

# **sFundamental studies of surface-enhanced Raman scattering (SERS) using aerosolized substrates**

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## **ABSTRACT**

The research presented in this paper improves potential for the application of surface-enhanced Raman scattering (SERS) in remote detection and analysis. Remote (stand-off) Raman sensing, with its ability to “fingerprint” analyte based on their unique vibrational spectra, offers great potential to address the challenging analytical problem of identifying unknown substances in low concentrations in the form of vaporous emissions or clouds. An inexpensive nebulizer/spray chamber was designed to study the mixing of aerosolized SERS (surface-enhanced Raman scattering) active nanostructures with a vapor phase analyte, the fluorophore Rhodamine 6G (R6G). Improved signal intensities (EF=200) are gained *via* SERS. Vapor phase mixing of the analyte and substrate is rapid (< 5 seconds).

**Keywords:** SERS, remote sensing, nanoparticles, Raman, spray chamber, stand-off detection, aerosol substrate, ~~XXX~~, ~~XXX~~

## **1. INTRODUCTION**

In their early days, both ~~the~~ lasers and Raman spectroscopy were frequently cast as “answers in search of a problem.” Currently, lasers are integral components in everything from DVD players to scanning confocal microscopes, and Raman spectroscopy rivals infra-red absorbance its popularity as quantitative and qualitative analytical technique. Similarly, surface-enhanced Raman spectroscopy (SERS) has been broadly viewed as more of an interesting phenomenon, rather than a useful analytical method. While SERS remains a difficult technique with which to quantitate, recent results show that the enormous relative increase in Raman scattering enables an increasing number of sensitive applications including the detection of chemical warfare agents and toxins, single molecules spectroscopy and dynamics, and biosensing *in vitro* and *in vivo*.<sup>1-5</sup> We believe that we can further extend the usefulness of SERS by combining with the nascent field of remote Raman sensing.

The identification of unknown substances in low concentrations in the form of vapors emissions or clouds is challenging analytical problem. Remote Raman sensing offers great potential to address this problem, most notably the ability to “fingerprint” analyte based on their unique vibrational spectra. Remote Raman sensing is a promising technique, yet the inherent weakness of the Raman scattering effect severely limits its practical application. SERS can enhance Raman scattering by orders of magnitude, yet there remains the difficulty in combining the techniques of remote sensing with the inherent need for a surface and analyte proximity to that surface for SERS occur.

This paper describes the development of a model system to study the potential application of surface-enhanced Raman scattering (SERS) in remote detection and analysis. Among the most extensively studied SERS active substrates are colloidal hydrosols. Dispersion of nanoparticle hydrosol by a nebulizer results in a nanoparticle/aerosol. Herein, it is demonstrated that improved Raman scattering intensities can be gained via SERS of aerosolized analytes.

## **2. REMOTE (STAND-OFF) RAMAN SPECTROSCOPY**

~~The identification of unknown substances in low concentrations in the form of vaporous emissions, clouds, or on contaminated surfaces is challenging analytical problem. There are many circumstances where it is desirable to identify a substance remotely, e.g. for reasons of accessibility (such as analysis by extraterrestrial probes, or tall smoke stacks), or where a potential for harmful exposure exists (such as in the detection of chemical warfare agents as in the Tokyo Sarin gas attacks, or toxic emissions like Bhopal).<sup>6,7</sup> Remote Raman sensing offers-possesses great potential to address this problem.~~ advantages over competing techniques in that most notably the ability to unambiguous molecular identification

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by the unique characteristics of vibrational spectroscopy—“fingerprint” analytes based on their unique vibrational spectra.<sup>8</sup> Typically, when a photon scatters off a molecule, it Rayleigh scatters; it undergoing-undergoes no change in energy-or-wavelength. In the Raman scattering process the scattered photon loses (Stokes shift) or gains (anti-Stokes shift) an amount of energy equal to that of a vibrational mode of the molecule. If the electron returns from the virtual energy state to a lower energy state than

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when it started, the photon has gained energy and has a shorter wavelength, and if the final energy level of the electron is greater than the original level, the scattered photon is of a longer wavelength than the original incident photon. Raman scattering occurs for vibrations that result in a change in the polarizability of the molecule's electron cloud. Not all vibrations are Raman active, but for the vast majority of substances (including homodiatomics) there are sufficient Raman scattering lines in the spectrum to uniquely identify the molecule. It is this ability to molecularly "fingerprint" a molecule by its vibrational spectrum that makes Raman scattering such an appealing method for identification of unknown substances, particularly in potentially hazardous situations where proper identification of the target analyte is necessary for correct remediation methods to be implemented.

