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Particle analysis by laser mass spectrometry (PALMS) studies of ice nuclei and other low number density particles

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Abstract

It has been shown that particles which effectively initiate freezing, known as ice nuclei (IN), are normally found at concentrations less than 10 l^{-1} in the background atmosphere. The low number density of these particles has presented significant analytical challenges, and determination of the size and composition, and thus the origin, of these particles has historically relied upon electron microscopy (EM). Single particle mass spectrometers can provide better time resolution and reduced sampling artifacts. The modifications to the particle analysis by laser mass spectrometry (PALMS) instrument, a laser desorption/ionization mass spectrometer, required to efficiently size and analyze particles with very low number density, are described here. A comparison to traditional EM studies is made and future applications of this method to solve other contemporary atmospheric problems are also discussed.

Keywords: Aerosol mass spectrometry; Laser desorption/ionization; Ice nuclei

1. Introduction

The first attempts several decades ago to desorb and ionize aerosol components and analyze them using mass spectrometry were hampered by inadequate technology [1]. With the advent of adequate vacuum systems and lasers, several groups were able to produce high signal-to-noise mass spectra in laboratory experiments and at field sites [2–5]. Since that time single particle mass spectrometers have improved significantly. These instruments have provided a previously unavailable means of determining the chemical composition of atmospheric aerosol particles which has changed many of our previously held views regarding atmospheric particle formation, transformation and removal [6–8]. The vast majority of data taken by aerosol mass spectrometers has been at ground level. While the number density of particles between 200 nm and 2 μm diameter, a fairly average window of accessible particle sizes for contemporary instruments, is highly variable, it is normally no less than 100 cm^{-3} in remote locations [9]. Even in cases where single particle instruments have been flown into the stratosphere number densities at the highest attained altitudes (~20 km) in this size window normally exceed 0.5 cm^{-3} [10].

There are atmospherically relevant issues, which are dependent on particles with much lower number densities, however. For example, cirrus ice clouds are known to exert a large radiative forcing on the Earth's climate system due to the combination of their high altitude and large global coverage [11]. Experimental studies of the aerosols which readily nucleate ice, and thus likely form the basis for ice cloud formation, have shown that such particles, termed ice nuclei, have a typical abundance of only between 1 and 10 l^{-1} [12]. Past studies of IN size have relied on electron microscopy because the technique is sensitive at the single particle level. Studies in the free troposphere over the central United State, for example, found a mode size for efficient ice forming aerosols between 100 nm and 1 μm geometric diameter with a peak at ~200 nm [13]. With the addition

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of energy dispersive X-ray analysis, chemical composition of IN was made possible and it was found that most IN are composed of refractory elements, such as mineral dust or metal oxides [13–15]. EM is, however, an off-line technique and significant care must be taken to prevent artifacts during sample handling and preparation [16]. The labor intensity required has restricted past studies to 100's of particles. Analysis takes place in vacuo and volatile materials are not discernable. IN components are also indistinguishable if they have the same composition as the sample substrate.

Laser desorption/ionization mass spectrometry is known to have several important limitations [17]. For example, ionization efficiencies for common aerosol components can be widely disparate, mass spectral characteristics can be highly dependent on particle matrix and the surface of large and/or highly refractory particles can be over-sampled with respect to the bulk [17]. Despite these limitations, the on-line nature, high signal-to-noise and sensitivity to volatile and refractory components renders laser desorption/ionization mass spectrometry superior to traditional electron microscope analyses of ice nuclei.

Several groups now employ techniques to determine the size and chemical composition of atmospheric aerosols using mass spectrometry. Other instruments, many of these described in detail within this special issue, have comparable, and in some cases superior, capabilities. The purpose of this publication is to describe the modification made to the particle analysis by laser mass spectrometry instruments to facilitate our investigation of low number density species, such as ice nuclei, to document the current status of the instruments and to quantify the performance of these modifications.

