Review of “Physicochemical analysis of individual atmospheric fine particles based on effective surface-enhanced Raman spectroscopy”

Summary

This study describes the use of Ag foil as a potential SERS substrate for the analysis of atmospheric aerosols. The concept is interesting is the nicest thing I can say about this work. From start to finish the manuscript is poorly written, poorly referenced, has poor data, and makes improper and incorrect use of the data. Key information is not provided, figures are not labeled, and assumptions are made without explanation or justification. An example that really stuck out was in Figure 4A where an AFM image of the foil with linear grooves is shown (with many issues noted below), but then the authors decide to represent the surface as spherical nanoparticles and then do modeling based on this. Perhaps I misunderstood something, but if I didn’t, I cannot remember such an egregious misuse of data in a paper I have reviewed. Another example of the poor scientific quality is the discussion of Figure 6 where the authors justify that their intensities are better than prior work, by comparing spectra from their paper and 2 others that are all given in “arbitrary units”. The problem is, that arbitrary units are in fact arbitrary and highly dependent on user settings, instrumental design, and a host of other factors. If the other studies had simply collected the spectra 8 times longer they intensities would have been the same, not 8 times lower. This is magnified by the fact that no information is given about how long spectra were collected in this work. That kind of analysis is simply unscientific and not publishable. On the whole the paper does not provide very much information and what it does provide is not of sufficient quality for AMT. There are numerous other issues listed below, but I am recommending for the first time in many reviews for EGU journals that this manuscript should be rejected. Unless the authors completely redo the paper with new and better data, better analysis, better writing, and better understanding of atmospheric particles it should not be published. My apologies that this all comes across so harshly, but this is really poor work.

Comments

- Overall the quality of the grammar and writing needs to be improved in a revised manuscript. Proper singular versus plural, spacing, and other issues cropped up repeatedly.
- Page 1 Lines 24-27: This sentence on single particle methods lists multiple method used for single particle analysis, but only includes a single reference for each method and mostly (except AFM) chooses recent work and not the original work. As an example single particle mass spectrometry in its different forms has been around for 25 years, yet the only paper cited is from 2015 and is not one of the early or seminar works. Someone reading this paper wouldn’t realize that these methods were not recently developed or that there were 3-4 groups that developed this in the early 90’s. I realize this is a long comment, but better use of citations would improve the manuscript considerably.
- I think it would be worth noting that SERS using silver foil has been around since the 1970’s and was the initial substrate used by Van Duyne and others to study the SERS effect. From reading the introduction, the reader would have no knowledge of the fact silver foil has been used for decades in SERS studies and some context would be helpful.
- Page 3 Lines 1-2: The authors say that sampling time was chosen to “ensure particle monodispersion”. Monodispersive means that only one size of particles is in a population, which is impossible in an ambient environment, particularly a polluted location like Beijing. The sentence should be revised to clarify what the authors meant.