Remote (or stand-off) Raman spectroscopy essentially takes Sir C.V. Raman's original experiment and stands it on its head. Rather than using a telescope to gather and concentrate the sun's light into an intense source of photons with which to generate Stokes shifted photons from a sample, remote Raman spectroscopy uses a telescope to collect the Raman scattering from a sample that is irradiated with monochromatic light (*viz.*, laser).<sup>9,10</sup> Remote Raman spectroscopic techniques can be categorized into two broad classes: hyperspectral or chemical imaging methods, and more traditional single point analysis. In the single point configuration, a laser is shone on a sample, and the Stokes-shifted photons gathered with a telescope and passed to a spectrometer for analysis. Stand-off ranges of tens of meters have been achieved with impressive results. Chemical imaging approaches generate similar spectral information, but rather than obtain information from a single point, *x* and *y* spatial data are paired with each spectrum. This results in a data cube, or, when projected into two dimensions, a chemical image where pseudocoloring can be used to indicate a particular chemical species as identified by its spectral signature.<sup>11,12</sup> The *x* and *y* information is obtained by rastering the laser across the sample, or by use of a tunable filter, such as an LCTOF. Within the past decade, both types of stand-off detection have seen a dramatic increase in interesting and resultant publications. Remote Raman spectroscopy has found applications in geology, extra-terrestrial chemistry, and environmental and atmospheric analysis.

However, Raman scattering is an inherently weak process, with only about 1 in 10<sup>8</sup> incoming photons undergoing inelastic Raman scattering.

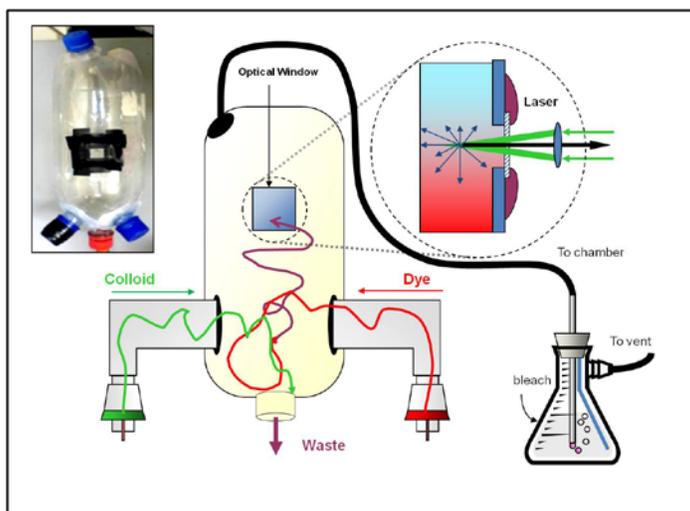


Figure 1. Schematic diagram of the spray chamber. A 2 L soda bottle serves as the body. Holes were drilled on opposite sides to accommodate tubing from medical grade nebulizers. Solutions of analyte and SERS active colloid could be vaporized from either side. Mixing of vapor droplets occurs within the body of the chamber. An optical window was fitted orthogonally to the two nebulizers. Spectra were obtained through the glass by focusing the laser excitation/photon collection volume within the interior of the chamber. Liquid waste was drained from the bottom, and excess gas phase materials vented through the top and were sent to a bleach trap (left inset). A photograph of the chamber is shown in the upper right inset.

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### 3. SURFACE-ENHANCED RAMAN SPECTROSCOPY

Since its initial discovery in the 1970s, SERS has been an attractive option to regular Raman scattering, in that the intensity of the observed scattering is enhanced greatly, thereby enabling lower limits of detection. When an analyte is adsorbed at or near a nanoscale roughened noble metal surface, the intense electromagnetic fields generated by the localized surface plasmons (collective oscillations of the conduction band electrons), act like a “lightning rod,” increasing the intensity of both the incoming excitation photon as well as the outgoing Stokes shifted photon. Typical enhancements are on the order of a million fold, while in some cases the enhancement factors can be as large as  $10^{14}$ .

This positions SERS as the only vibrational spectroscopy capable of single-molecule detection. SERS experiments are traditionally performed either in aqueous phase or on metal surfaces *in vacuo*. Recently, SERS has been applied to difficult sensing problems where spectral identification of an analyte at low concentrations is the target molecule, *e.g.* the *in vivo* detection of glucose or a cancer tracer, or the detection of the chemical warfare agent (CWA) stimulants half-mustard and malathion. While the latter case demonstrated that SERS can be used to detect vapor phase analytes, the SERS aspect of the experiment required a surface, and a complex sampling system to get the vapor to said surface.

