

Single particle analysis of soil dust by aerosol time-of-flight laser mass spectrometry

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A laboratory study was carried out to investigate the single particle soil dust using aerosol time-of-flight mass spectrometry. The presence of crustal elements is observed in the mass spectra of individual particles. Potassium and iron constitute the two most commonly detected cations. Other common cations observed in the mass spectra of soil particles include sodium and magnesium. According to a large number of single aerosol diameters, we obtained the size distribution. Peaks in the positive ion mass spectra enable us to identify individual dust particles in atmospheric samples and track chemically distinct dust particles in the atmosphere using aerosol time-of-flight mass spectrometry.

Keywords: mass spectrometry, aerosols, trace elements, particulate matter.

1. Introduction

Atmospheric aerosols are receiving increased attention by governmental, industrial, and scientific communities due to recent studies that report a correlation between high levels of particulate pollution and adverse health effects [1]. Both natural and anthropogenic sources contribute to atmospheric aerosols with concentration reaching up to 10^8 particles/cm³ in some polluted regions. Soil dust is a significant contributor to anthropogenic particulate matter throughout the world. On a global scale, it is estimated that production of dust is of the order of 250×10^6 tons annually, ranking it as the second larger primary particle source after sea salt [2]. The transport of soil dust over very long distances has been shown on numerous occasions. Further studies have shown that mineral dust can play a role in light scattering, and climate forcing [3]. In order to enhance our understanding of the role of aerosols in atmospheric processes and to identify aerosol sources, the ability to characterize ambient particles in real time is of primary importance.

Microanalysis techniques, such as laser microprobe mass analysis (LAMMA), are currently the most utilized methods for complete characterization of individual aerosol particles [1]. Current microanalysis tools include mass spectrometry [4], optical

spectroscopy [5], and electron microscopy [6]. The chemical composition of size segregated soil dust has been obtained for several soil sources. Typically, the chemical composition data obtained during such studies is acquired using bulk analysis of the samples by techniques such as proton induced X-ray emission (PIXE), or X-ray fluorescence (XRF) [7]. The use of bulk analysis techniques inherently complicates the possibility of assessing the contribution of dust particles originating from different soil sources, since all particles are collected and analyzed as an integrated sample. However, these techniques suffer from being off-line analysis methods, and the majority can only be used for quantitative determination of either particle size or composition. An ideal aerosol analysis instrument would allow simultaneous determination of all physical properties of an aerosol. The size and composition of an individual particle not only reflects the nature of the source of the particle but ultimately determines the particle's environmental and biological effects.

Source identification is a major goal of aerosol characterization studies. Specific chemical compounds associated with certain size modes allow sampled particles to be traced back to a single emission source. The purpose of this study is to characterize individual particles resulting from the suspension of soil dust. Data on the size and sets of chemical markers are used for the identification of individual soil dust particles in the atmosphere and monitoring their temporal profiles using the real-time capability of aerosol time-of-flight mass spectrometry. The temporal profiles obtained can then be correlated with meteorological factors such as wind speed and direction to assess the relative influence of transport. In addition, source apportionment of soil dust on an individual particle basis will allow for better quantification of the relative contribution of suspended soils to ambient particulate matter and the effects that ensue from their presence in the atmosphere.

2. Experiment – materials and methods

Soil samples were collected from a number of locations in China for the purpose of determining the size and chemical composition of dust particles derived from different areas. Approximately 10 g of each soil sample were introduced into a glass sampling bottle. Introduction of the sample in the container causes the suspension of dust particles in the air space above the soil.

The particle sample is then transferred to an aerosol time-of-flight mass spectrometer through an outlet valve and a plastic transfer line. A HEPA Capsule Filter is attached to an inlet valve on the glass container. The filter allows particle-free air to be pulled through the container to allow for a consistent flow of soil-entrained air into the instrument. This sample introduction procedure has also been employed for studies of automobile exhaust and biomass burning particles [8].

An aerosol time-of-flight mass spectrometer (ATOFMS) provides size and chemical composition information for individual particles. It operates in a continuous

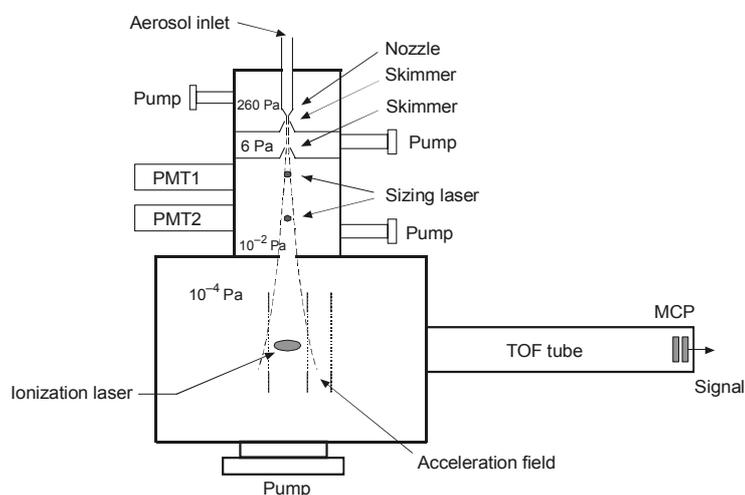


Fig. 1. Schematic diagram of aerosol time-of-flight mass spectrometer (ATOFMS).

