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## Automated aerosol Raman spectrometer for semi-continuous sampling of atmospheric aerosol



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### ABSTRACT

Raman spectroscopy (RS) is useful in characterizing atmospheric aerosol. It is not commonly used in studying ambient particles partly because automated instrumentation for aerosol RS has not been available. Battelle (Columbus, Ohio, USA) has developed the Resource Effective Bioidentification System (REBS) for automated detection of airborne bioagents based on RS. We use a version of the REBS that measures Raman spectra of one set of particles while the next set of particles is collected from air, then moves the newly collected particles to the analysis region and repeats. Here we investigate the use of the REBS as the core of a general-purpose automated Aerosol Raman Spectrometer (ARS) for atmospheric applications. This REBS-based ARS can be operated as a line-scanning Raman imaging spectrometer. Spectra measured by this ARS for single particles made of polystyrene, black carbon, and several other materials are clearly distinguishable. Raman spectra from a 15 min ambient sample (approximately 35–50 particles, 158 spectra) were analyzed using a hierarchical clustering method to find that the cluster spectra are consistent with soot, inorganic aerosol, and other organic compounds. The ARS ran unattended, collecting atmospheric aerosol and measuring spectra for a 7 hr period at 15-min intervals. A total of 32,718 spectra were measured; 5892 exceeded a threshold and were clustered during this time. The number of particles exhibiting the D-G bands of amorphous carbon plotted vs time (at 15-min intervals) increases during the morning commute, then decreases. This data illustrates the potential of the ARS to measure thousands of time resolved aerosol Raman spectra in the ambient atmosphere over the course of several hours. The capability of this ARS for automated measurements of Raman spectra should lead to more extensive RS-based studies of atmospheric aerosols.

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## 1. Introduction

### 1.1. Importance of atmospheric aerosol particles and their size and composition

Atmospheric aerosols can cause diseases, degrade visibility, and affect the weather and global climate. Atmospheric

aerosols are associated with increased cardiovascular disease, chronic obstructive pulmonary disease, and other illnesses [1]. Many harmful components of aerosols are known, e.g., carcinogens such as benzo[a]pyrene and other polycyclic aromatic hydrocarbons in soot, or heavy metals such as mercury in emissions from coal-fired power plants. However, there are many unknowns regarding the compositions and sizes of particles that contribute most to the harmful effects of aerosols on health [2–4]. Some diseases of humans (e.g., [5]), other animals (e.g. [6]) and many plant pathogens

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[7] are transmitted through the air by fungal spores, bacteria, and viruses. Aerosols affect climate and weather by scattering, absorbing, and reemitting radiation, and acting as cloud [8] and ice [9] condensation nuclei. Bioaerosols such as bacteria and fungal spores may be significant contributors to ice nucleation under certain conditions [10,11]. There are large uncertainties regarding the effects of biological and other aerosols on climate [12]. As a result, improved techniques for characterizing atmospheric aerosol size and composition are needed for a better understanding of the effects of aerosols on health, agriculture, visibility, climate, and weather.

To address these needs, improved instruments that can run continuously and provide information on the composition and size of individual aerosol particles are needed. Single-particle measurements are important for quantifying minority species in a population, determining the mixing state of aerosols [13,14] and its relation to climate forcing [15], and understanding the processing of particles in the atmosphere. Examples of single-particle instruments include aerosol mass spectrometers [16], aerosol fluorescence spectrometers [17,18], and instruments which measure Raman spectra [19] or electron-beam excited x-rays [20] from collected particles. The topic of this paper is Raman spectroscopy (RS) for deriving information about single particles in the atmosphere using an automated measurement method.

