

# CHARACTERIZATION OF SUB-MICROMETER URBAN AEROSOLS WITH EMILIE™

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While ultrafine aerosol particles typically have significant number concentrations, their total mass is typically very low, which makes their chemical characterization extremely challenging. AFM-IR (atomic force microscope - infrared spectroscopy) TEM-EDX (transmission electron microscopy with energy dispersive X-Ray spectroscopy) and SEM-EDX (scanning electron microscopy with energy dispersive X-ray spectroscopy) allow for the chemical characterization of individual ultrafine nanoparticles, but the process is time-consuming. We propose nanoelectromechanical Fourier-transform infrared spectroscopy (NEMS - FTIR) with EMILIE™ as an alternative for the rapid bulk chemical characterization of ultrafine aerosols.

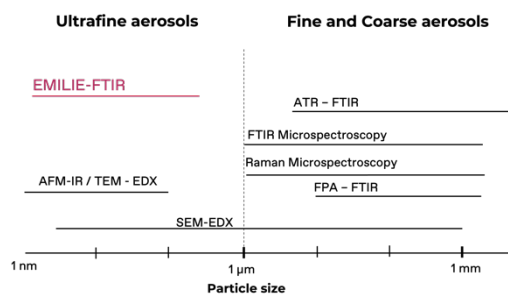


Figure 1. Overview of spectroscopic methods available for the analysis of aerosols

The measurement principle of EMILIE™ is based on the photothermal heating of the sampled nanoparticles, causing a measurable frequency detuning of the EMILIE™ resonator chip [1,2]. The frequency detuning, which is measured by the frequency tracking electronics PHILL™, is a direct measure for the absorbed light power [3]. With the photothermal sensing principle, EMILIE™ has a limit of detection in the lower picogram range [4].

## SAMPLING OF AEROSOLS ON EMILIE™ CHIPS

The system is centered around perforated NEMS resonator chips, which are used both as a filter for aerosol collection, and as a detector for bulk chemical characterization.

The sampling and measurement concept is illustrated schematically in Figure 1. The efficiency of the sampling technique is visualized in Figure 3. For 10 nm-sized nanoparticles, sampling times can vary from minutes to a day, depending on concentration.

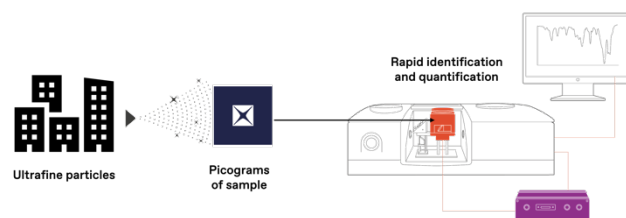


Figure 2. Aerosol samples are deposited directly on the surface of the EMILIE™ nanomechanical sampling and sensing chip prior to analysis by NEMS-FTIR.

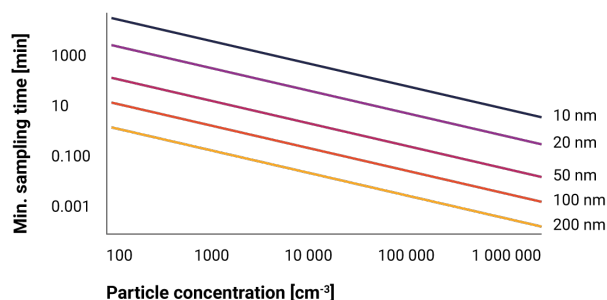


Figure 3. Estimated minimal sampling time for different particle sizes for a flow rate of 1 L/min

## URBAN AEROSOL ANALYSIS WITH EMILIE™

To demonstrate the EMILIE™ technology for the analysis of urban aerosols down to ultrafine particles, samples were collected in clean (ISO 5 / Class 100 cleanroom) and urban environment (central Vienna) for analysis by NEMS-FTIR. The sampling conditions in both cases were 15 min collection time at 1 L/min. An impactor with a 700 nm cut-off was used at the entrance of the sampling chamber to eliminate larger particles.