2. Experimental

The particle analysis by laser mass spectrometry instrument has been described in detail previously [18,19]. There are two PALMS instruments. The 'ground instrument' was originally designed and built in the early 1990's. It serves dual functions as a ground based single particle instrument used in laboratory [20,21] and field [22,23] studies and as a prototype and testbed for the second 'flight instrument'. The PALMS ground and flight versions have essentially identical components and performance with the exception of the aerodynamic inlets and computers described in the next sections. The other major difference between the two instruments is that the flight instrument is more compact so as to fit within the confined space of the nose of a NASA WB-57F high altitude research aircraft and later a wing pod on the NOAA P-3 [19,24]. Additional differences, related to the power, heating and vibration isolation requirements of a flight instrument, also exist but are not relevant to the discussion here. Since the previous PALMS instrument technical publications the ground and flight instruments have undergone changes. In the case of the ground instrument, these modifications were undertaken in order to perform studies of the chemical composition of ice nuclei at the Desert Research

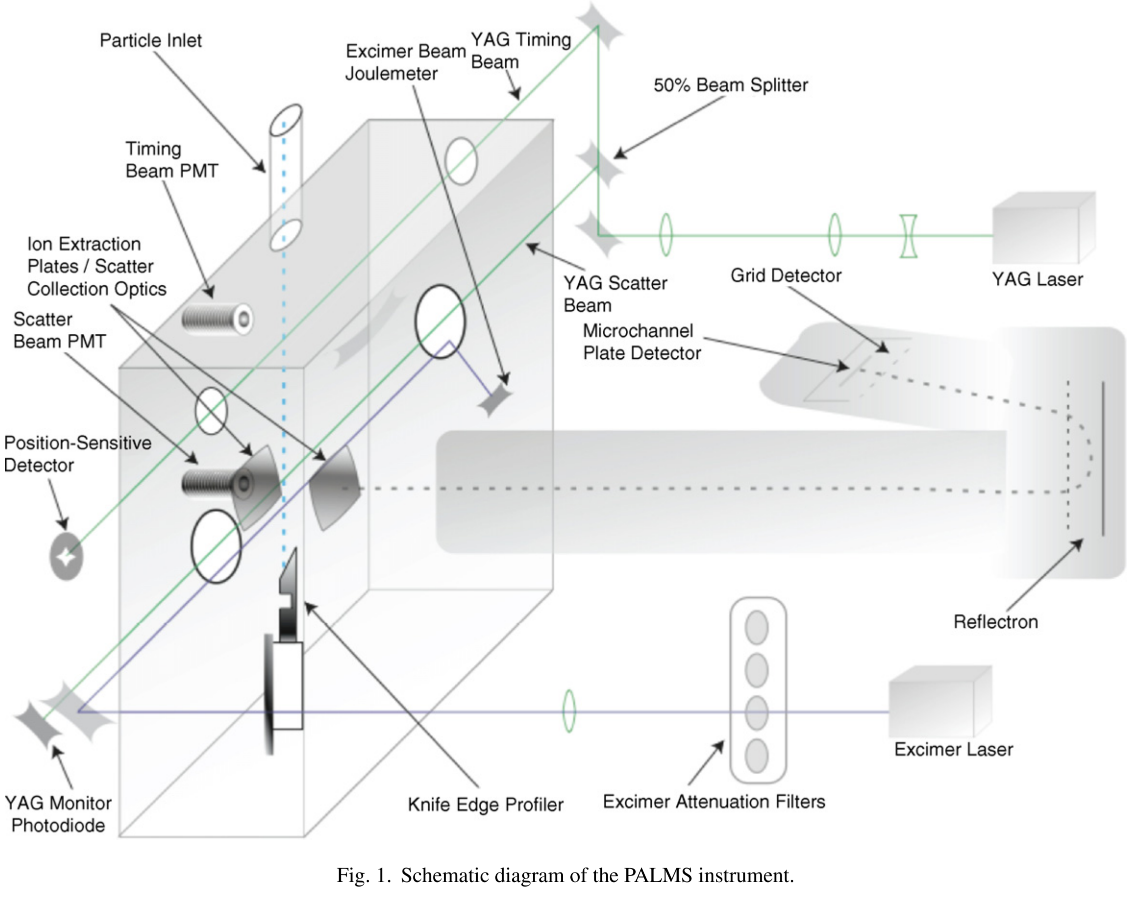

Fig. 1. Schematic diagram of the PALMS instrument.