

COMPARISON OF FT-IR AND RAMAN SPECTROSCOPY: IDENTIFICATION OF COMMON CHEMICALS IN SAFETY & SECURITY APPLICATIONS

Correct and timely identification of chemicals and chemical compounds are required to ensure safety. In this work, a comparison of two proven techniques is performed on a set of chemicals considered “materials of interest” in safety and security applications.



INTRODUCTION

FT-IR and Raman are proven optical-based techniques used to identify a variety of chemical substances and compounds in a number of industries. Sometimes used as complimentary technologies, each provides benefits and advantages. However, for safety and security applications, FT-IR has often been regarded as the most effective analytical technique for identification of many chemical substances and compounds. In comparison, Raman has not been considered as a technically equal or superior method for identification or verification purposes. Since these previous studies had focused on 785 nm Raman instruments, we decided to expand the study and compare the 785 nm Raman and the Rigaku CQL™ 1064 nm Raman analyzer with FT-IR results.

The scope of the study involved analyses of common household chemical substances, specifically those sold as consumer goods but also utilized as clandestine laboratory materials. By themselves, these chemicals may be innocuous, but are frequently used in combination to manufacture compounds that pose a threat to public response teams and environmental safety. A variety of chemical types were selected, with a focus on materials considered best suited for FT-IR (Fourier transform infra-red). Approximately 60 materials were evaluated, covering materials from acids/bases, over-the-counter (OTC) products, fuels, biologicals and proteins, organic and inorganic salts, and a catch-all category for miscellaneous household chemicals commonly found in a basement or garage. The expanded test set provided a better representative sample of chemicals commonly found in a household, yet potentially used in a clandestine lab.

RESULTS

The easiest chemical set to consistently identify across all the instruments was the small organic molecules. These are molecules such as acetaminophen, ethanol, and other organic solvents and active pharmaceutical chemicals or chemical precursors to active ingredients. These types of chemicals tend to be short chain or smaller molecules and pose no problem in any of the molecular systems as they contain both polar side groups and multiple centers of symmetry and also often contain delocalized electron systems that make them easy to polarize. Thus, both FT-IR and Raman give reasonable and reproducible spectra. As the spectra have sufficiently intense and strong peaks, there tends to be no issue with selectivity as well. This also means that with strong FT-IR signals, there is still sufficient intensity to produce strong overtones and combinations for the NIR spectra.

Conversely, the biological and protein materials were the most difficult group to identify. For this group, the most consistent response was in NIR, followed by the 1064 nm Raman. FT-IR spectra tended to be noisy in most cases or, because biologicals (as in plant materials) tend to be mostly water, the spectra gave little information. For 785 nm Raman, no useable spectra were found due to extreme fluorescence issues that even with mathematical processing made it either time-consuming or not possible to extract out the small signals. In these instances, 1064 nm Raman (with the consequent lower fluorescence) was able to produce useful and reproducible spectra.

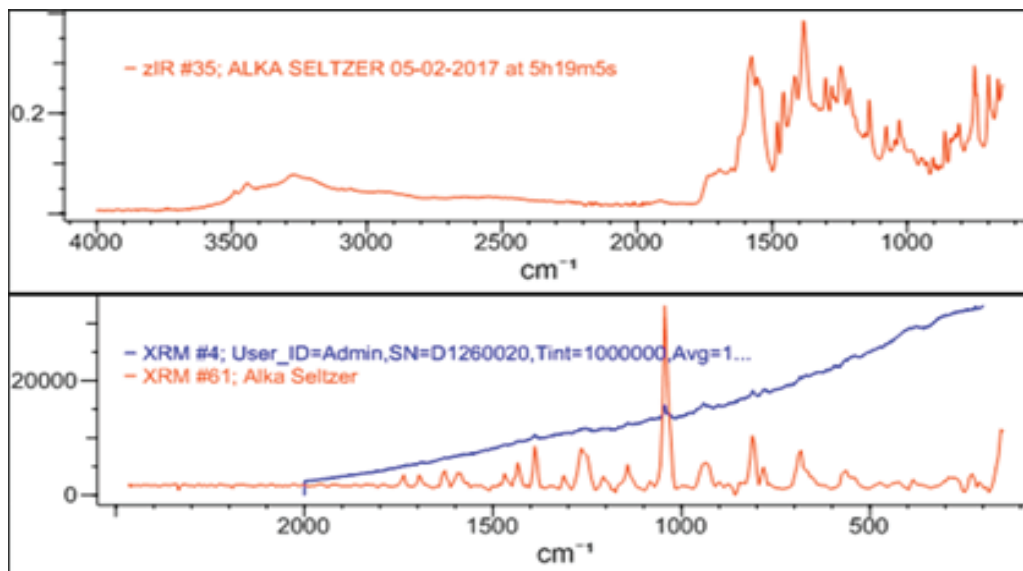


Figure 1. Comparison of spectra for FT-IR (top) and Raman (bottom): 785 nm in blue and 1064 nm in red for Alka Seltzer.

