



Final CTAP Report
National Technology & Engineering Solutions of Sandia, LLC
 Technical Assistance
 With
 Diné College

STATEMENT OF WORK

Under the CTAP Statement of Work, Sandia was tasked with providing technical assistance to Diné College to create a testing program to determine hazardous contaminant levels in donated hand sanitizer. Sandia will loan instrumentation, provide a procedure, and act as technical advisor. The challenge for on-site testing lies in a balance of testing capability/speed, complexity, and cost of operations. Instruments that allow fastest and least expensive operation will be validated for performance for this sample problem (hand sanitizer w/ poisonous methanol or 1-propanol). The objective of this project is to enable Diné College personnel to perform on-site testing.

BACKGROUND

The first goal of this technical assistance was to determine whether the Thermo First Defender (Raman spectroscopy) instrument, available for loan to Diné College from Sandia, was capable of detecting 1% methanol or 1-propanol (n-propanol) contamination in both ethanol- or isopropanol-based hand sanitizer. This is the level which has been deemed hazardous by the FDA, which issued warning statements at the height of the COVID-19 pandemic about brands/manufacturers whose hand sanitizers exceeded this level, even recalling multiple sanitizers. While literature suggests both Raman and FTIR are capable of measuring for these constituents, portable form factors are less established for this application. The second goal of this assistance will be to create a procedure enabling Diné to calibrate the selected instrumentation, and collect/process data, determining the contaminant levels in donated hand sanitizer and, thereby, evaluating their safety (i.e., are they below the 1% FDA guidance?).

METHOD

Measurement of methanol and 1-propanol contamination is technically challenging due to the variability of hand sanitizer formulations. Therefore, to validate the Raman measurements, hand sanitizer formulations were created in the lab and spiked with known contamination levels. This allowed for instrument suitability (ease of use and data processing along with performance), parameters, and calibration to be determined using 'clean' hand sanitizer samples, prior to using commercially available, highly variable formulations.

A total of twenty-six lab formulated reference standards were made, varying the concentration of the spiked contaminants, methanol and 1-propanol. Due to the small amount of material being spiked into a viscous media (glycerol-based), gas chromatography pulsed discharge ionization detector (GC-PDID) was

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used to verify the spiked concentrations of the contaminants. While GC-MS is a better standard for measuring these contaminants (Figure 1), portable options are not readily available.

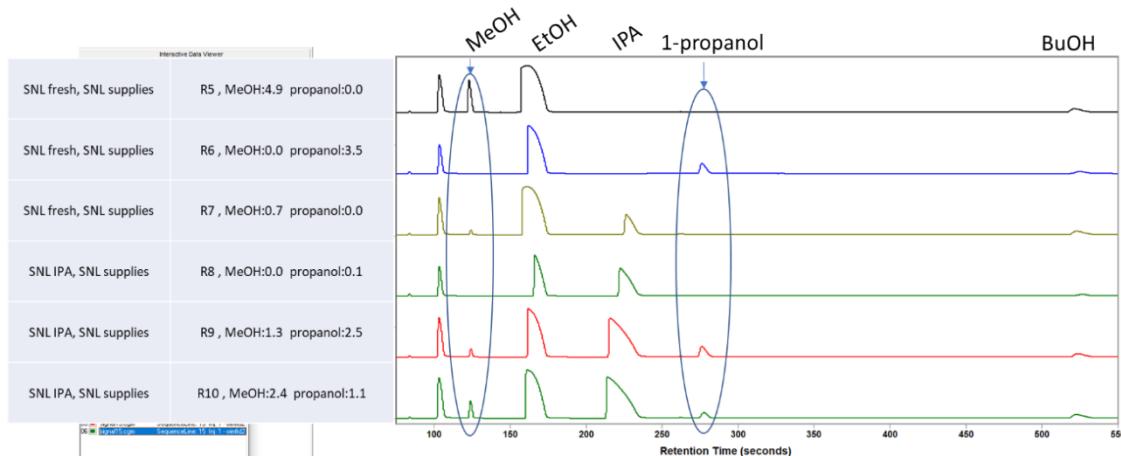


Figure 1: Example of GC-PDID chromatographs with clear resolution of methanol and 1-propanol contaminants.

CONCLUSION

Raman Suitability

All standards were analyzed by a handheld Thermo First Defender Raman spectrometer to determine methanol and 1-propanol signal resolution and attempt to calibrate the instrument for varying levels of these contaminants. However, there were issues observed in resolving both contaminants. As is evident in the pure reference spectra (Figure 2a), where methanol (MeOH) Raman signals overlap with multiple signals observed in ethanol (EtOH) and n-propanol (N-Prop). Figure 2b then illustrates the difficulty in observing changes to a lab formulated hand sanitizer mixture where 1-propanol is spiked.