Recent experiments have successfully combined SERS with remote detection. The results of those studies impressively demonstrate that SERS signals can be acquired over large distances, but the experiment involved dosing a SERS active substrate with an analyte, and then detecting the signal down range. Truly remote sensing would require us to get the surface to the analyte cloud or contaminated surface, and to then spectroscopically interrogate the system via a Raman capable telescope. Dispersal of an aerosolized solution of SERS active colloids, *e.g.* by munitions or up-wind spraying, seems the most likely method of bringing the enhancing surface to the remote location. This research demonstrates proof-of-concept that an aerosolized substrate can be successfully used to generate SERS from a gas phase analyte.

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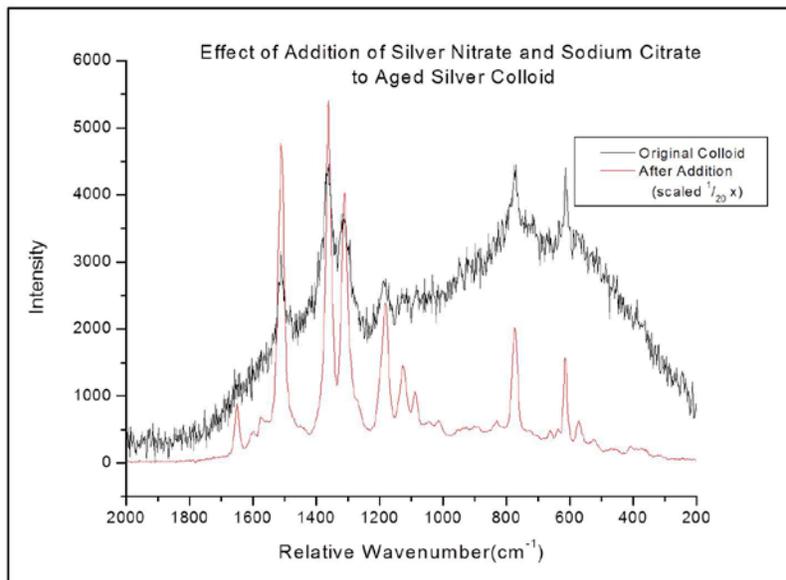


Figure 2. Recovery of SERS activity. The SERS spectra of R6G incubated an aged colloid (lower, less intense curve), and of R6G incubated in the aged colloid after has been “refreshed” by addition of silver nitrate and sodium citrate (upper, more intense curve).

## 4. METHODOLOGY

### 4.1 Design and construction of the spray chamber

The spray chamber was constructed from two disposable medical nebulizers with T connections (Vixone, U.S. Medical Supplies), an empty two-liter soda bottle, one 500 mL plastic bottle, and an 18 mm circular #1 microscope cover glass (Corning). First, two holes approximately 1.5 inches in diameter were drilled on opposite sides of the bottle. Flexible tubing from the nebulizers was inserted into each hole, and sealed with silicone sealant (StarBrite). To form a gas vent, a 1 inch hole was made in the rounded portion bottom of the bottle, and the top of a 500 mL water bottle (including the cap and threading) was grafted onto this hole and sealed with silicone sealant. A second bottle cap was drilled and fitted with a length of tubing. The tubing was then run to metal rod inserted into a rubber stopper on a side arm flask filled with bleach. The rod was below level of the bleach, ensuring destruction of the vapor phase material as it passed through the bleach. Escaping gas was vented via the side arm, and routed to the fume hood. The cover glass was functionalized with trimethoxy(propyl)silane (Sigma-Aldrich) or Rain-x spray to prevent droplet formation. An optical window was fabricated by drilling a 1 cm hole in the bottle orthogonal to (and vertically offset from) the two nebulizers, and covering the hole with the functional, and sealing carefully with the silicone sealant. The bottle was mounted in an inverted position, allowing the original cap to be used as a drain for accumulated liquid waste.

### 4.2 Synthesis and reactivation of colloids

Silver colloids were synthesized according to the Lee and Miesel procedure. Briefly, ~25 mg of  $\text{AgNO}_3$  in 250 mL of deionized water was brought to a rapid boil with stirring. While boiling, 5 mL of a 1% sodium citrate (Sigma-Aldrich) solution was added. The initially clear solution turned transparent yellow, then an opaque greenish-grey. The colloid was permitted to cool to room temperature, and stabilized with additional citrate. To make colloids stored for extended periods of time SERS active again, 0.0138 g of silver nitrate and 1 mL of 1% citrate were added under mild stirring at room temperature. The colloid was mixed with  $1 \times 10^{-4}$  M R6G in a small glass sample vial, and spectra acquired (1 sec) on a DeltaNu Advantage NIR Raman system (default settings:  $\lambda_{\text{ex}} = 785$ , power = 120 mW).

### 4.3 Concentration studies: determining limits of detection

A series of dilutions of from  $1 \times 10^{-3}$  to  $1 \times 10^{-6}$  M R6G were prepared. Aliquots of the R6G were incubated with 300  $\mu\text{L}$  of silver colloid and water was added to reach a final volume of 0.6 mL. Final concentrations ranged down to  $1.3 \times 10^{-7}$  M R6G. The solutions were placed in small glass sample vials, and spectra accumulated for 9 seconds.

