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Review article

Techniques and instruments used for real-time analysis of atmospheric nanoscale molecular clusters: A review

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ABSTRACT

The extremely high concentrations of $PM_{2.5}$ (particulate matter with an aerodynamic meter $\leq$ 2.5 μm) during severe and persistent haze events in China have been closely related to the formation of secondary aerosols (SA). New particle formation (NPF) is the critical initial step of SA formation. New particles are commonly formed from gas-phase precursors (e.g., SO_2, volatile organic compounds) *via* nucleation and initial growth, in which molecular clusters with a mobility diameter smaller than 3 nm (hereafter referred to nanoscale molecular clusters) will be involved throughout the whole process. Recently, significant breakthroughs have been obtained on NPF studies, which are mostly attributed to the technical development in the real-time analysis of size-resolved number concentration and chemical composition of nanoscale molecular clusters. Regarding the detection of size-resolved number concentrations of nanoscale molecular clusters, both methods and instruments have been well built up; practical application in laboratory-scale experiments and field measurements have also been successfully demonstrated. In contrast, real-time analysis of chemical composition of nanoscale molecular clusters has still encountered the great challenges caused by the complex organic compositions of the clusters, and improvement of present analytical strategies is urgently required. The better understanding in NPF will not only benefit the atmospheric modeling and climate predictions but also the source control of SA.

Contents

1. Introduction

Accompanied with the rapid industrialization and urbanization of China, extremely severe and persistent haze events have occurred with increasing frequency; great concerns have been aroused on this environmental problem due to its negative effects on regional and global climates, air quality and human health [1–6]. According to a recent report on the serious haze event in January 2013 in China, the measurement results from 74 major cities indicated that the highest daily concentration of $PM_{2.5}$ (particulate matter with an

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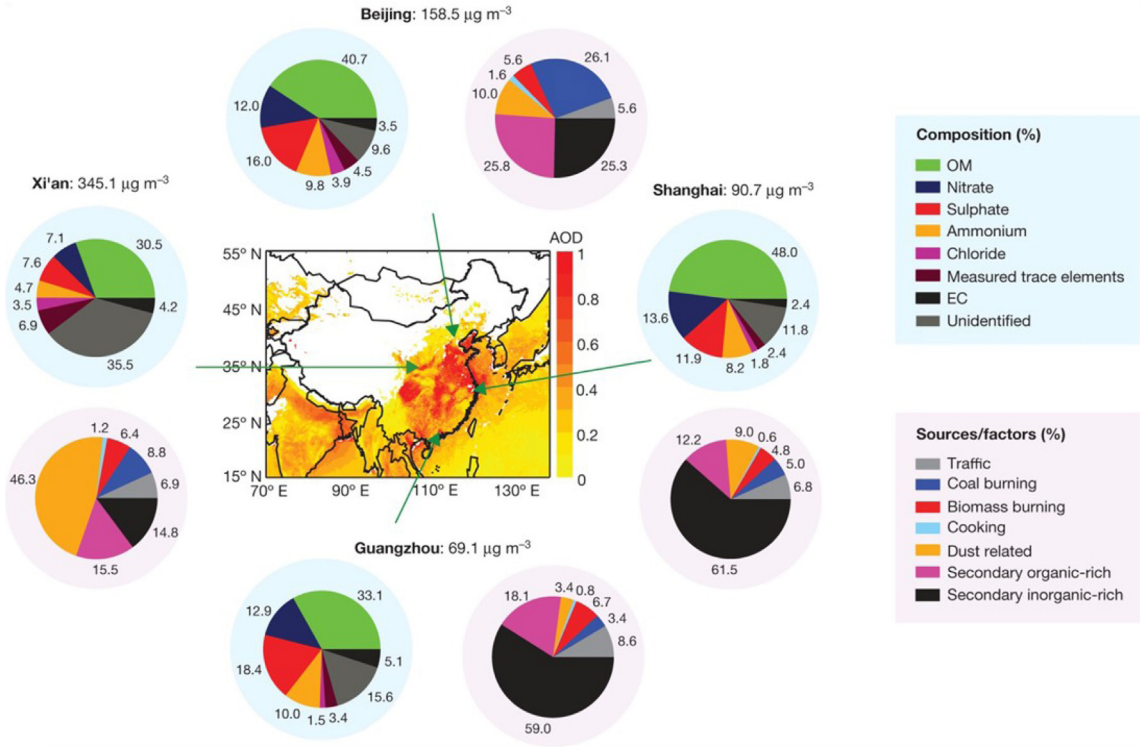

