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Review

Secondary ion mass spectrometry: The application in the analysis of atmospheric particulate matter

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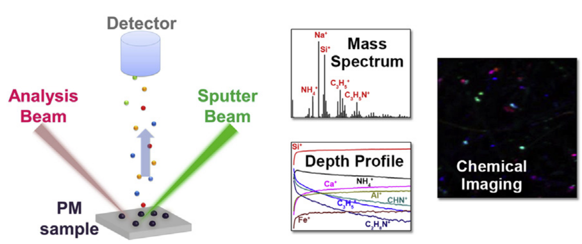
HIGHLIGHTS

- Significance for the study of surface chemistry and chemical heterogeneity between surface and bulk of PM are presented.
- Recent SIMS applications in PM analysis concerning various sources are summarized.
- Advantages and limitation of SIMS application in PM analysis are discussed.
- Future development of SIMS analysis of PM is proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Currently, considerable attention has been paid to atmospheric particulate matter (PM) investigation due to its importance in human health and global climate change. Surface characterization, single particle analysis and depth profiling of PM is important for a better understanding of its formation processes and predicting its impact on the environment and human being. Secondary ion mass spectrometry (SIMS) is a surface technique with high surface sensitivity, high spatial resolution chemical imaging and unique depth profiling capabilities. Recent research shows that SIMS has great potential in analyzing both surface and bulk chemical information of PM. In this review, we give a brief introduction of SIMS working principle and survey recent applications of SIMS in PM characterization. Particularly, analyses from different types of PM sources by various SIMS techniques were discussed concerning their advantages and limitations. The future development and needs of SIMS in atmospheric aerosol measurement are proposed with a perspective in broader environmental sciences.

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1. Introduction

Atmospheric particulate matter (PM), also known as aerosol, is generally defined as a heterogeneous solid or liquid mixture of micro-aggregates consisting of complex components in the Earth's atmosphere [1]. PM in ambient air is either emitted directly from various sources (primary aerosols) or formed from aerosol precursors through complicated physical and chemical reactions (secondary aerosols) [2,3]. Primary anthropogenic sources include coal combustion, industrial emission, vehicular emission and biomass burning [4–7]. Natural sources include sea salts, wildfires, windblown dusts and biogenic emissions [8,9]. The potential for these primary emissions to contribute to secondary aerosol formation requires more investigation [10]. In the last decades, increasing attention has been paid to PM as it plays an important role in atmospheric visibility, human health, rainfall and global climate change [11–13]. Specifically, PM in atmospheric pollution is typically accompanied by visibility decrease, which could have significant impact on human daily life. Furthermore, numerous hazard components in PM are known to induce serious diseases such as asthma and cardiovascular diseases [14], making PM a threat to human health. On the other hand, by acting as cloud condensation nuclei (CNN) or ice nuclei (IN), PM is one of the key factors in the formation process of clouds. As a result, PM could change the distribution of droughts and storms, and therefore impacts precipitation [15]. In addition, PM not only causes regional haze pollution but also influences the scattering and absorption of incident solar radiation. The out-of-balance climate system therefore leads to disordered phenomenon such as global warming, El Nino and extreme weather [16].

Mass spectrometry (MS) is one of the most frequently used techniques for the analysis of PM chemical compositions with short response time and high sensitivity. Generally, mass spectrometry in PM analysis is divided into two categories: on-line MS and off-line MS. On-line MS such as aerosol mass spectrometer (AMS) and aerosol time-of-flight mass spectrometer (ATOFMS) provides high time resolution in PM measurement and could avoid potential artifacts associated with sample preparation procedure [17]. Off-line MS including gas chromatography mass spectrometry (GC-MS), electrospray ionization mass spectrometry (ESI-MS), matrix-assisted laser desorption/ionization mass spectrometry (MALDI) etc. gives a more detailed insight into the structure of PM at molecular level for a better understanding of PM composition. Comprehensive review about the application of on-line and off-line MS in PM analysis were seen elsewhere [17,18].

Owing to relatively large specific surface area and interactions between reactive gases and condensed phase surfaces, harmful gases and microorganisms tend to adsorb on the surface of PM. These surface adsorbates, especially organic matter, affect the behavior of PM in various aspects, such as chemical reactivity, the formation of CCN or IN, and particle optical properties [19,20]. Thus, it is of significant importance to analyze the surface composition of PM, because it can differ from that in the bulk [21,22]. However, most existing studies on PM focused on ensemble measurements rather than surface chemical analysis of single particles. The primary reason is that the most frequently used PM analysis tools, including above mentioned on-line/off-line MS and other techniques were either designed for ensemble measurements or tend to destroy the surface structure during the sample preparation or measurement processes. Therefore, analysis techniques that can measure surface chemical information of single particle and distinguish the chemical heterogeneity between surface and bulk of PM with reasonable accuracy and sensitivity will substantially improve our understanding of the relationship between the chemical structure of PM and its impact on human health and environment. Among surface analytical techniques, secondary ion mass spectrometry (SIMS) is a popular choice in various applications, such as self-assembly monolayer characterization [23,24], solid-electrolyte interphase analysis [25–27], single cell chemical imaging [28,29] and environmental related particle investigation. High surface sensitivity and remarkable lateral/depth resolution of SIMS makes it a useful tool for the analysis of single particles and distinguishing chemical composition between PM surface and bulk [30,31].

Another technical challenge for PM analysis is the chemical heterogeneity among single particles. The impact of PM on climate and health depends largely on property of individual particles [32]. Owing to the small size (ranging from nanometer to micrometer) of aerosol particles, sufficiently high sensitivity and lateral resolution are needed to meet the requirement for single particle analysis. Recent years have witnessed the development of various single particle analysis techniques such as electron probe microanalysis (EPMA), micro-Fourier transform infrared spectroscopy (μ-FTIR) and micro-Raman spectroscopy (μ-Raman) [33,34]. On the other hand, SIMS could provide a high lateral resolution better than 100 nm. Besides, mass-resolved analysis of SIMS provides a better chemical specificity over other techniques. Thus, SIMS showed great potential in the analysis of individual aerosol particles.

Here, we aimed to survey current progresses of SIMS applications in PM analysis. Specifically, surface mass spectrometry, chemical imaging and depth profiling results revealed rich information regarding the spatial composition of PM collected from various origins. Based on these results, we summarized the challenges remaining in SIMS applications in PM analysis. A future