- Page 3 Lines 10-12: What grating is in the spectrometer? How many grooves per mm? What is the spectral range? What is the spectral resolution? All of this info may help explain understand the rather unconvincing data in Figure 3 below.
- Page 3 Lines 13-14: Almost no information about the AFM used is given. For example, what kind of tip was used? Most AFM studies have at least a few sentences describing the system and how it was operated, nothing is provided here beyond the model name, please expand this considerably.
- Page 3 Lines 22-23: This sentence should be revised and broadened as filter sampling has been occurring for 50 years (not just since 2001) and the readers could be directed to many of the seminal reviews and books rather than a single paper on a field study in Beijing from 2001.
- Page 3 Line 26: how long were samples collected? Only the time of 16:00 is mentioned, but no information on the duration of sampling was provided.
- Figure 1: It is unclear what the top portion of this figure adds to the paper. The operation of cascade impactors and Raman microscopes is very well established. The inset with the magnifying glass is fine, but similar in concept to many of the prior SERS of atmospheric particles papers in the literature. I would remove the entire top portion as it is does not provide any scientific information (would work for a TOC figure, though AMT does not do those).
- Page 3 Line 29 – Page 4 Line 2 and Figure 2: It is very well established how difficult it is to do optical microscopy-based spectroscopy methods on Teflon and quartz filters (again going back decades), but this is presented as a finding. Also, Al foil has been used in dozens of papers with Raman analysis and Ag foil in a few, so the sentence would be improved if it said "As prior work has shown (REFS), the flat surfaces…"
- Figure 2 (cont'd): The stage of the impactor is used for the particles in Figure 2 is not stated. Since the abstract focuses on particle aerodynamic diameter, this needs to be clearly stated.
- Page 4 Line 5: Space needed between Fig. and 3
- Figure 3: This figure has a number of flaws that need to be addressed.
    - The authors state this is 25 randomly selected points from Al foil and Ag foil. Based on Figure 2 the particles were not evenly distributed across the substrate. Thus, how do the authors' know that they are getting sample from particles at all 25 points. Also, why sample randomly, instead of focusing on particles that can be identified with the microscope prior to Raman analysis. Lastly, were individual particles being analyzed or was there enough overlap and a high enough loading that each point could have had multiple particle contributing.
    - 1) The signal for both Al foil and Ag foil is really weak in comparison to ambient samples from the literature. In particular, 987 and 1040 cm^{-1} is incredibly weak and poorly resolved from the background. What objective was being used (not listed)? In the methods all the options on the instrument are listed, but I can't find where the ones being used for this data are given. This might help explain this incredibly low signal.
    - Why is only 600-1750 cm^{-1} shown? The author state an interest in organics, but one of the main regions with the most intensity for Raman of aerosols is the C-H stretching region (2800-3050 cm^{-1}).
        - The authors don't discuss in the text the peaks due to the D and G bands of soot between 1300-1650 cm^{-1}. They should read and reference Doughty and Hill (2017), which has a detailed exploration of soot and Raman for ambient particles.
- Figure 4: If I am understanding this figure properly, this has fatal flaws that should not be published

- A) All the caption says is this is an AFM image. Is this a height map? Deflection map? Where is the color scale to allow the reader to interpret the image? Why is there a blue line across it? If this is foil, why is there a particle at 0.5 microns y-axis and 0.3 microns x-axis? The information provided and description need to be substantially improved for this to be a publishable image.
- B) If I am understanding correctly, the authors too the foil image and somehow said that b) represents the surface roughness. Forgive the casual language, but how on earth did the authors describe the straight lines of the foil in part a as spheres with a regular pattern in part b? Woah! This is not okay! Also no information is given about how this was done or justification for using something in the model that looks nothing like the AFM image it is nominal based on.
- C) What is the y-axis? Nanometers? What is the spatial and height resolution of the instrument? If the x-axis is microns, how was that used to justify a surface roughness of 5 nm? It also does not appear as regular as the model conception of evenly spaced 5 nm balls in part b. Is the spatial resolution in 4C even 5 nm? If so it is barely that low from looking at the data.
- D) What parameter were used to run the model in 4D? What does the color bar represent?
- E) How was crystal violet applied to the substrate? Was it aerosolized beforehand? If so, how? Was it impacted? Was a drop placed on the surface? None of this information was provided. A nice touch would be labeling the peaks with frequencies or modes.
- F) Why are doesn't the spectrum in 4F have the silicon phonon mode ~1000-1100 cm^{-1}. This seems like a poorly functioning Raman or some sort of issue. I get that the authors are trying to show on the same scale as 4E, but it is not possible to see the modes in the spectra well as presented. This should be amplified by at least a factor of 10 (just note it) so that the modes can be seen. At 10 mM I am surprised the signal is so low.

- Page 4 Lines 14-15: The authors state that "The FDTD model was setup for Ag foil according of the AFM results with a surface roughness of AgNPs of about 5 nm". How did the authors get from the AFM results to silver nanoparticles of 5 nm? No information is given and it seems to contradict the image in 4A.
- Page 4 Lines 23-24: The authors state "However, the experimental SERS enhancement factor in this work (4.3×10^4) was very close to the FDTD simulation result (4.6×10^4)". Given that the data put into the simulation as far as I can tell is incorrect, the similarity of these values is not meaningful, which calls into question the subsequent conclusions in that sentence. When it comes to models, even ones as good as FDTD, it may sound harsh but "garbage in, garbage out".
- Page 4: Line 30: fluorescence not fluorescent
- Page 5 Lines 1-4: That higher intensity Raman spectra are obtained for lower wavelength is well established and in any spectroscopy textbook.
- Page 5 Lines 9-11: The authors state "Based on our previous studies, PM2.5 is composed of various chemical species, which can be divided into three main groups based on bulk analysis: (1) inorganic ions; (2) carbonaceous species; and (3) trace elements (Cheng et al., 2016; Xu et al., 2017)." This all has been well known for half a century and the authors state it as though it was their discovery. This should be revised.