Figure 4 shows microscopy images of EMILIE™ nanomechanical sampling and sensing chips after collection in clean and urban environments. The average particle concentration (n=3) was 5702, 5287, and 5239 ultrafine particles per cm<sup>3</sup> with average diameters 77, 79, and 77 nm collected during morning, midday, and evening, respectively. After sampling, the resonator chips were transferred directly to the EMILIE™ nanomechanical analyzer chamber for NEMS-FTIR analysis without any further sample processing. NEMS-FTIR spectra feature a large photothermal silicon nitride peak centered at 866 cm<sup>-1</sup> due to the absorbance of the EMILIE™ chip. This feature is used as an internal standard in all measurements. Urban air samples were background corrected using the spectra recorded for clean air.

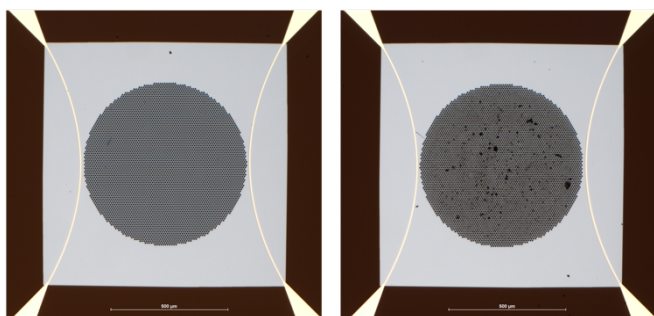


Figure 4. Left: An EMILIE™ chip after sampling cleanroom air (ISO 5 / Class 100). Right: An EMILIE™ chip after sampling in an urban environment.

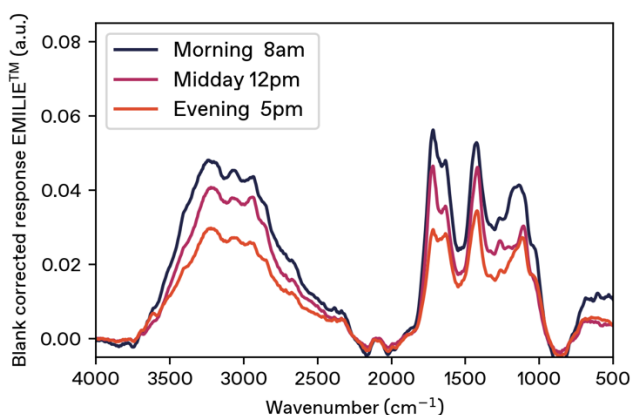


Figure 5. FTIR spectrum of ultrafine aerosols (10-700 nm) collected in urban environment. Each spectra represents the average of two spectra from two separate chips.

The background corrected spectra of urban aerosol shown in Figure 5 reveal several peaks that can be attributed to organic and inorganic-based aerosols, in particular SO<sub>4</sub><sup>2-</sup>

(1101 cm<sup>-1</sup>), NH<sub>4</sub><sup>+</sup> (1417 and 3190 cm<sup>-1</sup>), NH<sub>2</sub> (1600 cm<sup>-1</sup>), carbonyl (1712 cm<sup>-1</sup>), aliphatic CH (2900 cm<sup>-1</sup>), and aromatic CH (3040 cm<sup>-1</sup>) [5,6]. The intensity of the morning spectrum is higher than midday and evening, in accordance with the average particle counts recorded. This indicates the large potential of the technique for the chemical characterization of aerosols towards ultrafine particles.

#### BENEFITS OF USING EMILIE™

- Rapid collection of aerosols (10 nm - 1500 nm) directly on the surface of the sensing element.
- Rapid NEMS-FTIR characterization of ultrafine aerosols.
- No sample transfer from a filter for further analysis.
- No time-consuming scanning.
- High sensitivity without cryogenic cooling.

#### REFERENCES

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- [2] Yamada, Shoko, et al. "Photothermal infrared spectroscopy of airborne samples with mechanical string resonators." *Analytical chemistry* 85.21 (2013): 10531-10535.
- [3] Schmid, Silvan, Luis Guillermo Villanueva, and Michael Lee Roukes. "Responsivity and Sensitivity." *Fundamentals of Nanomechanical Resonators*. Springer International Publishing, 2023. 175-203.
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