sampling manner, allowing for real-time analysis of particles with high time resolution. The operating principles of ATOFMS have been described in detail before, so only a brief description is presented here [9]. The principle is shown in Fig. 1. Particles are introduced into the instrument through a nozzle and undergo a supersonic expansion. The particles are accelerated to a terminal velocity that is proportional to their aerodynamic diameter. The particles then enter a sizing region where they pass through two continuous wave laser beams. Scattering signals are collected as each particle passes through each laser beam. A particle time-of-flight is measured that can be converted to aerodynamic size with a calibration curve. After being sized, the particle travels to the ion source region of a time-of-flight mass spectrometer. Chemical species in the particle are desorbed/ionized, using the pulsed output from an ultraviolet laser, and separated and detected using a time-of-flight mass spectrometer equipped with multichannel plate (MCP) for ion detection.

The experiments described in this paper were performed using the laboratory-based ATOFMS. A red, diode-pumped laser (operating at 650 nm) was used for the aerodynamic sizing region of the instrument, with size calibrations indicating a lower size limit of 0.3 μm for these experiments. Laser desorption/ionization of chemical species in the particles was accomplished using a Nd:YAG laser operating at 266 nm. Positive and negative ions were acquired separately by changing the applied voltages for the source of the time-of-flight mass spectrometer.

The instrument has proven useful for determining size and chemical correlation information of individual particles for complex atmospheric samples, for tracking particles with distinct chemical signatures in the atmosphere, and for observing meteorological effects on particulate pollution.

3. Results and discussion

3.1. Particle size distributions

Analysis of ATOFMS data shows that suspension of soil dust results in the formation of mostly large-sized particles. This is expected, since it is known that large-sized particles tend to be derived from mechanically generated processes including wind blown dust and sea spray [10]. Figure 2 shows a size histogram for the particles generated by the suspension of a soil sample. This distribution is not corrected for instrumental biasing or sampling efficiencies. The dust particles analyzed exhibit a broad size distribution, measuring from approximately 0.4 μm to about 2.2 μm in aerodynamic diameter. In the ATOFMS system, few particles are observed above 2.2 μm due to losses in the current sampling inlet system. This size distribution is typical of the soil samples that were analyzed. It reflects the known contribution of dust as a dominantly coarse mode particle source that occasionally dominates mass distributions.

3.2. Chemical composition

Figure 3 shows the laser desorption/ionization (LDI) mass spectra from four individual particles showing representative positive ions common to soil dust. All the soil was used to cultivate baccy. The chemical heterogeneity of particles resulting from the suspension of soil dust is comparable to the measured composition of bulk soil dust observed in previous systematic studies [1]. The four spectra shown in Fig. 3 are the most typical types observed out of the particles in the soil samples that were analyzed.

In Figure 3a, a positive ion mass spectrum of a 1.2 μm particle is shown. This particle resulted from the suspension of a soil sample acquired from the Si Chuan

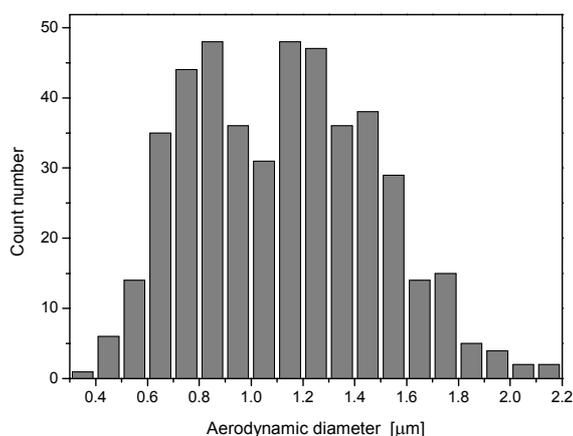


Fig. 2. Size distribution of particles resulting from the suspension of soil.

