

Identification of hazardous compounds and illicit drugs with the handheld Raman spectrometers

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1. Introduction

Raman spectrometry is becoming a common method for identification of hazardous compounds and illicit drugs. Historically, infrared absorption spectroscopy was the common method, but the mainstream has gradually shifted to Raman spectroscopy. In particular, Raman spectrometry has a couple of advantages over infrared spectrometry for onsite rapid analysis. First, handheld Raman spectrometers can analyze contents through transparent or translucent containers, which infrared absorption spectrometers cannot. Second, Raman spectrometer can analyze wet samples, but infrared absorption spectrometer cannot.

In the past, handheld Raman spectrometers had issues with overlap of fluorescence, depending on sample type. The reason behind this was that the wavelength of excitation laser was mostly 785 nm. The novel handheld Raman spectrometers for hazardous materials and drugs with 1064 nm excitation laser described in this article can reduce the overlap of fluorescence drastically. Other advantages of the novel handheld Raman spectrometers are described in the later sections.

2. Excitation wavelength

Short excitation wavelength results in high Raman scatter intensity. However, excitation wavelength dependence of fluorescence intensity⁽¹⁾⁻⁽³⁾ is more drastic. Thus, short excitation wavelength makes fluorescence intensity much higher than Raman intensity for some kinds of samples. Figure 1 shows the raw Raman spectra of brown sugar by 785 nm excitation and by 1064 nm excitation. For 785 nm excitation in (a), the fluorescence background is too high to visually identify the Raman spectrum. This means that it is difficult to identify the substance correctly even in the automatic library search of the Raman spectrometer. On the other hand, in the 1064 nm excitation in (b), the influence of the fluorescence background is negligible, so the Raman spectrum of sucrose can be clearly seen and a reliable result in the automatic library search is expected.

3. Advantages of 1064 nm excitation in the identification of threat agents

Figure 2 is an example of a chemical warfare agent, the spectra⁽²⁾ of HN3 (nitrogen mustard 3). (a) is the spectrum for 785 nm excitation which is common in conventional portable Raman spectrometers. However,

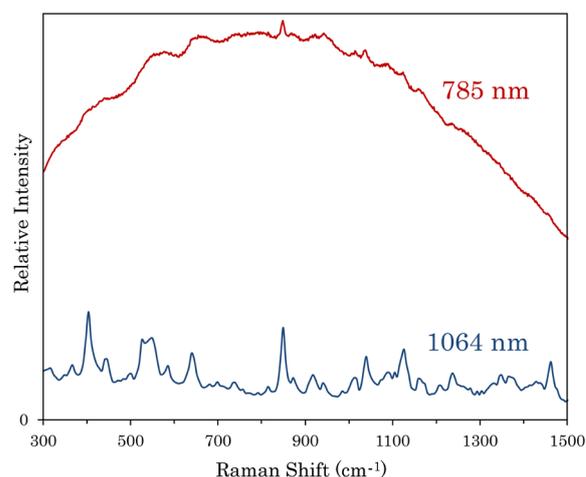


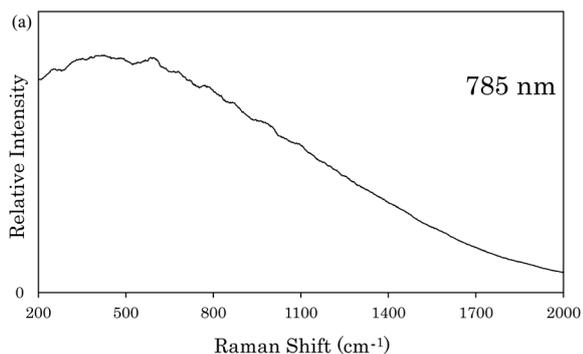
Fig. 1. Raman spectra of brown sugar collected with 785 nm and 1064 nm laser excitation.

the spectrum posted here is taken at about half of the maximum laser power 490 mW to prevent saturation of signal. (b) is the spectrum obtained by 1064 nm excitation. The laser output was at a maximum value of 490 mW, because there was no problem of fluorescence.

