Comparison of FT-IR and Raman Spectroscopy: Identification of common chemicals in safety and security applications

Dr. Suzanne Schreyer
Sr. Applications Scientist
Rigaku Analytical Devices

Abstract

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.

1. INTRODUCTION

FT-IR and Raman are proven optical-based techniques used to identify a variety of chemical substances and compounds in a number industries. Sometimes used as complimentary technologies, each provide 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.

The purpose of the study was two-fold. First, to gain a better understanding of the differences and similarities between the two techniques by comparing results generated by FT-IR and Raman systems. Second, to provide tangible data that decision makers involved in safety and security applications can utilize to select the technology best suited for their requirements.

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 team, 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).

In this work, the materials were analyzed using FT-IR along with Raman spectroscopy of varying wavelengths. Analyses data using NIR (near infrared) was also collected and presented. When possible, different instrumentation manufacturers were included.

Spectral results were collected using a variety of instruments. The results were compared to the instrument manufacturers' published results. As a secondary method of accuracy verification and to eliminate unnecessary bias, the data was evaluated for spectral quality using external databases. This extra measure was performed to confirm true positive results.

2. EXPERIMENTAL

2.1 Materials

A base list of chemicals was initially selected. These materials were best suited for analysis by FT-IR and not considered appropriate for analysis using Raman. To this list, other chemicals were added to include; 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.

The tables below show the solid and the liquid materials used in the study. They are listed by common name and synonym if applicable. The common ingredients in the mixture are also listed.

Figure 1 (a) Solid materials used in testing and Figure 1(b) liquids

Number	SOLID	Mixture components
1	Alka-Seltzer	Aspirin/Bicarbonate
2	Urea	
3	Aspirin	
4	Acetaminophen	
5	Gold Bond Foot Powder	Talc/Sodium bicarbonate
6	Epson Salt	Magnesium sulfate
7	Table Salt	NaCl
8	Comet	Calcium carbonate/Sodium carbonate
9	Sugar	
10	Egg Whites	Powder
11	Splenda	Sucralose based sweetener
12	Ammonium Nitrate	
13	Talc	Hydrated Magnesium silicates
14	Crushed Almond	peanuts/walnuts/etc
15	Tums	Sugar/Calcium carbonate
16	Benefiber	Wheat dextrin
17	Flour	
18	Baking Powder	Sodium bicarbonate/Starch/Calcium phosphate/Sodium Aluminum sulfate
19	Potassium permanganate	
20	Sodium Cyanide	
22	Cocoa Powder	Hot Chocolate mix Keurig
23	Aconitine	
24	Hexamine	Fuel Tablet
25	Castro Bean	Crushed castor oil seeds
26	Baking soda	Sodium bicarbonate
27	Sodium hydroxide	Pellets and solution (10%)
28	Talc	
29	Sulfur	

Number	LIQUID	Mixture Components
1	Acetone	
2	Hydrogen Peroxide	8% CVS brand
3	IPA	70% or 90%
4	Vinegar	Water/Acetic acid
5	Acetic Acid	
6	Sulfuric Acid	
7	Ethanol	
8	Methanol	
9	THF	Tetrahydrofuran
10	Gasoline	
11	Olive oil	
12	Diesel Fuel	
13	Motor Oil	5W-30
14	Albanian moonshine	
15	Brake fluid	Ethylene Glycol-ethers
16	Ethyl Acetate	
17	Ethylene Glycol	
18	Fuel oil	Heavy oil/Diesel
19	Citronella	Mineral oils/Fuel oils
20	Nitrobenzene	
21	Pool Shock	sodium hypochlorite (12.5%)
22	Triethylamine	
23	Perchloric acid	PERC
24	Kerosene	Lamp oil/Red dye added
25	DEET	Diethyltoluamide
26	Glycerine	
27	Polysorbate 20	
28	Nitric acid	
29	Antifreeze	Ethylene glycol
29	Toluene	
29	Ammonium hydroxide	Solution (30%)

2.2 Sample preparation and presentation

Each individual sample was run on all the instruments used in the study. For Raman, the samples were tested through glass vials. For FT-IR a portion of the sample was aliquoted and placed on the ATR crystal. The crystal was cleaned with IPA between uses. Pure chemicals were obtained from Sigma Aldrich. Household chemicals, OTC and fuels and food items were brand name products obtained from general stores.

