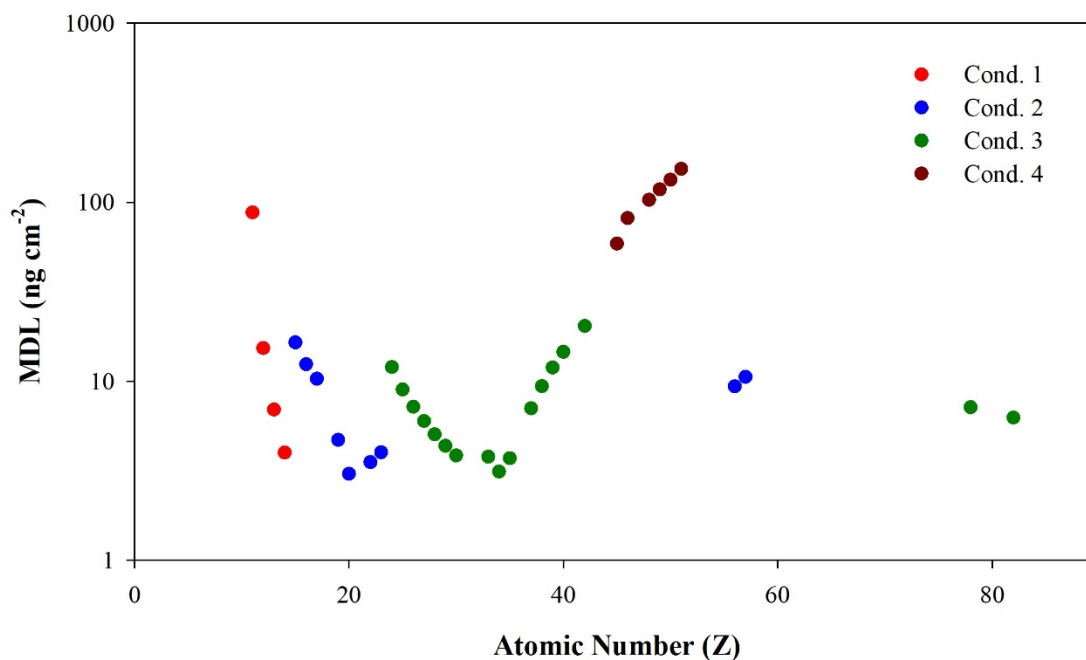


Figure 2: Minimum detection limits for the Epsilon 4 spectrometer obtained under the operating conditions listed in table 1.

### 3.2 LAB OC/EC AEROSOL ANALYZER

The instrument is a LAB OC/EC manufactured by Sunset Laboratory INC (figure 1). This instrument uses a proven thermal-optical method to analyze OC-EC aerosols collected on quartz filters. In the Lab OC-EC Aerosol Analyzer, samples are thermally desorbed from the filter medium under an inert helium atmosphere followed by an oxidizing atmosphere using controlled heating ramps. A flame ionization detector (FID) is used to monitor the analysis.