- Page 5 Line 12: The authors refer to Figure S2 and Table S2. There are two major issues with these figures.
    - First many salts were analyzed that would never appear in any appreciable amount in the atmosphere. For example bismuth nitrate, lanthanum nitrate, mercury sulfate, and many more.
    - Secondly, the salts that would appear in the atmosphere have almost all been run previously and published. Some going back 40-50 years, while others have been compiled more recently. Craig et al. (2017) and Ault et al. (2013) for example examined the frequencies of common sulfates and provide references to the initial spectroscopic identifications. No references are given to any prior published work on any of these common salts and a more systematic approach is needed for this work.
    - A minor issue is that none of the modes are identified. Peak frequencies are listed for a compound, but no information on the mode (symmetric? Asymmetric? Bending?) are given. For most spectroscopy publications this lack of detail would never be publishable.
- Figure 5: 5A-D the scale bar is barely legible. Does it say 10 microns? Also the loadings on these substrates are clearly quite high so and many particles overlap with other particles. Any analysis is thus an average of several particles and not individual particle analysis.
- Page 5 Line 22: What is the NanoMeasurer software? What does it do? How does it do it? None of this is explained. What are the value units? It is stated they agree with theoretical values? What are those theoretical values and how were they determined? Figure 5E-H? Is this supposed to be a size distribution of particle diameters from image analysis? If so, this cannot be used given that the particle loadings have overlapping particles, none of the dimeters on A, B, and possibly C would have any meaning.
- Figure 6: The authors state that many small peaks between 1250-1750 cm^{-1} could be organics, but all I see are graphitic peaks with a small amount of fluorescence on top. Without spectra out to 3000 cm^{-1} I'm not sure how this assignment can be supported.
- Page 6 Lines 3-10: The authors compare their work to other work based on intensity. However, this is done by comparing intensities that all 3 papers give as arbitrary units. This is a huge spectroscopy flaw, as arbitrary units are arbitrary and very dependent on setting and other instrumental factors. This should be removed as it is unscientific.
- Page 6 Lines 20-22: The authors comment that organic component identification is challenging, but this work, unlike most others does not look at the spectral range that gives key information about organic carbon (2800-3050 cm^{-1}). The authors need to note the limitations of their analysis.
- Figure 7: Why is the same schematic that was in Figure 1 shown again? This should only be used once.
- Figure S1: Are these of these of the same spot? If so, how do the authors know that? If not, how is it comparable? Also why are no peaks labeled? If the point is that as wavelength decreases intensity goes up, how come the 785 spectrum has a mode at 1600, but the 633 nm spectrum does not? Much more information is needed to be able to understand this figure.
- Table S1: Are these just the size cut points of the impactor? No information or explanation is provided as to what these values represent? If they are concentrations what are the units?

References:

Ault, A.P., Zhao, D., Ebben, C.J., Tauber, M.J., Geiger, F.M., Prather, K.A., Grassian, V.H., 2013. Raman microspectroscopy and vibrational sum frequency generation spectroscopy as probes of the bulk and surface compositions of size-resolved sea spray aerosol particles. Phys. Chem. Chem. Phys. 15, 6206-6214.
Craig, R.L., Bondy, A.L., Ault, A.P., 2017. Computer-controlled Raman microspectroscopy (CC-Raman): A method for the rapid characterization of individual atmospheric aerosol particles. Aerosol Sci. Technol. 51, 1099-1112.
Doughty, D.C., Hill, S.C., 2017. Automated aerosol Raman spectrometer for semi-continuous sampling of atmospheric aerosol. Journal of Quantitative Spectroscopy and Radiative Transfer 188, 103-117.