2.3 Instrumentation

All instruments were considered portable instruments and came from a variety of vendors: Smith Detection's HazMat ID using FT-IR, the Thermo Scientific FirstDefender using 785nm Raman, the Thermo Scientific MicroPHAZIR using NIR, the Rigaku 785nm Raman and the Rigaku Progeny ResQ using 1064nm Raman. All instruments were calibrated per manufacturers' instructions prior to use with the appropriate standard reference material. All testing was done using default conditions or in operator mode. Spectra were collected and downloaded from each instrument for off-line analysis. Results of the identification were also recorded from the instrument.

2.4 Analysis procedures

A two stage material verification was used to analyze the data (spectrum and match results).

For the first stage, sample identification and correlation were recorded on each instrument. The data was downloaded from the instrument. A correct response was recorded when the sample was correctly identified or if the mixture components were correctly identified. Spectra were also evaluated for noise and baseline effects as these tend to be limiting factors for selectivity required for positive identification and reproducibility.

For the second stage of data analysis, all spectra were downloaded to the BioRad KnowItAll (KIA) software and a spectral identification search was run against the KIA database appropriate to the type of analysis (FT-IR or Raman). Results were recorded and compared to the material (identification and correlation). If no match was found to the material in the external database, a search for the specific material was then performed to ascertain if the material was present in the KIA database.

A correct identification of the material or correct identification of the 2 largest components of the mixture – either from the instrument results or from the KIA database was considered an overall correct response. Spectra quality was also evaluated – spectra that were noisy or had baseline effects were repeated 3 times to check for reproducibility of response. Correct responses were color coded green in the summary of results.

If an instrument gave an incorrect response for the material and also a match could not be found in the KIA external database then the response was color coded red for No Match found. Again materials where the identification could not be found were repeated 3 times. The spectral quality was also evaluated as in these cases.

Any material giving a response that fell between the red and green was color coded yellow. In these cases, part of the response was correct. For mixtures, a yellow result was due to: 1. only one component was found from a mixture; 2. one component was not selective (calcium instead of magnesium ion for example). For pure components the ID was coded yellow if there were sufficient spectral effects that limited identification or reproducibility. The reasons are given in greater detail in the results section.

3. RESULTS

3.1 Infra-red analysis and results

The FT-IR instrument returned results within 1-2 minutes for all samples. However time of experimentation was much longer due to the required sample preparation on the ATR crystal. Overall results on the instrument were consistent with results obtained from the external library. The spectra quality overall was good.

Incorrect identification was due to inorganic materials not being identified correctly due to poor spectral quality (noise); biological materials also were not identified except as a generic mis-match of starches,

nutraceuticals; and there were issues where the components of a mixture could not be identified as in baking powder. These are summarized below:

Figure 2 Incorrect matches for FT-IR

Not ID or Incorrect	Resulting matches
Baking powder	Incorrect components
Castro bean	Incorrect components
Hexamine	Hexachloroethane
Perchloric acid	No match
Sulfur	No match
Table salt	No match
THF	Incorrect components

Results were consistent with FT-IR in general, mixtures are difficult to separate, especially for powders. Partially this is due to homogeneity issues, the single bounce ATR crystal has a small spot size so mixtures with salts tend to have issues with reproducibility. Also biological materials are harder to detect in FT-IR, in these cases NIR has been commonly used. For example, NIR can be used to both identify and quantify materials in food/feed/AG and other biological materials. NIR is also less susceptible to being overwhelmed by the water peak in aqueous solutions. In this set of experiments, when any aqueous material was present, the water band did overwhelm the signal and the results indicated water, but often missed the other components. This in fact was the main issue in the identification of the solutions in this data set, as seen in the yellow coded results below.