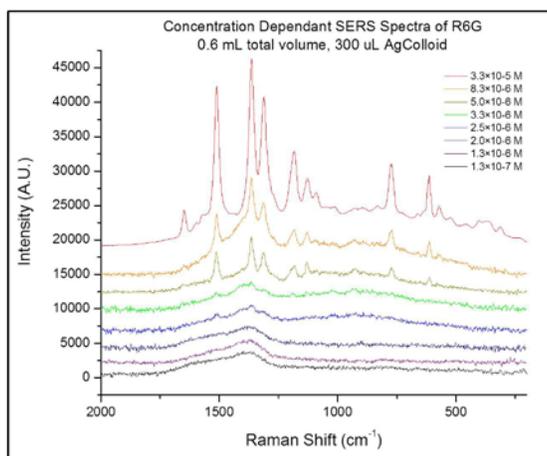


Figure 3. SERS spectra of varying concentrations R6G mixed with a fixed volume of colloid in a total volume of 0.6 mL. From top to bottom the concentrations are  $3.3 \times 10^{-5}$  M (scaled by a factor of 10),  $8.3 \times 10^{-6}$  M,  $5.0 \times 10^{-6}$  M,  $3.3 \times 10^{-6}$  M,  $2.5 \times 10^{-6}$  M,  $2.0 \times 10^{-6}$  M,  $1.3 \times 10^{-6}$  M,  $1.3 \times 10^{-7}$  M. Spectra have been offset for clarity.

#### 4.4 Proof of concept: SERS from aerosolized substrates

To test the proof of concept, the following experiment was conducted. A solution of  $1 \times 10^{-4}$  M R6G was placed in the left nebulizer, and a solution of freshly prepared colloid was placed in the right nebulizer. The distance attachment was affixed to the spectrometer, which was then moved into position such that the focal spot was through the optical window and inside the spray chamber. The software was set for 9 second spectral acquisitions. House air was applied to the nebulizers, which resulted in a fine mist of aerosol dye and colloid entering and mixing within the spray chamber. The two aerosol streams mixed, and spectra were obtained. For a positive control, colloid was mixed with  $1 \times 10^{-4}$  M R6G and placed into a single nebulizer, and ultrapure water was placed in the other nebulizer. Spectra were acquired as above. A blank was obtained by placing ultrapure water in both nebulizers, and recording the spectrum. Two negative controls were conducted. In the first case, colloid was placed into one nebulizer, and pure water in the other. In the second case, one nebulizer was filled with  $1 \times 10^{-4}$  M R6G, and the other with pure water. Spectra were obtained as above.

#### 4.5 Temporal response of the system

Airflow was applied to a nebulizer containing Ag colloid, and a 1 second spectrum collected. Airflow was then established to the nebulizer with dye, as rapidly as possible for the operator (~3 seconds) a spectrum (1 second) of colloid and  $1 \times 10^{-3}$  M R6G was obtained as above. Then, the airflow to nebulizers was cut, and a 1 second spectrum obtained as rapidly as possible by the operator (~4 seconds). Collection of the individual spectra and operator response time averaged below 5 seconds. Air flow volume was recorded at 5 L/min, and the mobilization rate was 0.25 mL/min.