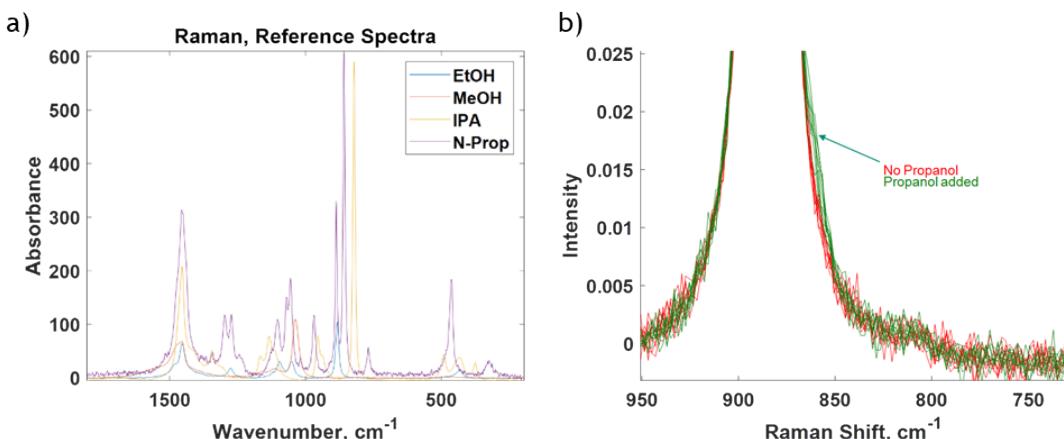


Figure 2: (a) Raman spectra of 'pure' reference materials. (b) Raman spectra (zoomed onto one signal) of lab formulated hand sanitizer solutions, one spiked with 1-propanol.

However, there was more success in comparison of other signals within the spectra, as can be seen in Figure 3. Based on the collected data, it was determined that the handheld Raman spectrometer was sensitive enough to provide the resolution needed to reliably measure the concentrations of hand

sanitizer contaminants above 1 vol%; however, it could not measure concentrations much lower than that 1 vol% (i.e., the method was able to determine if the contaminant level was above the recommended amount but could not provide a concentration below 1 vol%).

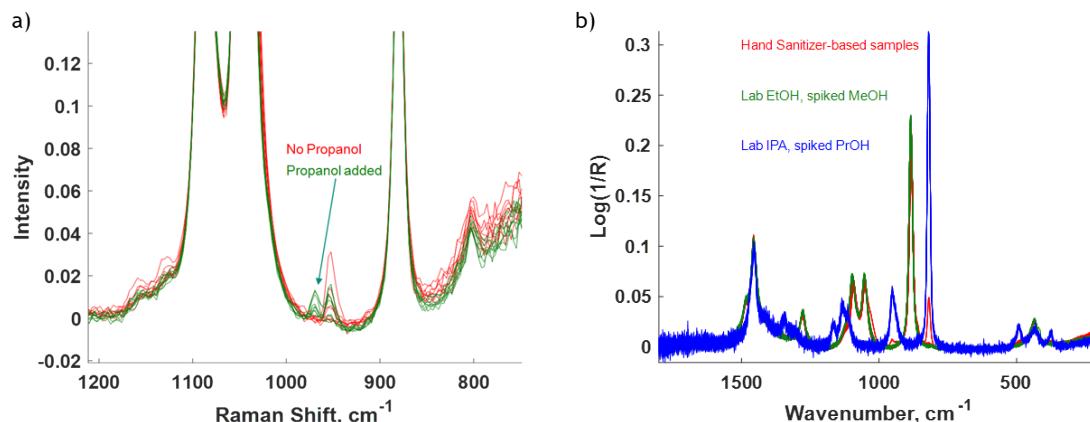


Figure 3: (a) Zoomed in view of a 1-propanol signal which was used for instrument calibration. (b) Overlaid Raman spectra of lab formulated and commercial hand sanitizers, some spiked with contaminants.

Changes to SOW

- **Extension from original completion date**

Due to the unexpected complexity of the Raman spectra of hand sanitizers, additional confirmational experiments were needed to support the Raman data and provide a procedure for Raman calibration and data processing.

- **Retirement of POC and assignment to new POC**

POC (C. Mowry) retired prior to the completion of this project and a new POC (J. Kustas) was assigned to complete the final reporting.

- **Companies retracted offer to provide Diné college with hand sanitizers**

Due to the unexpected complexity of the data analysis, there was a delay in providing a testing method to Diné college. During that time, the companies which were to provide the college with hand sanitizer retracted their offer. Therefore, the professor no longer needed to loan the spectrometer.

DELIVERABLES/OUTCOMES

From February-July, Sandia completed activities to support the creation of a testing program for Diné College to determine hazardous contaminant levels in donated hand sanitizer. The project resulted in the following:

- 1) Sandia determined the appropriate on-site instrumentation through thorough reference standard analysis.
- 2) Sandia established a data processing procedure which was suitable for undergraduate lab instruction.
- 3) Unfortunately, the professor no longer needed to request a loan of the handheld Raman instrument due to commitment changes in the acquisition of the hand sanitizers.