Figure 3 FT-IR results where issues were noted

Non selective/Missing component	Resulting matches
Brake fluid	Mixtures of glycols and ethers
Flour	wheat cereals and nutraceuticals
Metamucil	starches, carbohydrates
Vinegar	water
Hydrogen peroxide	water
Fuel oil	kerosene
Kerosene	mineral oil
Motor oil	mineral oil
Pool shock	water
Alka seltzer	Citrate and salicylates but wrong counter ions
Cocoa powder	Alfredo sauce, polysaccharides
Crushed almond	Yeast, various natural products
Potassium permanganate	Cesium permanganate, potassium chromate

These results show some of the difficulties associated with specificity and selectivity in this data set when analyzed by FT-IR. As noted, the food or biological samples tended to return generic results only, rather than specifics. In some cases the identification was completely wrong (cocoa powder as alfredo sauce) but was due to the instrument not being able to selectively identify the material. Also noted, the fuels tended to be grouped together into a generic mineral oil response. This is nonspecific for the materials and can be an issue if the different types of fuels have differing flammability hazards, thus requiring different handling procedures by hazmat responders and others. The issue with mixture analysis was again recorded, the wrong counter ions were reported or again generic results were obtained. Also

shown are some the responses to the solutions that were predominately aqueous. In these cases, the FT-IR response is overwhelmingly due to the large water band and this response prevails in the ID. This can be an issue in selectively identifying acids, which have different hazard levels as well.

The materials that did well and were easily identified were the smaller organic materials (common to all molecular spectroscopy) and also the inorganic and organic salts. As shown, FT-IR was able to correctly identify both strong acids and bases. The stronger organic acids such as sulfuric, nitric, phosphoric acid were easily identified, as well as the strong bases. For the weaker acid strength, when the water band overwhelms the signal, NIR instrumentation is required for correct identification. However the stronger acids could also be identified with 1064nm Raman, but the bases could not. So in the case of the strong bases, such as calcium or sodium hydroxide and ammonium hydroxide (both in solutions and as pellets), FT-IR was the only option that gave reliable results. The limitation is the water band as the bases get weaker, which causes the water band to dominate. Another traditional advantage for FT-IR has always been the ability to characterize the longer polymeric chains. These were not tested specifically in this case study, although we do have some longer chains that did reasonably well (carbohydrate results as a general category for the biological/protein materials). As observed, they were considered a yellow result in that the identification was more generic rather than selective. Also note that these materials were classically included in the list of materials commonly used in FT-IR, mostly due to fluorescence issues preventing correct identification when analyzed using a 785nm based Raman. In the cross testing with both 785nm and 1064nm Raman however, we did observe the fluorescence issues with the 785nm but not with the 1064nm. Thus we were able to get similar results with the 1064nm Raman as with the FT-IR instrument.

3.1 Raman analysis and results

The Raman results tended to be heavily dependent on the source laser wavelength. The two wavelengths, 785 and 1064nm will be discussed separately. In both cases, samples were in glass vials and were scanned in the appropriate vial holder. Default conditions for samples in vials were used for all Raman instruments.

Results were recorded and spectral quality assessed as described previously. All data was also analyzed in BioRad KnowItAll to check the identification of the samples or mixtures. As well any incomplete identifications or spectral issues limiting identification were retested 3 times. This mostly added additional time of testing to the 785nm Raman. There were issues with fluorescence which limited the identification and also added time of analysis both on the instrument and in completing scans.

Two different vendors' instruments for 785nm were used in this testing. Both gave similar spectra, so for the larger study only one was used continually. This was done mostly to offset the larger amount of time required to generate scans. In general, the 785nm systems took anywhere from 30 seconds to generate a result (for small organic molecules) to several minutes and up to an hour for severely fluorescing materials. For the 1064nm system results were generally obtained from 20 to 40 seconds.