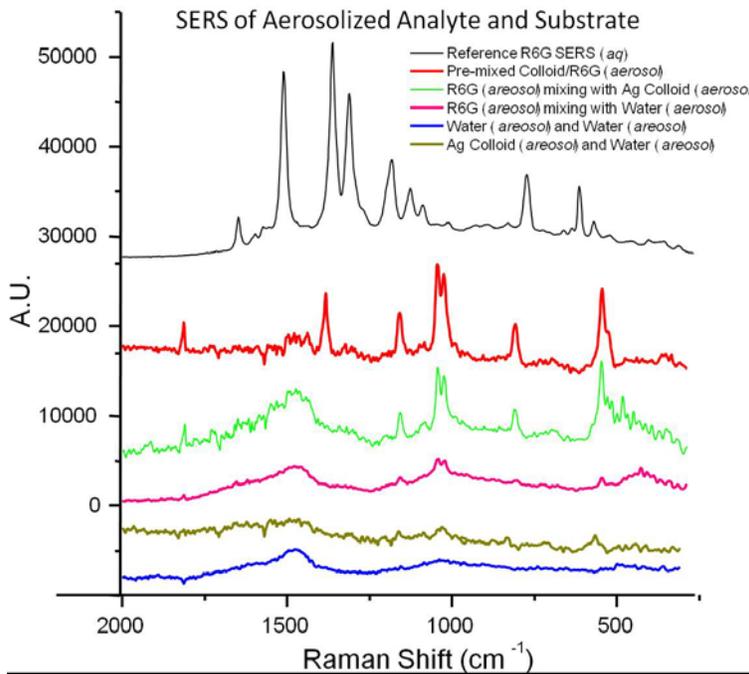


Figure 4. SERS of aerosolized substrates and analytes, and controls. From top to bottom, the spectra are of: 1) a reference SERS spectrum of R6G in aqueous solution, 2) the positive control where in colloid and analyte are mixed before spraying and detected, 3) Ag colloid and R6G (0.1 mM) sprayed from separate nebulizers, 4) negative control with R6G and pure water sprayed from opposite nebulizers (scaled up by a factor of 10 to show the vibrational peaks), 5) negative control with

Ag colloid and water sprayed from separated nebulizers, and 6) pure water aerosolized from simultaneously sprayed for both nebulizers. Spectra have been off-set for clarity.

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## 5. RESULTS AND DISCUSSION

### 5.1 Design of the spray chamber

Previous literature research revealed a dearth of simple and affordable designs for systems designed to study and simulate the effect of gas phase analytes. The present spray chamber was designed to be reusable, but of sufficiently low cost to be disposable should contamination occur. Figure 1 shows a simple schematic of the chamber, and a photograph. Disposable medical nebulizers were used to aerosolize both a solution of the target analyte and the SERS active colloid. Although these nebulizers do not give the same precision and control over droplet size and concentration as an ICPMS nebulizer, this is a reasonable approximation to “real world” conditions in which little to no control over dispersal conditions exist (such as a tear gas canister or smoke stack). These “chemical clouds” were then allowed to mix in a student designed and built spray chamber constructed from readily available inert plastic materials (*viz.* a 2 liter soda bottle). The glass window was cut into the spray chamber to enable acquisition of Raman spectra without interference from the plastic chamber itself. Silanization of the optical window prevented the accumulation of large beads of analyte on the surface (a possible false positive condition). The monolayer of silane provided minimal spectral interference, due to its very low effective concentration and the spatial distance from the focal volume of the spectrometer.

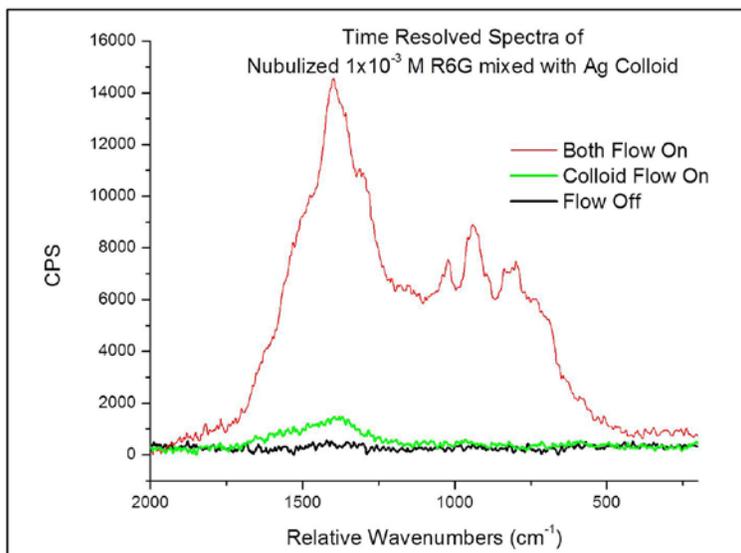


Figure 5. SERS spectra demonstrating temporal response of the system. Colloid and 1 mM R6G were placed in separate nebulizers, each nebulizer was attached to independent house air. Colloid was sprayed into the chamber, and spectrum recorded (middle trace). The nebulizer containing dye was then activated, and as rapidly as possible a 1 second spectrum obtained (upper curve). The flow to both nebulizers was cut, and as rapidly as possible the spectrum was obtained (lowest line).

## 5.2 Synthesis and reactivation of colloids

The temporal instability and lack of reproducibility on SERS substrates is a well-known and pernicious problem. Some of the causes of this great variation over time are known, such as oxidation of the surface and annealing of the nanoscale surface asperities. Great strides have been made in the development of methods that drastically improve both the life time and reproducibility of SERS surfaces including Ag island films (AgIFs), film over nanosphere surfaces (FONs), imbedding in hydro gel matrix, electron beam patterned surfaces (Klarite), and protection by atomic layer deposition (ALD) of alumina over nanosphere lithographically (NSL) fabricated arrays. Electrochemically roughened films can be regenerated by cycling the voltage. However, only sprayable colloid nanostructures are suitable for implementation in the above experimental scheme, and the phenomenon of colloids aging, and resulting in diminished SERS EFs is well known. Figure 2 shows that addition of additional AgNO<sub>3</sub> and reductant to an existing colloid will result in increased SERS. The lower trace shows the R6G SERS spectrum of the older colloid, and the upper (more intense) curve is of the same colloid after treatment with additional silver and citrate, followed by incubation in dye. The exact mechanism by which this occurs not known, but two possibilities exist: a) additional new particles are formed, and b) silver is reduced onto existing particles, regenerating their pristine surface. Absent access to a transmission electron microscope it is impossible to narrow down the possibilities, however, for the present case the fact that a method to “salvage” extant materials with less outlay of increasingly expensive noble metal reagents is useful.