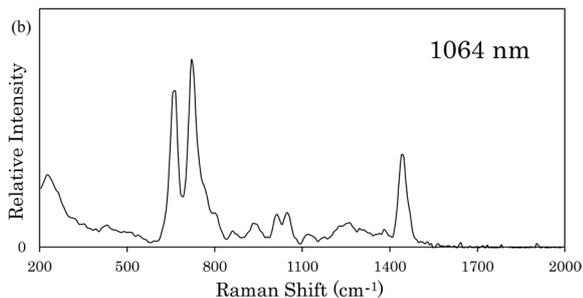
In chemical warfare agents, in addition to HN3 above, DM (Adamsite)⁽⁴⁾ is also extremely fluorescent at short wavelength excitation, and 1064 nm excitation is required. For explosives, substances such as TATP and HMTD often used by terrorists, and their precursors have particularly strong fluorescence at short wavelength excitation. In addition, illegal drugs of plant origin also may have significant fluorescence issues at short wavelength excitation due to varying degrees of purification. In general, there are many cases where fluorescence is an obstacle in short wavelength excitation.

On the other hand, even if the fluorescence of the substance itself is not a problem, the fluorescence of coexisting substances and impurities⁽⁴⁾ often becomes a problem in 785 nm excitation. In addition, for 785 nm excitation, fluorescence from the container also becomes a problem⁽³⁾. For example, brown glass bottles, colored plastic bottles and colored plastic bags are generally fluorescent for 785 nm light. In certain cases, it may be dangerous to open the container and expose investigators to a chemical hazard, therefore the material identification through the container becomes more important. The 1064 nm excitation often works well in this situation, but 785 nm excitation doesn't. Figure 3

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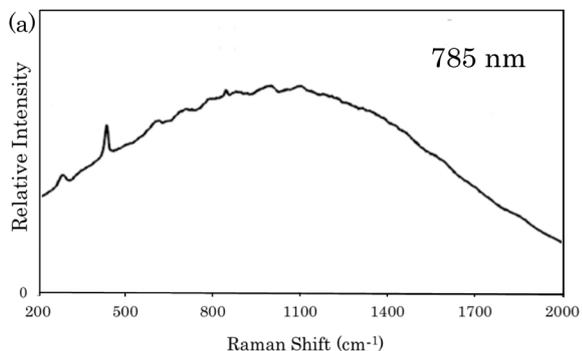


(a) Raman spectrum of HN3 with 785 nm excitation

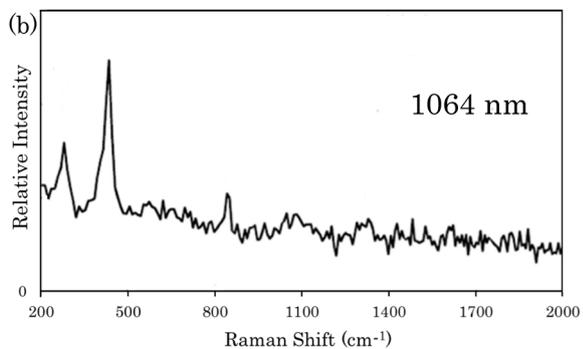


(b) Raman spectrum of HN3 with 1064 nm excitation

Fig. 2. Comparison of the Raman spectra of HN3 with 785 and 1064 nm excitation.



(a) Raman spectrum of PS in amber glass bottle with 785 nm excitation



(b) Raman spectrum of PS in amber glass bottle with 1064 nm excitation

Fig. 3. Comparison of the Raman spectra of PS in amber glass bottle with 785 and 1064 nm excitation.



Fig. 4. Progeny ResQ.



Fig. 5. Progeny ResQ CQL.

shows the results of analysis of PS (Chloropicrin) in a brown bottle at both 785 nm excitation and 1064 nm excitation. PS is a volatile warning agent, and it is desirable to analyze without opening the bottle. It can be seen that the degree of the effect of the fluorescence emitted by the glass of the bottle is significantly different depending on excitation wavelength.

4. Handheld Raman spectrometers for hazardous materials and illicit drugs

4.1. Basic functions

Below, we introduce two types of handheld Raman spectrometers for the security field. The common feature for both spectrometers is that accurate substance identification can be performed, with significantly reduced fluorescence interference, by the 1064 nm excitation, as described in the previous section. Progeny ResQ, shown in Fig. 4, is a model that has proven results in customs, police, military, border security, and drug control agencies around the world. Progeny ResQ CQL,

shown in Fig. 5 is a new model that includes additional features as well as further improvements to the Progeny ResQ.

In this section we describe the basic functions common to both models. The simplest and most important function is to identify a sample by positioning the spectrometer in front of a bottle or bag and scanning the contents. Once the sample is identified, an investigator or security inspector, can take appropriate action, since along with material identification, further chemical and hazard information about the material is shown. Substance identification is performed by finding the spectrum closest to the Raman spectrum of the contents of the bottle or bag by automatic library search. There are approximately 13,000 spectra of substances registered in the standard library, but it is also possible to create a user library that matches the purpose of use of the device.