3.1.1 785nm based Raman

The primary limitation for the 785nm systems was fluorescence. The main reason that the set of materials used was historically characterized as good in FT-IR and poor in Raman, was exactly for this reason. So as expected, fluorescence interference was the limiting issue for both selectivity and in certain cases positive identification of the materials. We had expanded out the basic set to also include materials that were also common household and OTC materials and in many cases these were readily identified in Raman.

There were only a few materials that could not be identified and showed up in the red results. In these cases the spectra were either too noisy or severely fluorescent. These are shown in the table:

Figure 4 Incorrect identification for 785nm Raman

Potassium permanganate	Barium peroxide
Sodium Cyanide	No match
Table salt	No match
Vinegar	No match

Aside from the lack of identification, the spectra quality was poor with both noise and fluorescence observed in the spectra. This also limited the ability of the KIA external software to return a reliable result. For the permanganate, the primary reason for the noisy spectra was probably due to the dark color of the material. This resulted in both fluorescence and noise in the spectra. The sodium cyanide peak is also very small in Raman, it is primarily an FT-IR signal. Table salt is an ionic salt so cannot be reliably analyzed using any of the molecular spectroscopic methods (FT-IR or Raman). As a further note, this is the same result for HCl, it also cannot be reliably measured with either Raman or FT-IR. The vinegar is a weak acetic acid, so the signal from the minor component is low and tends to get hidden in a noisy spectra.

The remainder of the spectra that had an issue with identification primarily exhibited varying degrees of fluorescence. This limited the ability to receive identification in reasonable time on the actual 785nm Raman instrument, and also limited the ability to use the spectra for external search as there were features hidden in the fluorescence hump. A reasonable amount of time was allowed to gather the spectra, but overall about 40% of the materials in the data set were limited by fluorescent issues, with some examples shown in figure 5.

Note that the issues with fluorescence that resulted in a No Match or a time-out because the scanning was taking too long arose predominantly for two reasons. First, colored materials do not scan well in the 785nm system. They are highly fluorescing in many cases. Hence they have been historically analyzed either in FT-IR or NIR. The second common type of material that displayed high fluorescence were biological or protein type materials. Again these tend to be analyzed using FT-IR or NIR historically, even though they are not highly specific even in those analyses. Our material list included materials that were colored and were also mixtures or materials that contained biological materials – such as flour, egg whites, castor beans (dark as well) and others.

Most of the fluorescence issues can be dealt with by using mathematical processing in the instrument. And in fact, this was commonly applied. The issue was and is that the time required for analysis becomes increasingly longer, and at a certain point, the scan was stopped (10 minute cutoff).

Figure 5 Materials shown to fluoresce in 785nm Raman

Alka-Seltzer	No match
Baking Powder	No match
Baking soda	No match
Brake fluid	No match
Castro Bean	No match
Citronella	No match
CoCo Powder	No match
Comet	No match
DEET	No match
Egg Whites	No match
Epson Salt	No match
Flour	No match
fuel oil	mineral oils
Gold Bond Foot Powder	No match
Hydrogen Peroxide	No match
Kerosene	No match
Metamucil (benefiber)	CD, celluloses, polysaccharides
Motor Oil	No match
Olive oil	No match
Perchloric acid	inorganic perchlorates as match
Polysorbate 20	No match
Pool Shock	No match

Finally the rest of the materials – mostly the white powders or clear liquids that were common organic chemicals – were correctly identified in the 785nm Raman. Without fluorescence issues, these materials had clean sharp spectra and showed high selectivity. As noted, these tend to be the smaller organic molecules such as ethanol, urea and hexamine that are commonly found to be precursors or potential hazards in a safety and security environment.