## 5.3 Concentration studies: determining limits of detection

The series of dilution experiments were conducted to determine the operational parameters and limits of detection of the experimental apparatus. Higher concentrations of dye would result in higher signals, but could also cause irreversible aggregation of the colloid. Figure 3 shows several representative spectra over a range of concentrations. At higher concentrations, the SERS spectrum is quite distinct, showing many sharp and intense peaks. At concentrations of  $3.3 \times 10^{-6}$  M and  $2.5 \times 10^{-6}$  M R6G the characteristic peaks are barely distinguishable ( $S/N = 2$ ). The signal obtained at  $1.3 \times 10^{-6}$  M R6G is vanishingly small, and only the strongest peaks are present, with a  $S/N$  ratio approaching 1. Therefore, standard procedure was to use a concentration that was well above the lower limit of detection for subsequent experiments to ensure that measurable signal could be obtained with a minimal amount of analyte.

## 5.4 Proof of concept: SERS from aerosolized substrates

The ability of SERS spectra to be collected from aerosolized substrates of aerosolized analytes is demonstrated in Figure 4. The uppermost trace in Figure 4 represents a positive control for mixing, *i.e.* the analyte and substrate were allowed to react before being mobilized, but not necessarily a positive control for detection. It was very uncertain whether the spectrometer would be able to detect flowing aerosol streams and analytes in vapor droplets, as the total effective concentration would be substantially less than in the condensed liquid phase. The total EF for this system is surprisingly low, only ~801, but still represents a many-multi-fold increase in total signal. This, which could be useful in applications with analyte concentrations below the LOD for regular stand-off Raman detection systems. The experimental run (second trace from the top) resulted in measureable enhancements of ~238. The negative control utilizing dye (middle trace) shows some spectral features, but of far less intensity than the SERS amplified signals described above. The negative control with water and colloid has a broad spectrum, typically ascribed to adsorbed citrate, that is devoid of meaningful features. The blank (lowermost trace) is the spectrum obtained from spraying water from both nebulizers. This spectrum shows only noise at the integration times selected, but some features, *e.g.* the “hump” generated by Raman scattering from the glass in the window, is-are barely detectable even at higher zoom levels. Shifts in the spectra peak are observed in the upper three traces. It is uncertain if this is due primarily due to the changing phase (*e.g.* the spectra of glucose<sub>(s)</sub> and glucose<sub>(aq)</sub> are considerably different), or because of variation in calibration from changing the input optics on the spectrometer.

## 5.5 Temporal response of the system

The system was able to respond rapidly to changes in flow rates. Figure 5 shows an increase in the Raman scattering can be realized on the sub 5 second time scale. The rapidity of the mixing of the analytes is greater than anticipated, and subsequent experiments will address dependence on the mechanical operations of the experimenter. A reconfiguration of the chamber to spatially locate the optical window more proximally to the mixing site may result in greater time resolution, however it is strongly suspected that the mixing and enhancement occurs more rapidly than the 1 second minimum acquisition time available with the current instrumentation. It is not anticipated that longer acquisition times, slower flow rates, or greater spatial displacement of the window relative to the mixing point will reveal any particularly useful information regarding the kinetics of the system, as the enhancement factors for the positive control and

experiment described in section 5.4 are very similar in magnitude, suggesting that the subsequent reactions are minimal. The quick results are highly encouraging from a practical ~~stand point~~<sup>standpoint</sup>, as speed is often a decisive factor in being able to apply proper remediation or control measures.