Figure 6 shows examples of basic function, Threat/No Threat Judgment. Both samples are transparent liquids, but (a) is a toxic and flammable chemical, and (b) is a household chemical.

Figure 7 shows an example of Caution. Usually, the material is No Threat, but it can be Threat if combined with a specific material.

4.2. Novel functions and important functions

In addition to the 1064nm excitation, Progeny ResQ and Progeny ResQ CQL have unique functions important for security applications, that are not found in other handheld Raman spectrometers.

1) 4C mode

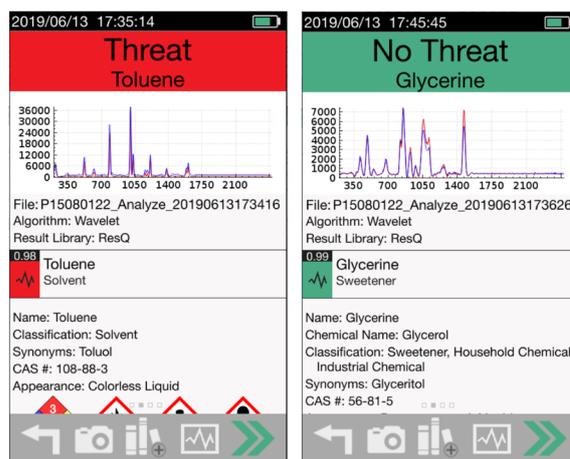
A unique function called 4C mode can be used for the purpose of foreseeing the preparation of dangerous materials. If two or more precursors for the same dangerous material⁽⁵⁾ are found when testing multiple suspicious items in a specific place or specific baggage, a warning screen is displayed showing the possibility of dangerous material production. In the example shown in Fig. 8, the first measured sample is Acetone, and 4C warning is not displayed. However, once the next sample, hydrogen peroxide solution was identified, an instantaneous warning was displayed. The warning is due to the fact that both Acetone and Hydrogen Peroxide solution are precursors of the explosive TATP which are often produced by terrorists.

2) Picture of sample

In the identification result screen, there is also a camera icon for taking sample pictures. By pressing it, the picture of the sample can be stored together with the data. When the data is downloaded to PC, the picture is downloaded together. This is important for pictorial evidence of the sample. Figure 9 shows an example of hazardous industrial material in a bottle.

3) Mixture mode

Sometimes, hazardous materials or illicit drugs are mixed with other compounds intentionally or for other reasons. If both target material and mixed material need to be identified, Mixture mode can be used. Figure 10 is



(a) Threat

(b) No Threat

Fig. 6. Threat/No Threat Identification.

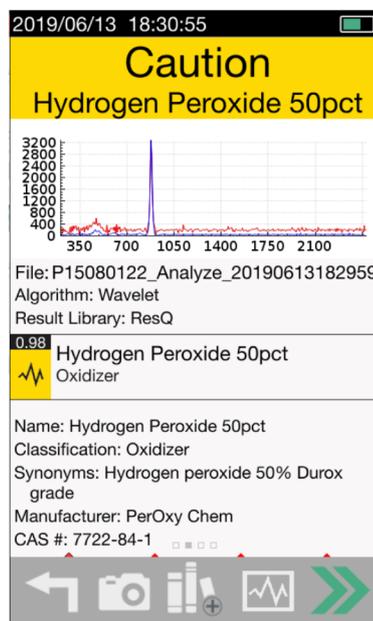


Fig. 7. Caution.

an example of controlled substance mixed with cutting agent.

4) Optimization of relative focus position

At the front of the device is a relative focus position adjustment mechanism with a dial. Figure 11(a) is an example of the tip position setting when measuring the powder in the thin plastic film bag. The dial value is set to 1 so that the focus of the laser light is directly inside the film. Figure 11(b) is an example of tip position setting when measuring liquid in a glass bottle having a glass thickness of about 2.5 mm. The tip is adjusted so that the numerical value of the dial is 5 and the focus position of the laser is about 5 mm in front of the tip of the device. The focus on the position of the liquid inside the bottle is advantageous in terms of Raman signal intensity.