3.1.2 1064nm based Raman

By utilizing the 1064nm laser Raman instrument, the issues associated with fluorescence that were observed in the 785nm Raman were no longer a problem. Analyses were completed within 20-40 seconds on default conditions. Overall because of the lack of fluorescence limitations, the 1064nm was able to identify many of the same materials as the FT-IR system.

The only incorrect response for the 1064nm was the sodium chloride table salt, seen as red in the other systems as well. Again, this is expected as ionic chemicals are not appropriate for molecular spectroscopy.

For the yellow-tagged materials in the 1064nm Raman analysis, the main issue encountered was lower selectivity of the instrument. So in mixtures, the majority components were identified, but as the contribution of the material to the spectra decreased we observed the lower selectivity. For example, the major component of Comet and Benefiber was identified but not the minor components. These results are similar to those observed with the FT-IR, but for different reasons. FT-IR had problems identifying

mixture components due to small sample area and test area; while in Raman it is more often due to lower selectivity. Also, since water does not give a signal in Raman, any of the aqueous solutions only showed the components other than water. This is equivalent to what is seen in the 785nm Raman results as water does not produce a signal in Raman analysis.

For biologicals and proteins, similar results were generated as to those observed with the FT-IR instrument in that the materials were identified as generic groups. Not shown in this set of tests, but as an example-lactalbumin and casein tend to be grouped together (as a generic milk protein group). In our set of materials, flour is identified as starch (similar chemical structures of long chain polysaccharides). This was also observed in the FT-IR.

Results for the materials that were yellow tagged are shown below in Figure 6. This shows that the major components in a sample or mixture were identified, but with less selectivity on the smaller quantity components

Figure 6 Yellow tagged material ID in 1064nm Raman

Sample	ID, 1064nm
Albanian moonshine	ethanol
Brake fluid	hexa ethylene glycol
Citronella	WD 40
Cocoa Powder	sucrose+tripiperinphosphine
Comet	calcium carbonate+ rhodium chloride
Flour	wheat starch
fuel oil	WD 40
Gold Bond Foot Powder	baby powder
Kerosene	WD40
Metamucil (benefiber)	maltotriose
Motor Oil	pentadecane+diesel
Pool Shock	perchloric acid
Talc	Talc

Most materials in the data test set were correctly identified using the 1064nm Raman. Avoiding the issues of fluorescence also opened the testing to allow for colored materials, as well as the biological and protein samples. The results from the 1064nm system were thus more similar to that seen in the FT-IR results, rather than those associated with the 785nm Raman. The only obvious commonality between the Raman systems was their non-response to water.

3.2 Overall comparison of techniques

Upon comparison of all the systems with one another, we split the data into categories –biologicals, small organic molecules, organic salts, acids/bases and household chemicals. 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.

The overall result for these types of materials is shown in the data set below, where ignoring the information on the bases for now, it is obvious that these types of chemicals are easily identified across all systems.

Figure 7 Identification of common organic chemicals in all systems

Chemicals	NIR/IR	785nm	1064nm
Ethanol	Yes	Yes	Yes
Methanol	Yes	Yes	Yes
1, 5, and 10 N NaOH	Will see water band; concs not distinguishable	No	No – Si-O-H spectral effects; non selective
N-Methylimidazole	Yes	Yes	Yes
Dichloroacetic acid	Yes	Yes	Yes
Ammonia hydroxide	Yes	No	No- same as NaOH solution
50% Triethylamine in acetonitrile	Yes	Yes	Yes
Acetonitrile	Yes	Yes	Yes
Toluene	Yes	Yes	Yes
Pyridine	Yes	Yes	Yes
Acetic acid	Yes	Yes	Yes
Acetic anhydride	Yes	Yes	Yes
3-Picoline	Yes	Yes	Yes

Sodium Acetate	Yes	Yes	Yes
4,5-Dicyanoimidazole	Yes	Yes	Yes
Phenylacetyl disulfide	Yes	Yes	Yes