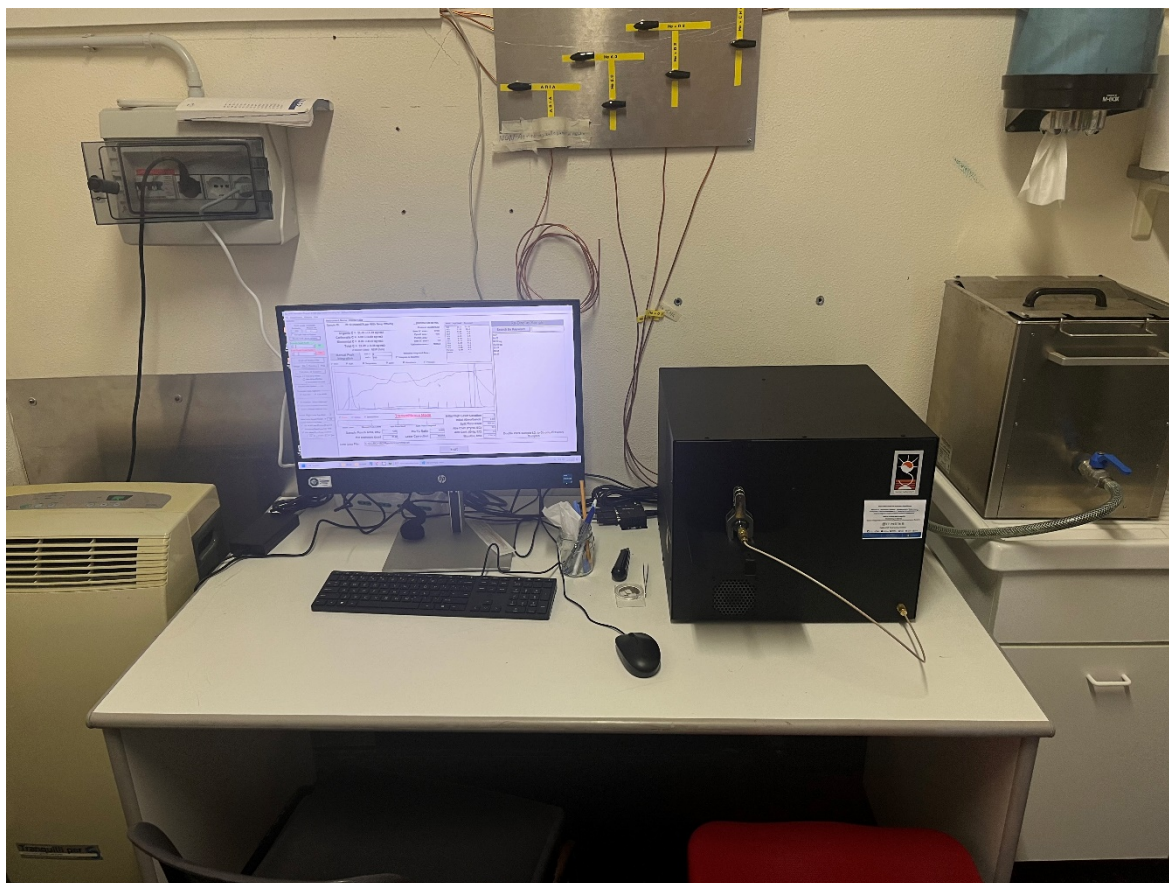


Figure 3: The LAB OC/EC Analyzer installed at the ChAMBRé facility.

## 4. TESTS AND RESULTS

### 4.1 ED-XRF EPSILON 4

The elemental thickness [ $\mu\text{g cm}^{-2}$ ] in the samples is obtained by comparing the filter yields with a sensitivity curve (figure 2) obtained by measuring a set of thin standards certified within 5% (Micromatter Inc.). The standards were measured with the 4 conditions listed above.

