

Aerosols and Mass Spectrometry Instrumentation

Aerosols are tiny particles of matter in liquid or solid state that are suspended in a gas or in air. They range in size from 3nm to 200 μm . Aerosols in our atmosphere are constantly undergoing chemical and physical changes, which affect not only the atmosphere, but also other realms of the Earth system such as the hydrosphere, biosphere, and the cryosphere.

There are various classification systems for aerosols. Aerosols can be referred to by their chemical composition; for example, there are organic aerosols and inorganic aerosols. Organic aerosols are further classified into two groups based on how they were formed: Primary Organic Aerosols (POA) and Secondary Organic Aerosols (SOA). POA are directly released into the atmosphere as condensed particles. Some common sources include fossil fuel burning, biomass burning, wind-driven or human-driven suspension, biological material, and sea-spray. SOA are formed from the condensation and nucleation of gases in the atmosphere or as a result of chemical reactions of volatile gases in the atmosphere. Another category is carbonaceous aerosols, which are also classified into two groups: organic/brown carbon, which consists mostly of hydrocarbons, and elemental/black carbon, material like soot. Carbonaceous aerosols are classified based on their thermal and refractivity properties. Elemental/black carbon absorbs more light and has a greater index of refraction than organic carbon. Inorganic aerosols are grouped into categories based on chemical composition like sulfates, nitrates, and ammonium.

Aerosols are of particular relevance in human affairs because of their effects on climate and human health. Aerosols affect the “energy balance” of our Earth, known as radiative forcings. Solar and terrestrial radiation cause changes in the energy fluxes of the earth, causing either a cooling effect (negative forcing) or a warming effect (positive forcing). It is estimated that the direct, net affect of aerosols is a negative forcing, since most aerosols reflect incoming solar radiation. Aerosols indirectly complicate one of the greatest uncertainties in climate modeling, clouds. Cloud condensation nuclei (CCN) are particles with condensed water on their surfaces. The clouds with CCN have smaller water molecules, resulting in greater reflectivity and a greater net cooling effect on the earth. Ultra fine particulate matter, aerosols with a diameter less than 100 nm, have been linked to a variety of pulmonary illness because of their ability to penetrate deep into human lungs and enter the blood stream. There lies a great uncertainty in the role aerosols play in the effecting the quality of human health and one of the major crisis facing the world today, climate change.

Atmospheric scientists use a variety of instrumentation to take quantitative and qualitative measurements of aerosols. Unfortunately, not all the instruments needed are commercially available, so the need to build a custom instrument arises; Time-of-Flight Mass Spectrometers (ATOFMS) fall into that class of instruments. A mass spectrometer identifies compounds based on its mass-to-charge (m/z) ratio by ionizing the compound and accelerating it through an electric or magnetic field. The mass spectra produced are a graph charting the relative intensities (y-axis) of the m/z peaks (x-axis). There are many different types of mass spectrometers, but an ATOFMS determines the m/z of an aerosol by

measuring the amount of time it takes the ionized particles to reach the detector from the moment it is ionized. The fundamental concept of an ATOFMS is that the duration of time the ionized compounds spend in “flight” in the field free region is proportional to the square root of the mass-to-charge ratio.

The ATOFMS analyzes one particle at a time, as opposed to a bulk quantity, so one is able to acquire an entire mass spectrum per particle. The instrument also analyzes particles in real time, as opposed to analyzing the particles after an elapsed time period. These two properties of the ATOFMS are essential because aerosols are constantly undergoing changes; they vary in the atmosphere throughout space and time. In a bulk quantity, the nature of these changes is harder to pinpoint when one cannot distinguish between particles in a mass spectrum. And the real-time measurements are crucial because a particle can easily undergo a chemical or physical reaction after an elapsed period of time.

The ATOFMS is divided into three regions: the inlet, the sizing region, and the mass analyzer. The inlet consists of a Po neutralizer, critical orifice, and an aerodynamic lens. The neutralizer is packed with radioactive polonium. The polonium emits ionized alpha particles, ionizing the surrounding air molecules. When charged aerosols pass through this region, they attract charged air molecules that neutralize their charge by imparting a Boltzmann charge distribution. (The particles need to be neutralized so the pulse laser will be less likely to miss the particles when it enters the ionization region located in an electric field.) The function of the critical orifice is to introduce particles from the atmosphere into a vacuum via a dramatic drop in pressure and accelerate them to a “critical” velocity. The aerodynamic lens then collimates the particles into a beam by accelerating them through a series of chambers, each of decreasing pressure and decreasing outlet diameter. It is important that the particles travel in a straight line to be perpendicular with three laser beams in the other two regions of the mass spectrometer.

The sizing region has two continuous laser beams, 504 nm and 588 nm. When a particle passes through the first beam, the light scattered by that particle is focused by an elliptical mirror into a photomultiplier tube (PMT). The PMT filters and amplifies the light and converts it to a 5 Volts electrical signal that is sent to a timing circuit. The timing circuit starts a counting clock. When the particle passes through the second laser, a second PMT tells the timing circuit to stop the clock. Since the distance between the two lasers is fixed, and the elapsed time is known, the velocity of the particle can be calculated. The velocity gives information about 1) the size and possibly shape of the particle and 2) where the particle will be in what moment in time. The electronics is set up so that when the two continuous lasers detect a particle, the timing circuit tells the pulse ionization laser when to fire.

The third and last region of the instrument is the mass analyzer, this is where the particles are ionized and fragmented by a 266 nm Nd:YAG solid-state laser. Afterwards, they are accelerated by an electric field until they reach the detectors, one for positive ions and another for negative ions. The distance traveled, in the mass analyzer, by the particles is elongated by use of a reflectron, a series of concentric, charged, ring plates. The reflectron acts as an ion mirror. The more kinetic energy a particle has, the deeper into the field it penetrates. The reflectrons improve the resolution of the mass spectra by elongating the relative time of arrivals between the particles. A mass spectra is finally generated by the computer with a source-apportionment software that interprets the series of bits from

the detector and groups the particles into clusters such as organic carbons, elemental carbon, sulfates, organic aerosols, etc.

Understanding the changing chemistry of the atmosphere is what drives the study of aerosols. Most of the organic aerosols in the atmosphere have yet to be classified. We remain largely in the dark about what kinds of chemical reactions and physical alterations are taking place in the atmosphere involving aerosols. The ATOFMS is particularly suited for taking measurements of aerosols because it measures single particles in real time; we get to measure how our atmosphere changes with respect to space and time. Expanding our knowledge about aerosols can help guide policy decisions aimed at improving and protecting our health and mitigating the anthropogenic effects of climate change.

References:

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