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 1064nm 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. In these cases when the organic plant materials limited the spectra, NIR was the most useful. For 785nm 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, 1064nm Raman (with the consequent lower fluorescence) was able to produce useful and reproducible spectra. One point about the 1064nm Raman for these types of materials is that with the lower selectivity, it is best to classify the proteins or biologics by group rather than assume that the specific protein is identified. For example the milk proteins can be identified in a generic milk protein group, but not individually (as Casein or Lactalbumin). Based on the relative success of identifying proteins and biologicals we were able to build a library for the biologicals– of which the castor beans are an example – and get consistent identification. It would be interesting to add to this list and include more toxic biologicals and see how selective this group would be to separate out the biological toxins. An example of the results is shown in Figure 8 for 4 types of biological/protein samples or mixtures.

*Figure 8 Instrument response for biologic/protein materials*

Sample	IR	785nm	1064nm
Castro Bean	brewers yeast, hummus, etc	No match	castor bean
Egg Whites	dried egg white	No match	Egg Whites
Flour	wheat cereal	No match	wheat starch
Metamucil (benefiber)	corn starch (carbohydrates)	CD, celluloses, polysaccharides	maltotriose

The third point to raise about the overall comparison in general, is the identification of mixtures. In most cases, the identification of mixture components is highly dependent on the mixture algorithm present in the instrument. For this reason, the data was not only analyzed on the instrument but also analyzed in external databases. Additionally, 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 785nm Raman. For 1064nm 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 1064nm instrument may have selectivity issues with counter ions. An example of the results is shown in the Figure 9, and also a comparison of the spectra in the Figure 10.

Figure 9 Instrument responses for common household materials

Sample	IR	785nm	1064nm
Alka-Seltzer	ferric citrate+sodium salicylate	No match	sodium hydrogen carbonate+ salicyclic acid
Baking Powder	minerals, composites, dextran	No match	baking powder
Comet	calcium carbonate	No match	calcium carbonate+ rhodium chloride
DEET	DEET	No match	DEET

Figure 10 Comparison of spectra for FT-IR (top) and Raman (below, 785nm blue; 1064nm red) for Alka Seltzer
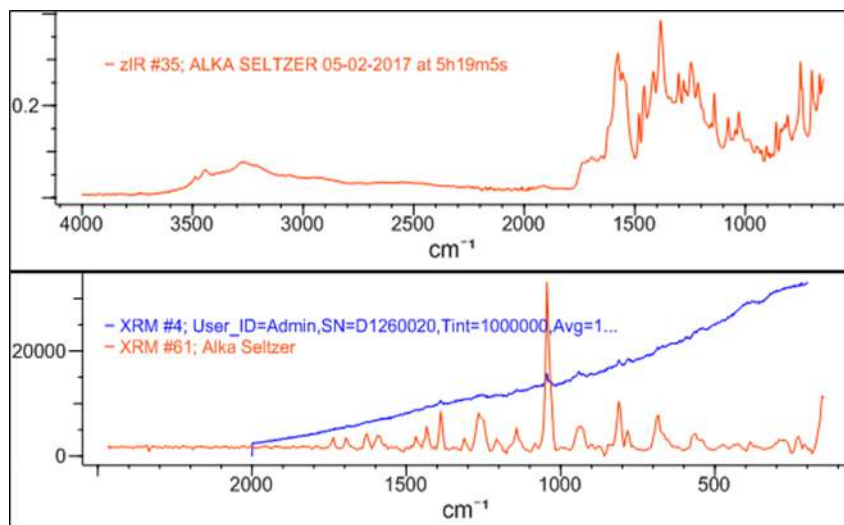
For solutions of two or more materials, FT-IR had more consistent identification of the components as heterogeneity is not an issue. This is the same for Raman identification. Limitations for liquids tend to be water for FT-IR, the water band dominates the spectra, and smaller components may not be visible, 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. The second reason for yellow tag and incomplete identification in the data generated with FT-IR was the incomplete identification of mixture components. Examples of solutions with water and the subsequent effect on identification are shown in Figure 11 which contains examples where the non-water components are above 10% (and identify correctly in FT-IR) and where the other components are below 10% and have issues in identification for FT-IR.