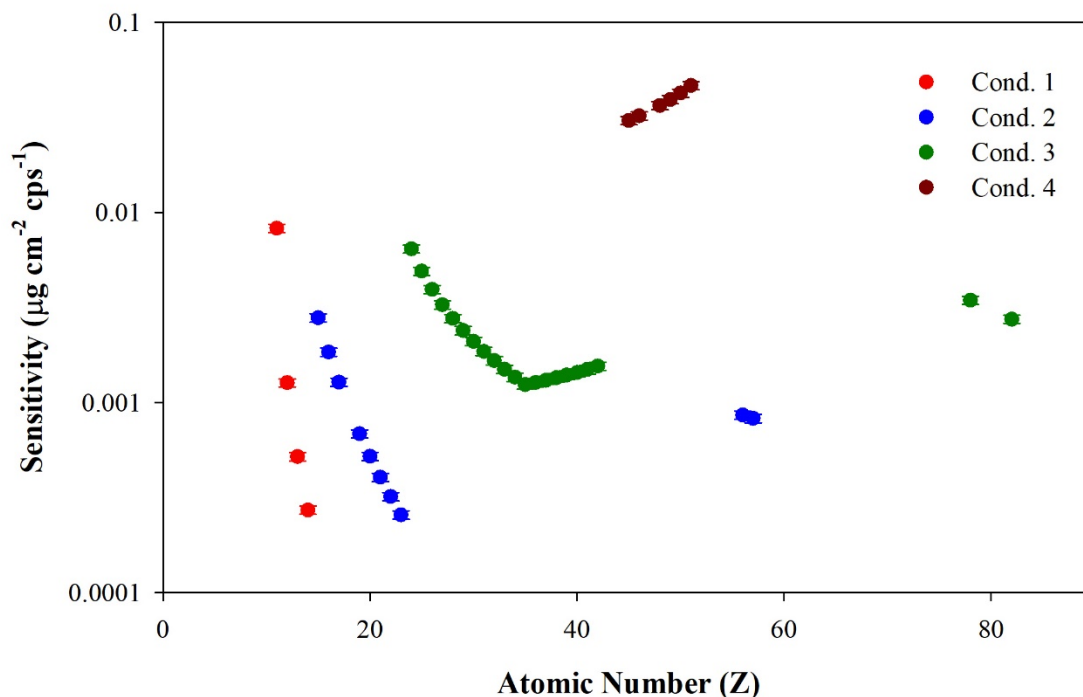
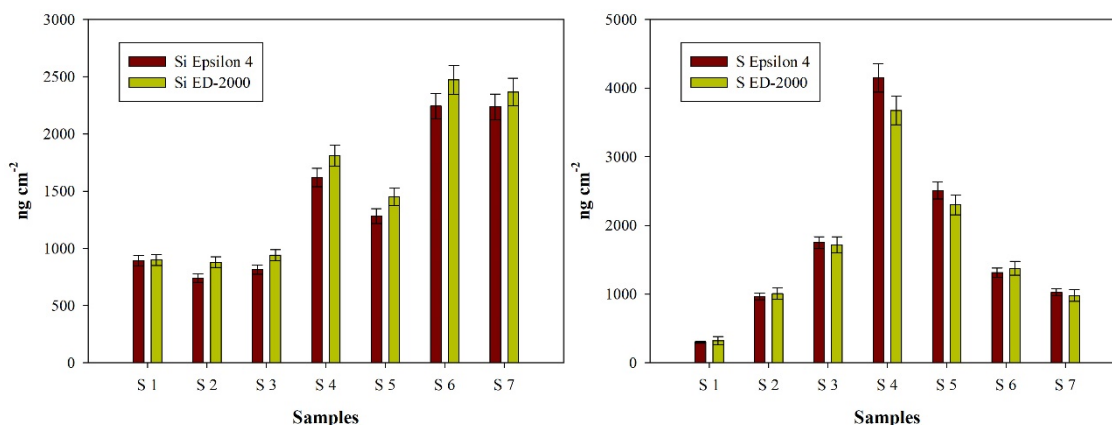


Figure 4: Sensitivity response of Epsilon 4 spectrometer obtained with elemental standards in the four exciting conditions.

Finally, we compared the results of elemental concentrations on seven PM10 filters obtained with Epsilon 4 and one ED-XRF spectrometer (ED-2000 of Oxford Instruments) installed at the Department of Physics of Milan University. In the next figures, the results of some major elements found are reported.