## 1.2. Raman spectroscopy for characterization of atmospheric aerosols

Because the intended audience for this paper includes researchers who may have little familiarity with RS, we state here some of the features that make RS appealing for single-particle, and even semi-continuous, characterization, of atmospheric aerosol:

a) Raman spectra have a relatively high information content because, like infrared (IR) absorption spectra, they are dependent on the vibrational and, when applicable, rotational frequencies of the molecules in a sample. Typically, many or most of the vibrational bands in IR spectra also appear in Raman spectra. In RS, an electron, in a ground state with frequency  $\omega_0$ , is excited by a laser with photon energy  $hc\omega_L$ , where  $h$  is the Planck constant and  $c$  is the speed of light, to an intermediate transient state. The excited electron almost immediately drops to an energy level with vibrational frequency  $\omega_n$ . To conserve energy, a photon is emitted having an energy  $hc\omega = hc\omega_L - hc\Delta\omega$ , where  $\Delta\omega = \omega_n - \omega_0$ . Vibrations that are very weak in IR spectra may be strong in RS and vice versa. For many pure materials with molecular weights less than a few hundred daltons, Raman and/or IR spectra can serve as fingerprints. RS can differentiate between many different bacteria [21], fungal spores [22], and pollens [23]. RS may also be useful for differentiating types of soot [24], a feature important in studies of climate and the health effects of aerosols. The large majority of materials have readily measured Raman spectra. Although pure alkali halides (e.g., NaCl, KF) have negligible Raman spectra, sea spray aerosols,

which are primarily NaCl, contain other inorganic salts and biological and other organic materials that appear in Raman spectra [25]. The fluorescence of most pure materials, on the other hand, is negligible or very weak. There are limits on the information that can be obtained for complex mixtures using RS because weaker lines of primary compounds may overlap the strong lines of secondary compounds [19]. Similar limits apply when studying complex mixtures using other high-information content techniques such as mass spectrometry (MS), IR spectroscopy, or nuclear magnetic resonance spectroscopy.

- b) Raman spectra can be generated using one laser and one detector array, where the photon energies of the laser and the detected photons are far from the energies of photons at the vibrational frequencies of interest. A single laser in the visible or near IR can generate a Raman spectrum from 200 to 4000  $\text{cm}^{-1}$ . If, for example, the Raman spectrum is generated using light at 640 nm, the detector must only be sensitive to light at wavelengths from approximately 640 to 860 nm in order to measure the Raman spectrum from 0 to 4000  $\text{cm}^{-1}$ . Laser sources in the visible and near IR are relatively inexpensive. Charge-coupled device (CCD) detectors throughout the visible and near IR can be sensitive with low noise.
- c) Raman spectra can be measured from particles with volumes of less than  $1 \mu\text{m}^3$ , depending upon the material and the excitation and collection optics, because it is an inelastic scattering measurement. Raman microprobes, RS instruments with confocal, epillumination geometries, have been used for over 40 years [26]. IR absorption spectroscopy, in contrast, typically requires larger sample volumes. Attempts to develop techniques to measure the IR absorption by measuring and analyzing the elastic scattering patterns of individual particles have been made [27].
- d) RS has relatively simple instrumentation requirements that are relatively inexpensive. RS only requires a narrowband laser, a good CCD, a spectrometer, imaging optics and optical filters, and a way to collect the aerosol and move the sample into the focal plane under the excitation-collection optics. It does not require sample preparation or high vacuum.
- e) Raman spectra include contributions from the molecular vibrations of molecules throughout the particles, at least for particles with little or no black carbon or other particles that are not too large, e.g., greater than  $30 \mu\text{m}$ , depending upon the excitation wavelengths. This ability to include information about molecules throughout the particle (when not too large or absorbing) arises because Raman spectra can typically be measured with excitation and emission wavelengths where most of the light is not absorbed by the particle.
- f) The measured Raman spectrum is the sum of the Raman and fluorescence emission and therefore can also provide information about molecules that are fluorescent at the excitation wavelength. Although fluorescence spectra are broad and lack the informational content of Raman, we suggest that their combination with RS can be useful, especially regarding bacteria, pollens, and

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