## 6. CONCLUSION

There is a pressing need to be able to identify materials at long range. The past decade has seen a surge of interest in the field of stand-off Raman spectroscopy as a potential to fulfill this need.<sup>17-24</sup> This research demonstrates the potential for the application of surface-enhanced Raman scattering (SERS) in aerosolized samples, thereby expanding the reach of remote Raman to sample of low concentration. A spray chamber design was developed to test the feasibility of the aerosol SERS approach, and this equipment should prove useful for others in the field willing to trade precision of droplet size for savings in cost. The successful detection of mixed aerosolized substrate/analyte resulted in modest SERS enhancement factors of approximately 230, and measured EFs of 800 for pre-incubated dye/analyte aerosols. Determination of exactly quantitative results of SERS signals (*i.e.* a Beer's Law type of standard curve) is difficult under conventional experimental conditions, and made all the more difficult in the present work. The response time of the system was rapid, with mixing and spectral acquisition occurring at an operator limited rate of less than 5 seconds. Given the success of the initial dye studies, future research will focus on more realistic analytes, such as CWA surrogates or pesticide analogs, which show weaker SERS. More advanced studies will test and develop functional monolayer coatings to improve chemical selectivity of the nanoparticles with the vapor phase analytes and SERS active nanoparticle substrates.<sup>[3a, 4]</sup> The long-range impact of this project is expected have relevance to first responders, hazmat teams, environmental monitors, and defense agencies. The ability to detect and identify potentially life threatening or toxic chemicals from safe "stand off" distance would be invaluable to those professions, in that neither personnel nor equipment are placed at risk of exposure.

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## ACKNOWLEDGEMENTS

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## REFERENCES

- [1] Nie, S. and Emory, S. R., "Probing single molecules and single nanoparticles by surface-enhanced Raman scattering," *Science* 275, 1102 (1997).
- [2] Stuart, D. A., Yuen, J. M., Shah, N. C., Lyandres, O., Yonzon, C. R., Glucksberg, M. R., Walsh, J. T. and Van Duyne, R. P., "In Vivo Glucose Measurement by Surface-Enhanced Raman Spectroscopy," *Anal. Chem.* 78, 7211-7215 (2006).
- [3] Qian, X., Peng, X. H., Ansarin D.O., Yin-Goen, Q., Chen, G. Z., Shin, D. M., Yang, L., Young, A. N., Wang, M.D. and Nie, S., "In vivo tumor targeting and spectroscopic detection with surface-enhanced Raman nanoparticle tags," *Nat. Biotechnol.* 26(1), 83-90 (2008).
- [4] Stuart, D. A. Biggs, K. B. and Van Duyne, R. P., "Surface-Enhanced Raman Spectroscopy of Half-Mustard Agent," *Analyst* 131, 568-572 (2006)
- [4][5] Dieringer, J. A., Lyandres, O., McFarland, A. D., Shah, N. C., Stuart, D. A., Whitney, A. V., Yonzon, C. R., Young, M. A., Yuen, J., Zhang, X. and Van Duyne, R. P., "Surface-enhanced Raman spectroscopy: new materials, concepts, characterization tools, and applications," *Faraday Discussion* 132, 9-26 (2006).
- [6] Sharma, S.K., Lucey P.G., Ghosh M., Hubble H.W., Horton K.A. "Stand-off Raman spectroscopic detection of minerals on planetary surfaces," *Spectrochimica Acta Part A*, 59 (10), 2391-2407 (2003)
- [7] Misra, A. K., Sharma, S. K., Acosta, T. E., Bates, D. E., Clegg, S. M. and Wiens, R. C., "Standoff Bio-Finder For Planetary Exploration With Fast Detection," 43<sup>rd</sup> Lunar and Planetary Science Conference (2012).