Figure 11 Instrument responses for organic salts

| Sample	IR	785nm	1064nm
Albanian moonshine	water, ethyl alcohol	ethanol, 12% ethanol	ethanol
Hydrogen Peroxide	water	No match	Hydrogen peroxide
nitric acid	nitric acid	nitric acid	Nitric acid
Perchloric acid	no match	inorganic perchlorates as match	perchloric acid
Pool Shock	No match	No match	perchloric acid
Sulfuric Acid	sulfuric acid	No match	Sulfuric acid
Vinegar	water	No match	vinegar

For Raman, the major reason for lack of identification was due to the fluorescence of these samples for the 785nm Raman. The fluorescence and baseline noise also limited identification of colored materials. Conversely for the 1064nm Raman, all the materials that had severe fluorescence in the 785nm system were identified in the 1064nm system. There was also the ability to identify biological and protein materials for the 1064nm system. This gave results that had the 1064nm 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 785nm Raman systems, we consistently got correct identification with the 1064nm Raman instrument. A further advantage is that water did not limit the identification of many of the organic acids in this study for the 1064nm Raman as those observed for the FT-IR. As usual, there is

a tradeoff, while most materials could be identified reproducibly using the 1064nm Raman instrument, the 1064nm Raman did have lower sensitivity with mixture components when the component fell below 10%, as compared with the FT-IR. And as noted previously, the 1064nm Raman produces more generic results for the biologicals and also mixtures of poor Raman scatterers. An example would be mixtures of heavy oils which tended to give generic results of mineral oils rather than the specific type of oil. Note that this same effect was seen on the FT-IR instrument, while the 785nm instrument did not find any match due to fluorescence. To see the effect of fluorescence the results are summarized in Figure 12 below, and also in the comparison plot shown in Figure 13.

Figure 12 Instrument responses where fluorescence was issue for 785nm Raman

Sample	IR	785nm	1064nm
Alka-Seltzer	ferric citrate+sodium salicylate	No match	sodium hydrogen carbonate+ salicyclic acid
Baking Powder	minerals, composites, dextran	No match	baking powder
Comet	calcium carbonate	No match	calcium carbonate+ rhodium chloride
Gold Bond Foot Powder	Talc, calcium phosphate	No match	baby powder
Olive oil	glycerol trioleate; olive oil	No match	Olive oil
Polysorbate 20	polysorbate 20	No match	tween
Splenda	sweetener (dextrose, saccharin, other)	No match	splenda
tums	antacid (calcium carbonate, sucrose)	No match	calcium carbonate + sodium carbonate

*Figure 13 Compare response of 785nm (blue) to 1064nm (red) to a fluorescing material*
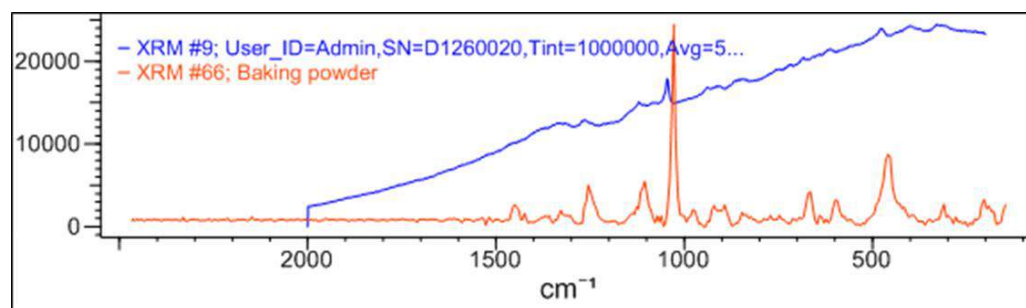
4. Summary and Conclusion

The overall results are presented in the summary table, Figure 14, below. The yellow tagged incomplete response of the FT-IR is similar to that of the 1064nm Raman. Incorrect responses (red) are lower for the 1064nm 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 785nm Raman.

