ADVANCES IN SPECTROSCOPIC METHODS FOR PARTICULATE MATTER SPECIATION

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1. Introduction

Speciation of airborne particulate matter (PM) and source apportionment is crucial for understanding the magnitude and impact of PM on the environment and human health. Identifying when there is need for mitigation strategies and monitoring the success of their implementation is best achieved when we can recognise individual particles and their source. Identifying, grouping, and quantifying particles at specific locations and times has historically been a challenging task. Early studies, regulatory standards, and current PM monitoring programs primarily focus on measuring total particle concentration and size distribution (Alfano, 2020; Amaral, 2015). While regulatory standards help determine PM mass concentration in various size fractions, identifying the chemical composition of particles and quantifying particles based on distinct chemical and morphological groups and their sources remains a complex challenge. Online measurement techniques such as Soot-Particle Aerosol Mass Spectrometry (SPAMS) and Long Time-of-Flight Chemical Ionization Mass Spectrometry (LTOF-CIMS) are costly and intricate to operate. For comprehensive particle characterization including morphology and chemical properties, offline measurements involving particle collection on filters are preferred (Galvão, 2018).

Environmental PM samples are highly complex, typically containing hundreds of thousands of unique particle species scattered randomly across sample filters. These particles originate from diverse sources, each influenced by various factors affecting their emissions profile. The surface chemistry of these particles is further affected by meteorological conditions and atmospheric chemistry changes. To manage this complexity, air quality specialists use specialized sampling devices and diverse approaches to strategically collect PM. These devices collect controlled fractions of particle size and density on tailored filter materials, often located alongside other instruments to gather comprehensive meteorological meta-data that can influence PM surface chemistry (Alfano 2020).

2. Spectroscopy based speciation and source apportionment of PM

In the past decade, advancements in chemical characterization and source identification of PM have been significant, driven by increased use of advanced materials chemistry techniques and improved data analysis software. Various instruments are employed to analyse PM chemistry on filters, typically using spatially averaged methods. X-ray spectroscopies like Energy Dispersive X-ray Spectroscopy (EDS), X-ray Fluorescence spectroscopy (XRF), X-ray Absorption Near Edge Structure (XANES), and X-ray Photoelectron Spectroscopy (XPS) excel in elemental analysis and oxidation state determination for heavy elements but are less effective for organic materials. Vibrational spectroscopies such Fourier Transform Infrared spectroscopy (FTIR) and Raman Spectroscopy (RS) provide molecular fingerprints and identify specific compounds like nitrates, sulphates, and carbon-containing species based on functional groups. Ion beam techniques like Secondary Ion Mass Spectrometry (SIMS) and Particle-Induced X-ray Emission (PIXE), offer quantitative elemental analysis with surface sensitivity and depth profiling, while PESA quantifies hydrogen content (Amaral, 2015; Correa-Ochoa, 2023; Ogrizek, 2022).

No single technique comprehensively characterizes environmental PM samples chemically. Typically, multiple filters and diverse characterization methods are necessary for thorough analysis. Many methods are sample-destructive, and filter material choice varies depending on the measurement method, environmental context and particle types present (Galvao, 2018).

To identify chemical species and their emission sources from averaged data collected across multiple methods, researchers combine datasets and apply multivariate statistical methods and machine learning techniques (receptor modeling). These methods include Chemical Mass Balance (CMB), Positive Matrix Factorization (PMF), Principal Component Analysis (PCA), Enrichment Factor, Cluster Analysis, Unmix, and Effective

Variance (EV). Hopke (2016) reviewed the evolution and application of receptor models in determining PM sources.

3. Hybrid instruments for single particle measurements

Morphological characterization of PM using microscopes with particle finder software has greatly improved speciation and source apportionment by providing detailed information on individual particle shape, size, and structure. Combining this with spectroscopy-based chemical analysis gives a more complete understanding of PM sources and the processes influencing particle formation and reactivity (Ogrizek 2022).

Measuring spectra of single particles is challenging due to low signal strength and poor signal-to-noise ratios, requiring long measurement times for high-quality spectra. Complex particle mixtures can also cause issues with matrix signals and fluorescing particles. Using high-powered, large-scale facilities like Synchrotrons and Ion Beams can enhance measurement speed and spectral resolution for single particle analysis (Shaltout 2021). However, these facilities are shared among researchers across various fields, which limits their availability.

Hybrid instruments combining microscopes and spectroscopic techniques are powerful tools for analysing individual particles based on their morphology. These instruments can perform 2- and 3-D hyperspectral imaging in the micron range. Optical microscopes coupled with vibrational spectroscopy (Micro-RS and Micro-FTIR) have recently been used in air quality research to image single particles and scan entire filter areas, obtaining molecular fingerprints of thousands of particles per filter, providing richer data sets for receptor modelling (Longoria-Rodríguez 2021). Olson et al. reported the first use of an Optical PhotoThermal InfraRed with Raman Spectroscopy (OPT-IR-RS) microscope for PM characterization. This instrument simultaneously measures FTIR and Raman spectra at single-particle resolution and is promising for PM speciation and source apportionment studies (Olson 2020).

Scanning Electron Microscopy (SEM) combined with EDS is commonly used in PM studies for semi-quantitative elemental analysis of single particles, along with their morphological characterization. Other SEM hybrid instruments include Raman-SEM, XPS-SEM, SIMS-SEM, and the more recently developed Raman-SEM-EDS, which combines two spectroscopy methods with morphological characterization (Cardell, 2023).

4. Conclusions

Advancements in spectroscopic methods are improving our ability to identify and quantify various particle types in the environment. Integrating optical and electron microscopy with vibrational and x-ray spectroscopy has created new opportunities for analyzing complex PM samples. Instruments like the OPTIR-Raman microscope, capable of simultaneously measuring FTIR and Raman spectra at single-particle resolution, demonstrate innovative approaches in PM research. Future research efforts should focus on refining these hybrid techniques and applying them to a wider range of environmental samples. By utilizing these advanced tools, we can gain deeper insights into PM composition and behavior, facilitating the identification and quantification of specific PM sources. This, in turn, enables the evaluation of mitigation measures, ultimately contributing to improved air quality and public health outcomes.

5. References

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