Application of SERS on the chemical speciation of individual nanoparticles

Ryota Kunihisa¹, Ayumi Iwata², Masao Gen^{3,4}, Chak Keung Chan⁴, *Atsushi Matsuki⁵

1. Graduate School of Natural Science and Technology, Kanazawa University, 2. Faculty of Science and Technology, Keio University, 3. Institute of Science and Engineering, Kanazawa University, 4. School of Energy and Environment, City University of Hong Kong, 5. Institute of Nature and Environmental Technology, Kanazawa University

The smallest of atmospheric particles are less than 100 nm in diameter and also termed as nanoparticles. The subset of particles in this size range can also act as cloud condensation nuclei and have significant impact on the regional and global climate. Also, human exposure to anthropogenic nanoparticles is an emerging health concern since their impact maybe overlooked by the conventional regulatory measures such as PM₂₅. However, the chemical speciation of nanoparticles is technically challenging because of the minute particle mass. There is a constant need for more effective collection method and sensitive chemical analysis, which can detect and resolve the evolution of the chemical compounds of nanoparticles in the atmosphere. In this study, we examined the applicability of surface enhanced Raman spectroscopy (SERS) on the rapid and sensitive chemical analysis of nanoparticles. SERS provides a drastic enhancement of the scattering efficiency over traditional Raman spectroscopy. The novelty of the proposed technique is that a SERS substrate was directly used as a sampling substrate of nanoparticles in the condensation growth tube (CGT) sampler (Series 110 Liquid Spot Sampler, Aerosol Device Inc.), which can activate nanoparticles into water droplets ($^{3} \mu$ m) and ensures their inertial impaction on the SERS substrate. Additional advantage is that while the SERS substrate requires the analyte in the form of water solution but Spot Sampler can activate nanometer-sized particles into large liquid droplets (~3 µm). Using the SERS method, we investigated laboratory generated ammonium sulfate and levoglucosan particles of 20 nm, 50 nm, and 100 nm, as well as ambient nanoparticles. Based on the successful detection of the peaks corresponding to sulfate $v(SO_4^{2-})$ and organics v(C-H) modes, our proposed method of combined CGT sampler and SERS technique showed sensitivity high enough for detecting major chemical components from nanoparticles as small as 20 nm. Furthermore, comparison of chemical composition inferred both from current method and that from hygroscopicity of ambient particles showed consistent results.

Keywords: nanoparticle, droplet activation, Raman spectroscopy, SERS