Fig. 1. Chemical composition and source apportionment of $PM_{2.5}$ collected during the high pollution events of 5–25 January 2013 at the urban sites of Beijing, Shanghai, Guangzhou and Xi'an. (Reprinted with permission from Ref. [1]. Copyright 2014 Nature Publishing Group).

aerodynamic meter ≤ 2.5 μm) has reached 772 μg m^{-3}, which is about ten times as much as the Chinese air pollution standard (75 μg m^{-3}), and the daily average $PM_{2.5}$ concentrations in Xi'an, Beijing, Shanghai and Guangzhou, four typical urban cities in China, were 345.1, 158.5, 90.7 and 69.1 μg m^{-3} (Fig. 1), respectively. Moreover, the concentrations of $PM_{2.5}$ in 69% of days in January could not meet the national air pollution standard [1].

These severe haze events have been closely related to the formation of secondary aerosols (SA), which probably has accounted for 30–77% of $PM_{2.5}$ (Fig. 1) [1]. SA are formed in the atmosphere from reaction products of gaseous precursors [7,8] and can be further divided into secondary inorganic aerosols (SIA) and secondary organic aerosols (SOA). The chemical composition of SIA is dominant by sulfate and nitrate. The gas precursors of sulfate and nitrate are mostly SO_2, NO_x (NO, NO_2) and NH_3 (Equations (1) and (2)). SO_2 is mainly from coal burning; most NO_x results from vehicle exhaust and power plants; NH_3 is ubiquitous in the atmosphere and could be emitted from both natural and human activities.

SOA are composed of low-volatile and semi-volatile oxidation products of volatile organic compounds (VOCs) through various photochemical reactions or gas-particle transformation (Equation (3)). The emission sources of VOCs include vehicles, coal-burning and biomass-burning. However, it should be noted that there are a large number of VOCs species involved in SOA formation and also the reaction pathways are various, both of which lead to the extremely complex chemical composition of SOA. Besides, trace metal elements have also been found in SA, including Cr, Pb, As, Ni, Cu, Cd, Fe, Al, Mn, *etc*; these metal elements are either from anthropogenic activities or natural processes [1,9].

$$SO_2 \xrightarrow{[O]} H_2SO_4 \xrightarrow{NH_3} (NH_4)_2SO_4 \quad (1)$$

$$NO_x \xrightarrow{[O]} HNO_3 \xrightarrow{NH_3} NH_4NO_3 \quad (2)$$

$$VOCs \xrightarrow{[O],gas-paricletransformation} SOA \quad (3)$$

The presence of $PM_{2.5}$ will not only cause environmental problems, but also pose a significant impact on human health. The health risk due to the exposure to $PM_{2.5}$ should be evaluated by considering not only their chemical compositions (e.g., oxygenated polycyclic aromatic hydrocarbons, heavy metal elements) but also the size of the particles. $PM_{2.5}$ could get down to the alveoli, which is the deepest portion of lungs, and penetrate the bloodstream, amplifying the harmful effects. Up to date, both experimental and epidemiological studies have demonstrated the possible association between $PM_{2.5}$ exposure with cardiovascular diseases, lung cancer, *etc*. [8,10–12].

The initial step of SA formation is new particle formation (NPF). Both ambient charged molecules or clusters and neutral molecules or clusters will participate into the process of NPF [13–17]. Actually, NPF is also the critical step for SA formation [7,18]. To be specific, NPF is considered to be a two-step process, i.e., nucleation and initial growth, and these two sub-processes are distinguished based on the formation of the critical nucleus or cluster (mobility diameter ~ 1.4 nm).

In the process of nucleation (before reaching the critical size), molecular clusters are created to form a new phase, and this is achieved through random collisions and rearrangements of gas-phase atoms and molecules (precursors). During the transformation from vapor, to liquid and finally to solid, there is a decrease in both enthalpy and entropy in the nucleating system, i.e., $\Delta H < 0$ and $\Delta S < 0$. As a result, nucleation is an exothermic process ($\Delta H < 0$) and thus thermodynamically favored based on the first law of