Figure 14 Summary of instrument performance

Result:	IR	785	1064
Incomplete ID	13	27	13
Incorrect ID	7	4	1
Correct ID	35	24	41
Total samples	55	55	55
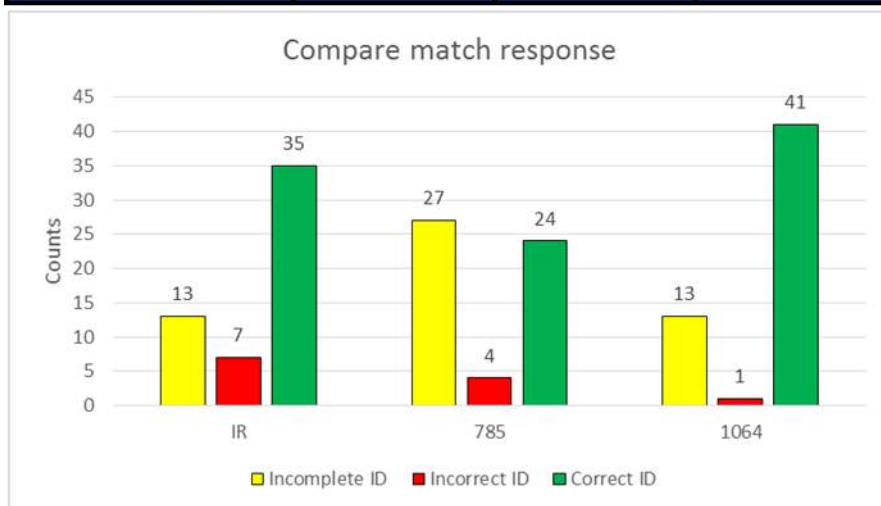
From this series of testing, we were able to compare FT-IR and Raman on a database that contained materials commonly believed to be more suitable for FT-IR, which was then augmented with a variety of other chemicals. Some of these comparisons were expanded out to include NIR – as prior to 1064nm Raman – this was the common instrument used to compensate for limitations of FT-IR such as water dominance and identification of protein/biologics. 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 provide below, in Figure 15. For the specific response and the identification, all results are shown in the Appendix.

Figure 15 Summary of best instrument across categories

Sample type	Instrumentation
• Biological materials	• IR, NIR, 1064nm Raman
• Colored materials	• IR, NIR, 1064nm Raman
• OTC	• IR, Raman
• Acids/Bases	• NIR, Raman
• Fuels/Distillates	• IR, Raman
• Aqueous materials	• Raman, NIR
• Ionic salts	• None
• Organic salts	• IR, 1064nm Raman
• Explosives	• IR, Raman
• Narcotics	• IR, Raman
• Trace analysis	• SERS, other method

Appendix A – Summary of results on all instruments

Sample	IR	785nm	1064nm
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+ salicyclic 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
CoCo Powder	long chain triols, polysaccharaides	No match	sucrose+tripiperinphosphine
Comet	calcium carbonate	No match	calcium carbonate+ rhodium chloride
DEET	DEET	No match	DEET
Diesel Fuel	lubricants; kerosene	diesel	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	ethyl acetate
Ethylene Glycol	ethylene glycol	ethylene glycol	ethylene glycol
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
Nitrobenzene	nitrobenzene	nirobenzene	nitrobenzene
Olive oil	glycerol trioleate; olive oil at 3rd match	No match	Olive oil
Perchloric acid	no similar match - 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
Colorcoded summary:			
red	7	4	1
yellow	13	27	13
green	35	24	41