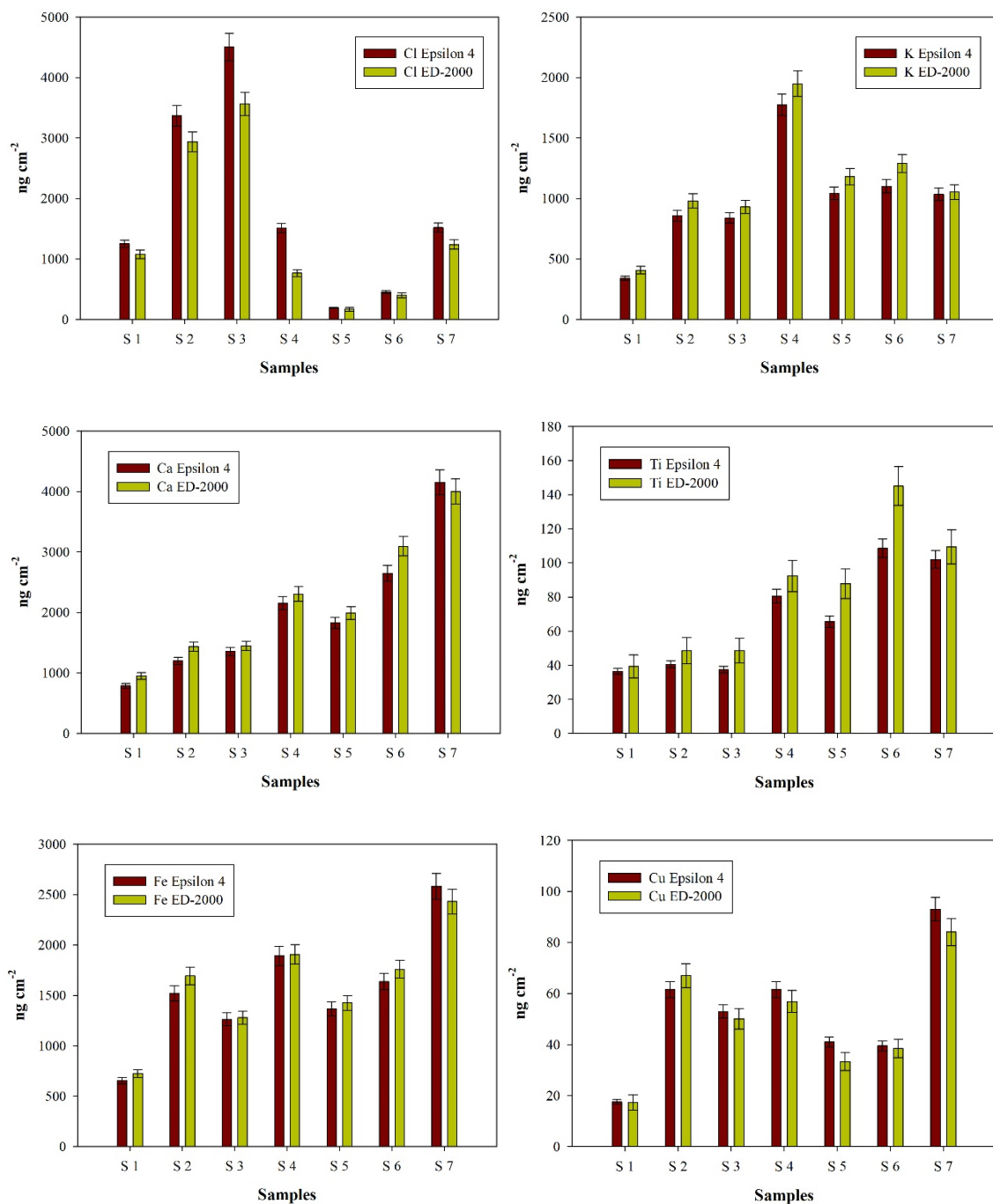


Figure 5: Comparison between elemental concentrations of some major elements in seven PM10 filters measured with ChAMBR-Epsilon 4 and ED-2000.

## 4.2 LAB EC/OC ANALYZER

The instrument was calibrated using Sucrose solutions as suggested by the manufacturer. Below the results obtained on 2 solutions of 53.70 and 22.13  $\mu\text{g cm}^{-2}$ .

Table 2: Results on SUCROSE standards.

	Measure 1		Measure 2		Measure 3	
	OC	EC	OC	EC	OC	EC
Std 53.7 $\mu\text{g cm}^{-2}$	53.11 $\pm$ 2.76	0 $\pm$ 0.10	51.07 $\pm$ 2.65	0 $\pm$ 0.10	51.13 $\pm$ 2.66	0 $\pm$ 0.10
Std 22.13 $\mu\text{g cm}^{-2}$	21.55 $\pm$ 1.14	0 $\pm$ 0.10	21.13 $\pm$ 1.16	0 $\pm$ 0.10	21.69 $\pm$ 1.18	0 $\pm$ 0.10

The instrument was checked measuring a performance evaluation sample of OC and EC supplied by the manufacturer, SN: 620120673. The figures below show the results and the certificate of analysis.