Another point to raise about the overall comparison in general, is the identification of mixtures. For FT-IR analysis the small spot size limits mixture analysis if the sample is heterogeneous and has varying particle sizes present. This was the results observed with common household materials that are mixtures of varying composition and colors. The heterogeneity tended to limit the identification in FT-IR and the fluorescence and colors limited identification in 785 nm Raman. For 1064 nm Raman, the colors and fluorescence were not an issue, although sample heterogeneity is still relevant, albeit to a less extent due to the larger spot size and the ability to quickly take multiple scans. In the cases of low concentration components in a mixture, the 1064 nm instrument may have selectivity issues with counter ions. Limitations for liquids tend to be water for FT-IR, the water band dominates the spectra, and smaller components may not be visible, especially as the percent of the minor component falls below 10%. The effect of diminishing results as the components fall below 10% is also present in Raman systems, but as water is not an issue for Raman, the systems can identify the minor components (down to a few %). This is an advantage in testing organic acids especially. The presence of water is the major reason for issues in FT-IR identification.

For Raman, the major reason for lack of identification was due to the fluorescence of these samples for the 785 nm Raman. The fluorescence and baseline noise also limited identification of colored materials. Conversely for the 1064 nm Raman, all the materials that had severe fluorescence in the 785 nm system were identified in the 1064 nm system. There was also the ability to identify biological and protein materials for the 1064 nm system. This gave results that had the 1064 nm system consistently performing similar to the FT-IR instrument for this data set. Recall that the reason the data set was initially chosen was due to the perception that this data was best suited for FT-IR and gave poor results in Raman. So while this still held true for the 785 nm Raman systems, we consistently got correct identification with the 1064 nm Raman instrument. A further advantage is that water did not limit the identification of many of the organic acids in this study for the 1064 nm Raman as those observed for the FT-IR.

The overall results are presented in the summary table (Figure 2), where the yellow Incomplete ID indicates either a missing component in a mixture ID or a non selective response for a counter ion. Red indicates an incorrect response and green indicates the material was correctly identified. Incorrect responses (red) are lower for the 1064 nm Raman than for the FT-IR, and this is due mostly to a lack of water interference. For correct identification (green) and reproducible spectra, the 1064nm Raman consistently performed better than both the FT-IR and the 785 nm Raman.

APPLICATION NOTE

Result:	IR	785 nm	1064 nm
Incomplete ID	13	27	13
Incorrect ID	7	4	1
Correct ID	35	24	41
Total Samples	55	55	55

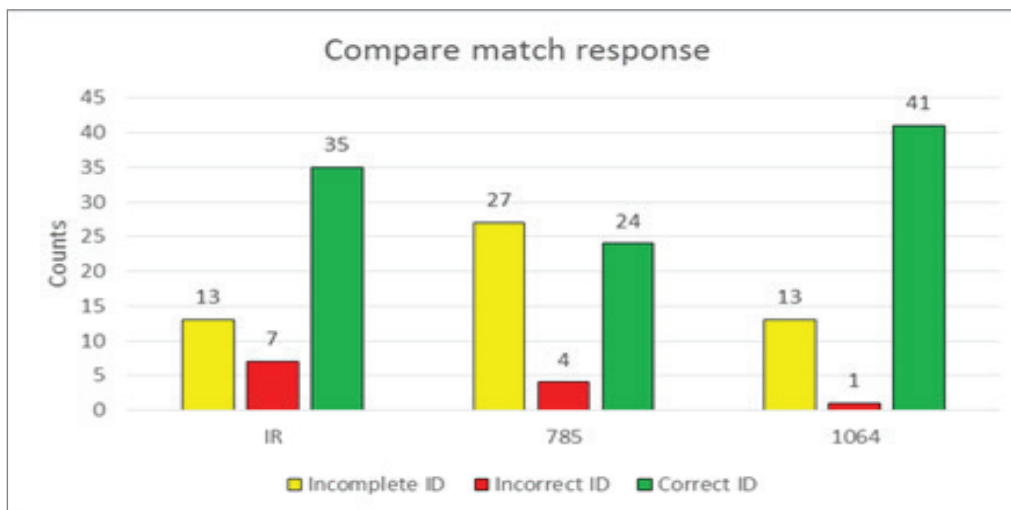


Figure 2. Summaries of instrument performances.*

CONCLUSION

From this series of testing, we were able to compare FT-IR and Raman on a database that contained materials commonly believed to be more suitable for FT-IR, which was then augmented with a variety of other chemicals. However, as shown in this analysis, the 1064nm Raman can clearly achieve reproducible identification for materials previously only able to be identified by FT-IR, and also can expand out the available chemical identification to many other types of material categories including colored materials - making this an effective all-purpose instrument for a variety of uses.

A general summary of instrument type that was found to be suitable in these different categories is provided in Figure 3. For the specific response and the identification, all results are shown in the Appendix.

