Optical Spectroscopy of Venus Aerosol Analogs and Substrate Survivability

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Introduction: Aerosol Rapid Analysis Combined Entry Probe/Sonde Technology (AERACEPT) is a dual descent probe and in-situ sampler of cloud and aerosol particles, used as part of the Nephele mission concept to study Venus cloud layers. Various optical spectroscopic characterization methods, including Raman spectroscopy and Surface Enhanced Raman Spectroscopy (SERS), Laser induced Breakdown Spectroscopy (LIBS), and absorbance and fluorescence spectroscopy are being assessed for viability for compatibility with AERACEPT. Specifically, the detection limits, sensitivity, specificity, and analysis cadence of these techniques for a set of Venus aerosol analogs and their mixtures are tested. We report on preliminary optical spectroscopy results of the Venus aerosol analogs, as well as optical substrate survivability in heated and acidic conditions, substrate physical robustness, and analyte wettability on substrates.

Venus aerosol analogs and test matrix: Table 1 shows a simplified Raman test matrix with non-SERS and SERS substrates, different laser wavelengths, and both single component and multicomponent aerosol analogs. The red aerosol analog shown forms after mixing propanal (0.1M) and sulfuric acid (81 wt%).

Table 1. Raman test matrix

Substrates	Lasers/method	Venus aerosol analogs
Reference substrates	405-Probe	***Single component***
Diamond wafter (CVD, but rough texture)	785-Probe	propanal
Si	405-microRaman	sulfuric acid + water
glass slide	532-microRaman	water
sapphire window	785-microRaman	tryptophan
stainless steel	1064-Raman desktop	anthrarufin
Teflon		DI H2O
SERS substrates		***Multicomponent***
Impossible Sensing Ag on Si SERS		propanal + sulfuric acid
Hydrophilic Ag SERS substrates on ITO glass		propanal + water
Hydrophobic Ag SERS substrates on ITO glass		
Hydrophilic Ag/Au SERS substrates on ITO glass		
Hydrophobic Ag/Au SERS substrates on ITO glass		
Graphene film on Quartz substrates		
Graphene film on SiO2/Si substrates		
Graphene film on Cu foil substrates		

Preliminary optical spectroscopy findings:

Raman. Fig. 1 shows example Raman spectra of propanal and sulfuric acid on monolayer graphene on Si (left) and Si (right), measured with 532 nm excitation laser. While both substrates show sulfuric acid and propanal peaks, graphene demonstrates a fluorescence quenching effect for sulfuric acid.

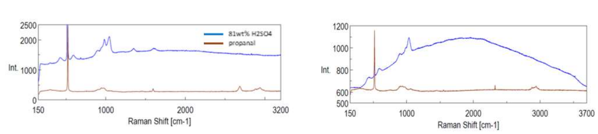

Figure 1. H_2SO_4 and propanal on graphene/Si (left) and Si (right)

SERS. In SERS, nanostructured materials, commonly Ag or Au, enhance signal through amplification of electrical fields or increased surface area. Fig. 2 shows an example of SERS spectra and analog interaction.

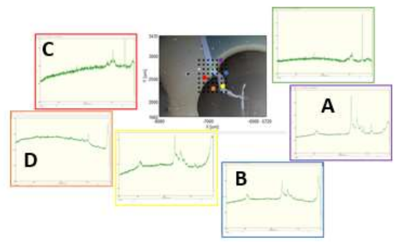

Figure 2. Raman mapping at 532 nm shows interaction of H_2SO_4 and propanal. H_2SO_4 reduced enhancement of organic and obscured the propanal signal. [A]: Ag SERS substrate, enhanced organic features [B]: Propanal, C-H stretch features evident near 2700 cm^{-1} [C]: H_2SO_4 [D]: Propanal interacting with H_2SO_4, loss of propanal features.

Raman Fluorescence. Fluorescence of propanal-H_2SO_4 mixture is evident at every excitation wavelength, obscuring features of both sulfuric acid and trace organic, as shown in Figure 3.

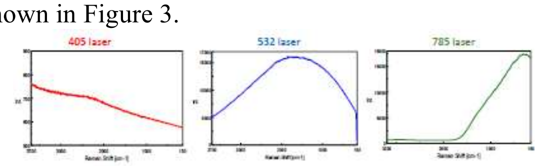

Figure 3 Fluorescence of H2SO4-propanal with different excitation wavelengths

Substrate Survivability: Ag SERS substrates were exposed to H_2SO_4 at room temperature and at 80°C. Substrates exposed to heated H_2SO_4 experienced complete delamination of coating, while substrates exposed to room temperature H_2SO_4 experienced coating degradation, but not complete delamination (Fig 4).

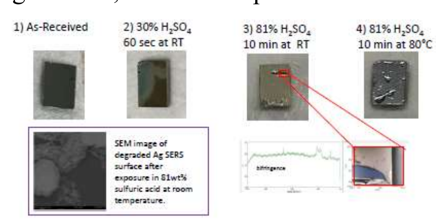

Figure 4. optical substrate heat and acid exposure

Substrate Wettability: Substrate wettability, from hydrophobic (left) to hydrophilic (right) in Figure 5, is an important consideration when detecting analytes as it can affect Raman signal as well as analyte chemistry.

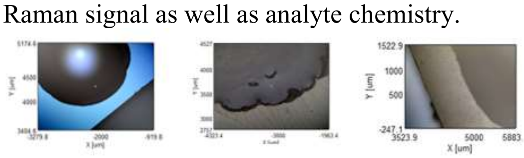

Figure 5. H2SO4 wettability on different substrate