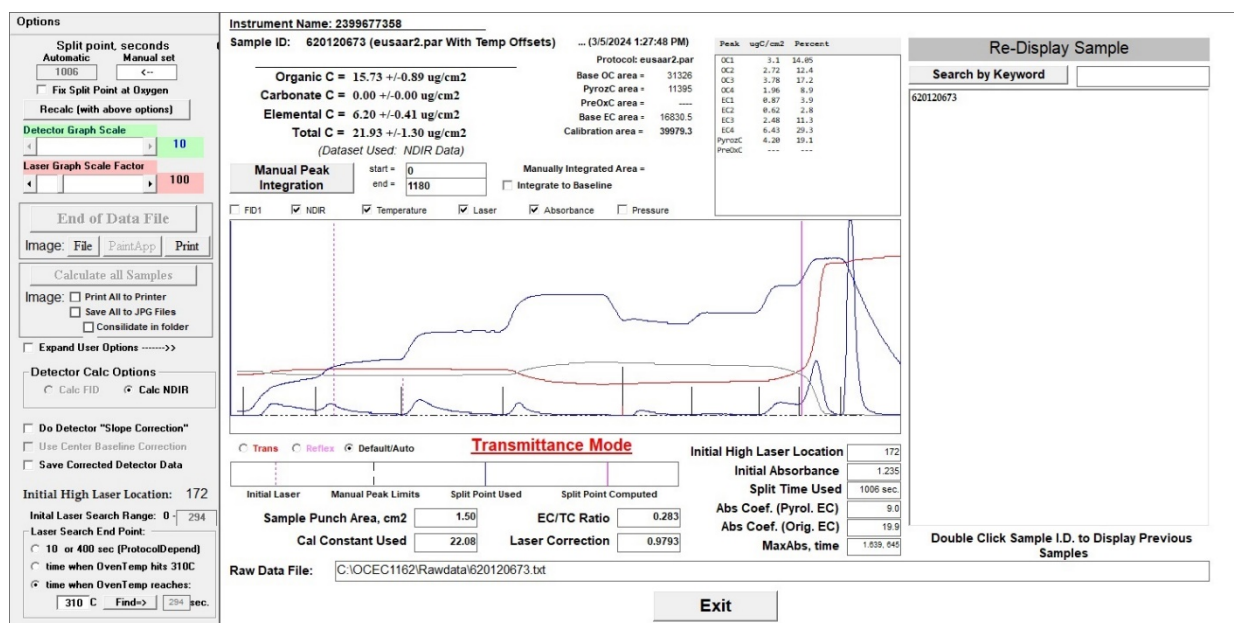


Figure 6: Results on certified standard SN: 620120673.



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## Certificate of Analysis

### Performance Evaluation Sample

PES Sample ID Number: 620120673

Date Prepared: December 13, 2023

PES Type: PES-MCB-E

### RESULTS

Serial Number	620120673					
Analysis Protocol	EUSARR2		Calculation Software	Version 464		
Sample ID	OC( $\mu\text{g}/\text{cm}^3$ )	EC( $\mu\text{g}/\text{cm}^3$ )	TC( $\mu\text{g}/\text{cm}^3$ )			
620120673-10	15.93	6.26	22.19			
620120673-12	16.79	6.01	22.80			
620120673-11	15.86	6.12	21.98			
<b>Reference Value</b>	16.19	6.13	22.32			
<b>Standard Deviation</b>	0.52	0.12	0.43			
<b>Expected Results Range</b>	<b>Min</b> 14.64	<b>Max</b> 17.75	<b>Min</b> 5.76	<b>Max</b> 6.50	<b>Min</b> 21.04	<b>Max</b> 23.60

This Performance Evaluation Sample was made according to Sunset Laboratory's procedures and analyzed on OCEC instruments calibrated and maintained according to the recommendations described in the instrument user's manual. Individual results may vary.

*Disclaimer: Obtaining results comparable to those listed above requires that the instrument being used is in good working order and is properly maintained according to Sunset Laboratory's recommendations. It is recommended that the instrument in use have all calibrations evaluated and corrected, if necessary. Please consult the instrument user's manual for a list of routine checks and calibrations.*

Approved for Release

Figure 7: Certificate of analysis of performance evaluation sample SN: 620120673

## 5. CONCLUSIONS

The use of ED-XRF and thermo-optical analysis helps to determine the composition of particulate matter, specifically the presence of metals (Na to Pb) and the carbonaceous fraction. Understanding the concentration of toxic metals in aerosols is crucial for monitoring air quality and identifying potential pollution sources. Additionally, the two main types of carbon, organic carbon (OC) and elemental carbon (EC), are significant in assessing air quality, with EC being a major contributor to atmospheric warming due to its strong sunlight-absorbing properties. The calibration procedures for the instruments have ensured accurate results, which can provide valuable insights into particulate

matter. The new equipment for off-line aerosol speciation at INFN paves the way towards a better characterization of PM and a greater understanding of its emission sources.