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- [8] Docherty, F.T., Monaghan, P.B., McHugh, C.J., Graham, D., Smith, W.E. and Cooper, J.M., "Simultaneous multianalyte identification of molecular species involved in terrorism using Raman spectroscopy," *Sensors Journal IEEE*, 5(4), 632-640 (2005).
- [9] Product information, Delta Nu OBSERVER-LR <<http://www.intevac.com/intevacphotonics/deltanu/deltanu-products/portable-raman-spectrometers/observer>> (1 April 2012).
- [10] Rentz, J., Schwarze, C., Vaillancourt, R. and Hercher, M., "Standoff Raman measurement with COTS components," *Proc. SPIE* 5268, 28-339 (2004).
- [11] Ehlerding, A., Johansson, L., Wallin, S. and Östmark, H., "Resonance-Enhanced Raman Spectroscopy on Explosives Vapor at Standoff Distances," *International Journal of Spectroscopy* 2012, Article ID 158715, 9 pages (2012).
- [12] Treado, P. J., Nelson, M. P., Schweitzer, R., Gardner, C. and Wentworth, R., "Standoff Raman Hyperspectral Imaging Detection of Explosives," [Laser Applications to Chemical, Security and Environmental Analysis], OSA Technical Digest (CD), Optical Society of America., paper LThB1 (2008).
- [13] Hobro, A. J., and Lendl, B., "Stand-off Raman spectroscopy," *TrAC* 28(11), 1235-1242 (2009).
- [14] Scaffidi, J. P., Gregas, M. K., Laully, B., Carter, J. C., Angel, S. M. and Vo-Dinh, T., "Trace molecular detection via surface-enhanced Raman scattering and surface-enhanced resonance Raman scattering at a distance of 15 meters," *Appl. Spectrosc.* 64(5), 485-492 (2010).
- [15] McCabe, A., Smith, W. E., Thomson, G., Batchelder, D., Lacey, R., Ashcroft, G. and Foulger, B. F., "Remote Detection Using Surface-Enhanced Resonance Raman Scattering," *Appl. Spectrosc.* 56, 820-826 (2002).
- [16] Docherty, F.T., Monaghan, P.B., McHugh, C.J., Graham, D., Smith, W.E. and Cooper, J.M., "Simultaneous multianalyte identification of molecular species involved in terrorism using Raman spectroscopy," *Sensors Journal IEEE*, 5(4), 632-640 (2005).
- [17] Van Neste, C. W., Senesac, L. R. and T. Thundat, T., "Standoff Spectroscopy of Surface Adsorbed Chemicals," *Anal. Chem.* 81 (5), 1952-1956 (2009).
- [18] Bugay, D. E. and Brush, R. C., "Chemical Identity Testing by Remote-Based Dispersive Raman Spectroscopy" *Appl. Spectrosc.* 64(5), 118A-152A and 467-561 (2010).
- [19] Carter, J. C., Angel, S. M., Lawrence-Snyder, M., Scaffidi, J., Whipple, R. E. and Reynolds, J. G., "Standoff Detection of High Explosive Materials at 50 Meters in Ambient Light Conditions Using a Small Raman Instrument" *Appl. Spectrosc.* 59(6), 120A-138A and 707-851 (2005).
- [20] Li, H., Harris D. A., Xu B., Wrzesinski P. J., Lozovoy and V. V., Dantus M., "Coherent mode-selective Raman excitation towards standoff detection," *Opt. Express.* 16(8), 5499-504 (2008).
- [21] Misra, Anupam K.; Sharma, Shiv K.; Bates, David E.; Acosta, Tayro E. "Compact standoff Raman system for detection of homemade explosives," *Proc. SPIE* 7665, 76650U-76650U-11 (2010).
- [22] Ehlerding, A., Johansson, L., Wallin, S. and Östmark, H., "Resonance-Enhanced Raman Spectroscopy on Explosives Vapor at Standoff Distances," *International Journal of Spectroscopy* 2012, Article ID 158715, 9 pages (2012).
- [23] M. Gaft and L. Nagli, "UV gated Raman spectroscopy for standoff detection of explosives," *Opti. Mater.* 30(11), 1739-1746 (2008).
- [24] Misra, A. K., Sharma, S. K., Acosta, T. E., Bates, D. E., Clegg, S. M. and Wiens, R. C., "Standoff Bio-Finder For Planetary Exploration With Fast Detection," 43rd Lunar and Planetary Science Conference (2012).
- [25] Rentz, J., Schwarze, C., Vaillancourt, R. and Hercher, M., "Standoff Raman measurement with COTS components," *Proc. SPIE* 5268, 28-339 (2004).
- [26] Vogel, B., "Raman spectroscopy portends well for standoff explosives detection," *Jane's Defense Security Report*. <<http://www.janes.com/products/janes/defence-security-report.aspx?id=1065927739>> (1 April 2012)
- [27] Rivera, W. O., [Standoff Raman spectroscopy system for detection of explosives, Chemical Warfare Agents Simulants and Toxic Industrial Compounds], University of Puerto Rico, Mayaguez (Puerto Rico), *en passim* (2008).
- [28] Product information, Delta Nu OBSERVER LR <<http://www.intevac.com/intevacphotonics/deltanu/deltanu-products/portable-raman-spectrometers/observer>> (1 April 2012).
- [29] Treado, P. J., Nelson, M. P., Schweitzer, R., Gardner, C. and Wentworth, R., "Standoff Raman Hyperspectral Imaging Detection of Explosives," [Laser Applications to Chemical, Security and Environmental Analysis], OSA Technical Digest (CD), Optical Society of America., paper LThB1 (2008).
- [30] Hobro, A. J., and Lendl, B., "Stand-off Raman spectroscopy," *TrAC* 28(11), 1235-1242 (2009).

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- [23] Dieringer, J. A., Lyandres, O., McFarland, A. D., Shah, N. C., Stuart, D. A., Whitney, A. V., Yonzon, C. R., Young, M. A., Yuen, J., Zhang, X. and Van Duyne, R. P., "Surface enhanced Raman spectroscopy: new materials, concepts, characterization tools, and applications," *Faraday Discussion* 132, 9-26 (2006).
- [24] B. Sharma, B. Frontiera, R. R. Henry, A-I. Ring, R and R. P. Van Duyne, R. P., "[SERS: Materials, Applications, and the Future](#)," *Matr. Today*, 15, 16-25, (2012).