Sample Type	Instrumentation
Biological materials	IR, NIR, 1064 nm Raman
Colored materials	IR, NIR, 1064 nm Raman
OTC	IR, Raman
Acids/Bases	NIR, Raman
Fuels/Distillates	IR, Raman
Aqueous materials	Raman, NIR
Ionic salts	None
Organic salts	IR, 1064 nm Raman
Explosives	IR, Raman

Figure 3. Summary of best instrument across categories.

*Schreyer, S. (PhD). (2017). Comparison of FT-IR and Raman Spectroscopy: Identification of common chemicals in safety and security applications [White Paper]. <https://www.rigakuanalytical.com>

APPLICATION NOTE

APPENDIX A – SUMMARY OF RESULTS ON ALL INSTRUMENTS

Sample	IR	785 nm	1064 nm
Acetaminophen	acetaminophen	APAP	acetaminophen
Acetic Acid	acetic acid	Acetic acid	Acetic acid
Acetone	acetone	Acetone	Acetone
Aconitine	aconitine	No match	aconitine
Albanian moonshine	water, ethyl alcohol	ethanol, 12% ethanol	ethanol
Alka-Seltzer	ferric citrate and sodium salicylate	No match	sodium hydrogen carbonate+ salicylic acid
Ammonium Nitrate	ammonium nitrate	Ammonium nitrate	ammonium nitrate
Antifreeze	ethylene glycol	ethylene glycol	ethylene glycol
Aspirin	ASA	ASA	aspirin
Baking Powder	various minerals and composites	No match	baking powder
Baking Soda	sodium bicarbonate	No match	sodium hydrogen carbonate
Brake Fluid	pentaethylene glycol	No match	hexa ethylene glycol
Castro Bean	brewers yeast, hummus, etc.	No match	castor bean
Citronella	mineral oil	No match	WD 40
Cocoa Powder	long chaintriols, polysaccharaides	No match	sucrose+tripiperinphosphine
Comet	calcium carbonate	No match	calcium carbonate+ rhodium chloride
DEET	DEET	No match	DEET
Diesel Fuel	lubricants; kerosene	disel	Diesel Fuel
Egg Whites	dried egg white	No match	Egg Whites
Epson Salt	sulfuric acid, Mg salt	No match	magnesium sulfate
Ethanol	top match is alcohol, second is ethanol	ethanol	ethanol
Ethyl Acetate	ethyl acetate	ethyl acetate	ethylacetate
Ethylene Gycol	ethylene glycol	ethylene glycol	ethyleneglycol
Flour	wheat cereal	No match	wheat starch
Fuel Oil	kerosene	mineral oils	WD 40
Gasoline	gasoline	unleaded petrol	Gasoline
Glycerine	glycerol	glycerol	Glycerine
Gold Bond Foot Powder	Talc, calcium phosphate	No match	baby powder
Hexamine	hexachloroethane	hexamine	hexamine
Hydrogen Peroxide	water	No match	Hydrogen peroxide
IPA	2-propanol	IPA	IPA
Kerosene	mineral oil	No match	WD40
Metamucil (benefiber)	corn starch (carbohydrates)	CD, celluloses, polysaccharides	maltotriose
Methanol	methanol	methanol	Methanol
Motor Oil	mineral oil	No match	pentadecane+diesel
Nitric Acid	nitric acid	nitric acid	Nitric acid

APPLICATION NOTE

APPENDIX A – SUMMARY OF RESULTS ON ALL INSTRUMENTS

Sample	IR	785 nm	1064 nm
Nitrobenzene	nitrobenzene	nitrobenzene	nitrobenzene
Olive Oil	glyceroltrioleate; olive oil at 3rd match	No match	Olive oil
Perchloric Acid	no similar matches - minerals	inorganic perchlorates as match	perchloric acid
Polysorbate 20	polysorbate 20	No match	tween
Pool Shock	No match - closest is anionic surfactants + wa	No match	perchloric acid
Potassium Permanganate	Cesium permanganate	barium peroxide	Potassium permanganate
Sodium Cyanide	sodium cyanide	No match	sodium cyanide
Splenda	sweetener (dextrose, saccharin, other)	No match	splenda
Sugar	sucrose	Sucrose	sucrose
Sulfur	No match	sulfur	Sulfur
Sulfuric Acid	sulfuric acid	No match	Sulfuric acid
Table Salt	silicate derivates and foaming agents	No match	No match
Talc	talc	No match	Talc
THF	Top match is retinol	THF	THF
Toluene	toluene	Toluene	Toluene
Triethylamine	triethylamine	triethylamine	Triethylamine
Tums	antacid (calcium carbonate, sucrose)	No match	calcium carbonate + sodium carbonate
Urea	urea	Urea	urea
Vinegar	water	No match	vinegar
Color-coded Summary	IR	785 nm	1064 nm
Red	7	4	1
Yellow	13	27	13
Green	35	24	41