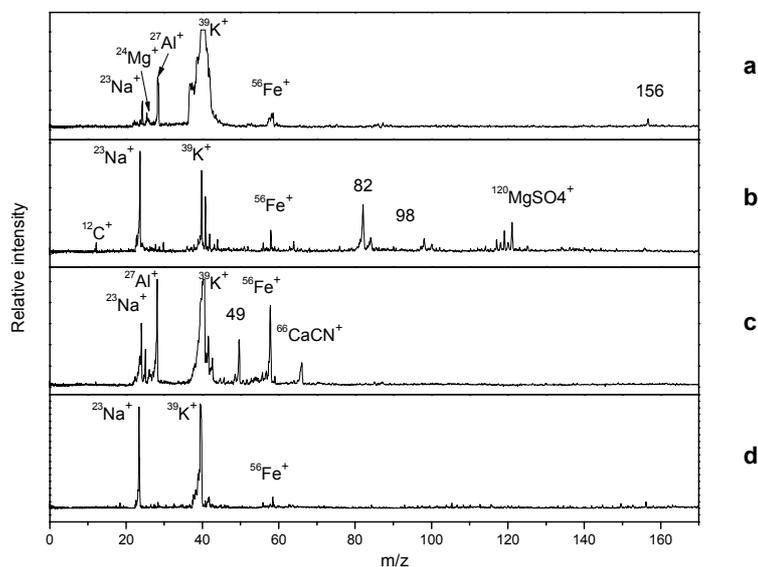


Fig. 3. Positive ion mass spectra of individual soil dust particles.

province. In this spectrum, dominate peaks are due to the presence of sodium, potassium, and iron. However, it also clearly contains peaks due to the three isotopes of magnesium (mass-to-charge ratio $m/z = 24, 25$). The peaks is very distinct, and seems to be more indicative of dust from sand sources, rather than fine soils. This particle type was observed frequently in the other three sand samples from other locations. The distinctive feature in this spectrum is the peaks at mass-to-charge ratio (m/z) equal to 156. This cluster of peaks appears to have isotope features that would be indicative of its being a silicon-containing cluster.

Figure 3b displays the positive ion mass spectrum of a 1.6 μm particle resulting from the suspension of a soil sample from the Nei Meng-gu province. The spectrum contains peaks due to sodium, potassium, magnesium and iron. The distinctive feature in this spectrum, however, that is, the relative ratios appear to vary considerably from one particle to another, indicating that several species may be responsible. Figure 3b shows the most common types of positive ion mass spectra observed during analysis of soil dust. However, the composition of soil particles shows considerably greater variability than those three mass spectra. In Figure 3, four more positive ion mass spectra are shown that display the diversity of the composition of soil particles. These particles are minor types that are observed in the soil samples analyzed. The chemical heterogeneity observed in soil dust particles is a result of the large number of mineral species that are present in soil, and thus one particle can be enriched with an element that is not present in another particle.

Figure 3c shows a positive ion mass spectrum for a 2.1 μm particle. This particle resulted from the suspension of soil from Hei Long-jiang province. In this spectrum,

several elements common to soil are observed, with the mass-to-charge ratio (m/z) being equal to 23, 27, 39 and 56. These peaks are due to the most common isotopes of sodium, aluminum, potassium and iron. Two peaks are also observed at m/z equal to 49 and 66, probably corresponding to the presence of carbonate ion. Mass-to-charge ratios of 49, 66 are observed in particles generated from all four soil samples studied, although they are detected less frequently than the more common cations, such as sodium, aluminum, potassium, and iron.

In Figure 3d, a positive ion mass spectrum for another soil particle from the An Hui province is shown, and it measures 1.4 μm in diameter. The presence of sodium, potassium, and iron in the spectrum is observed. Both elements are observed in particles from several soil samples, typically, in over 56% of all the particles.

The aerosol time-of-flight mass spectrometry is capable of providing real-time data on atmospheric particles over extended periods of time [11]. And it has been used to monitor real-time changes in the observed composition of sea-salt particles. The data acquired using ATOFMS show a variation in sensitivity toward different elements. Such differences in chemical sensitivity due to the laser desorption/ionization process have been reported previously for the analogous off-line technique, LAMMA [8]. In current studies, we have determined the ATOFMS instrumental response factors for a number of elements. Since sodium is the most commonly observed element in the soil particles, all response factors are scaled relative to the measured sensitivity of sodium. Furthermore, because it is an alkali metal, sodium is relatively easy to ionize, making ATOFMS sensitive to its presence in particles.

4. Conclusions

This paper demonstrates how ATOFMS can be used for characterization of individual particles from the soil dust. ATOFMS measures both the size and chemical composition for single particles. In general, the particles that result from suspension of dust are large ($> 1 \mu\text{m}$). Although the chemical composition observed in the particles is very heterogeneous, it is possible to identify several broad classes of soil dust particles based on the combination of elements present in the mass spectrum. These differences in composition can then be used to monitor the presence of those particle types in the atmosphere in real-time.

The presence of cations due to sodium, potassium, and iron is typically observed in positive ion mass spectra, except in potassium-rich particles, where potassium clusters dominate. Using these markers, particles resulting from the suspension of soil dust can be identified in complex ambient samples. Ultimately, by providing sufficient characteristics of soil sources, it will be possible to measure atmospheric contributions of dust particles from different sources or locations on an individual particle basis.

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