

# **Optimization of Time-Resolved Raman Spectroscopy for Multi-Point In-Situ Photon Counting**

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## **Abstract**

This study makes use of a Time-Resolved Raman Spectroscopy (TRRS) system developed in the Purdue Civil Engineering spectroscopy laboratory to advance technology critical to enable field deployment of Raman spectroscopic systems, with a primary focus on developing solutions to overcome two specific barriers to Raman analysis in the natural environment: (1) obtaining Raman spectra of chemical compounds at field-relevant concentrations, and (2) realizing economical spatial monitoring. To inform both streams of activity, this work first explores the role of component choice and apparatus design on Raman system output. A component-level Raman system transfer function is developed in terms of intensity, wavelength, and time which yields detailed insight into system performance that greatly exceeds traditional single “system factor” treatments of apparatus effects. The modelling frame provided by the transfer function is universally applicable in that it is inclusive of the majority of component choices that may be encountered in any open-path or closed-path Raman system, and is likely to be valuable in efforts to assess the performance benefits and limitations of system designs, modify or tailor apparatus layouts, facilitate experiment design, and compare results obtained on different systems.

The system characterization offered by the transfer function is then employed to develop a multi-photon counting algorithm realized through digital signal processing (DSP) which captures photon arrivals traditionally ignored in conventional counting methods. This approach increases acquired Raman intensity for any given analyte by using detector output voltage or a voltage-time product as an energy proxy – an approach that is likely broadly applicable to any spectroscopic techniques employing detectors that make use of the photoelectric effect. In experiments carried out on analytes (nitrate, isopropanol, and rhodamine 6G) in aqueous solutions, enhanced observations enabled by the multi-photon counting algorithm are shown to increase observed Raman intensities of low Raman-yield solutions 2.0-3.1-fold compared to single-threshold analysis, and also extend the upper observation limit of strong Raman-yield solutions that would

traditionally saturate detectors using a binary photon counting scheme. Notably, the improved performance offered by the multi-photon counting algorithm is realized through comparison of multi-photon and conventional counting algorithms applied to the same data in a post-processing exercise, thus eliminating any effects of test-to-test variation on results, and highlighting the ability to employ the developed counting approach without modification of traditional systems.

Additional insights from the system transfer function are also used to inform exploration of a novel approach to enable spatial environmental monitoring via Raman spectroscopy by combining fiber optics, optical switch technology, and the Raman system prototype. Tests designed to evaluate the system configured as a multiplexed optically switched fiber optic network demonstrate the potential to deliver excitation and collect Raman scattering from different desired monitoring locations with a sole excitation source and a single detector over substantial distances. Using nitrate as an example compound of interest, it is demonstrated that the system has a detection limit of 5 ppm within approximately 1.5 meters, which increases to 15 ppm at 100 m, and 38 ppm at 200 m. Modelling informed using the developed system transfer function highlights that improving the prototype by eliminating fiber connectors and making use of commercially available visible-light optimized fiber can substantially extend the range of the system, offering a 15-ppm nitrate detection limit at 2100 m. As increases in laser power, testing time, and collection optic efficiency are all also straightforward and viable, the prototype demonstrates realistic potential to achieve field relevant detection sensitivity over great distance.

As a final demonstration of system potential, a set of experiments on aqueous nitrate solutions is performed to understand the influence of turbidity, fluorescence, optics size, and varied raw data integration lengths on Raman observations. Results demonstrate that cumulative advances in the TRRS system establish a new generation of Raman spectroscopic sensing amenable to long-term environmental monitoring over significant spatial extent in complex in-situ conditions. Specific advances made herein include enhanced power delivery and scattered light collection informed by the system transfer function, increases in sensitivity from multi-photon counting, and incorporation of optical multiplexing. Overall, the Time-Resolved Raman Spectroscopic System (TRRS) now offers a set of capabilities that bring in-field deployment within practical reach.