5) Delayed trigger for explosives

It is important to follow proper safety procedures

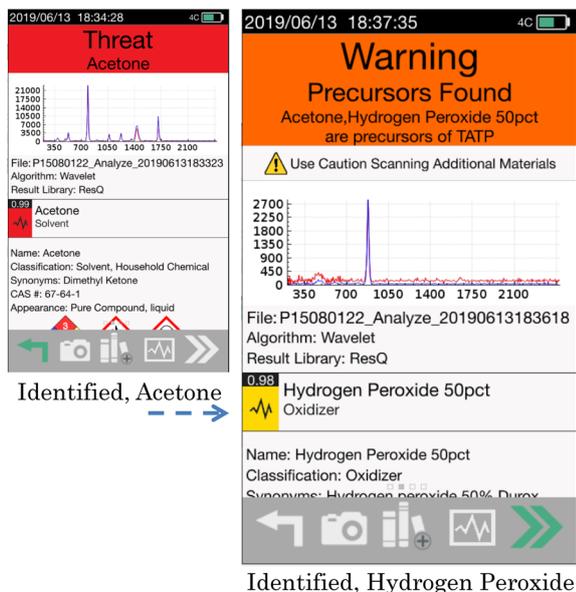


Fig. 8. 4C Warning for explosive precursors.



Fig. 10. Example of mixture mode.



Fig. 9. Pictorial evidence of sample.

when scanning explosive or potentially explosive materials. Additionally it is recommended to use the delayed trigger mode. Delayed trigger mode gives explosives investigators necessary evacuation time before scanning a potentially thermally reactive materials with a laser. The delay time can be selected up to 10minutes. During the delay, the screen shows remaining time before starting the laser.

5. Progeny ResQ CQL

There are many possibilities for the future of portable Raman spectrometers, but in particular, new applications based on the unique features and new functions of the latest Progeny ResQ CQL model are highly promising. The important points are described below.

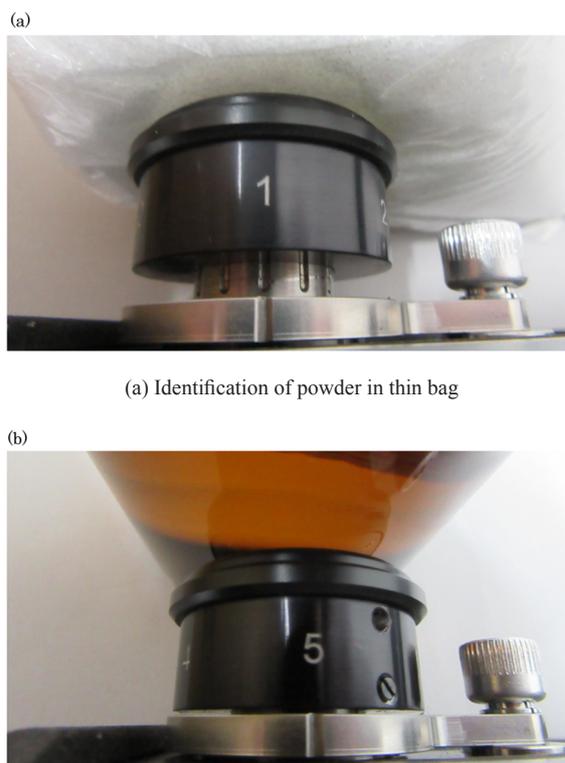
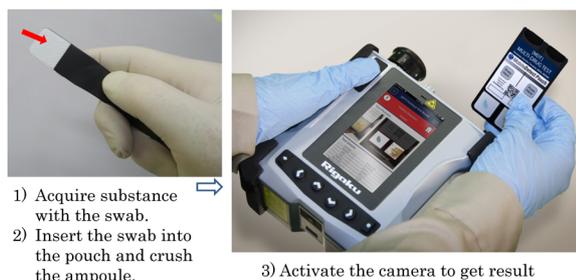


Fig. 11. Optimization of relative focal point.

5.1. Identification of trace amount of compounds with QuickDetect mode

In the past, it was generally understood that portable Raman spectrometers were good at bulk analysis and not suitable for Trace Analysis. For example, when attempting to scan trace amounts of powder on a desk or other surface, the predominant signal



- 1) Acquire substance with the swab.
- 2) Insert the swab into the pouch and crush the ampoule.
- 3) Activate the camera to get result

Fig. 12. QuickDetect mode for trace analysis.

is due to the surface material of the desk rather than the trace substance. However, with QuickDetect colorimetric software on Progeny ResQ CQL, trace analysis is now possible due to the combination of QuickDetect colorimetric chemical reaction with the color observation function of Progeny ResQ CQL. The analysis procedure is shown in Fig. 12.

Although SERS (surface-enhanced Raman spectroscopy) may be used for trace analysis, it takes long time for pretreatment, and running cost is very high. So, QuickDetect is much better for on-site trace material identification.

5.2. Other improvements and new features

1) Ergonomics

The weight has been slightly reduced to 1.4kg, and both one-handed and two-handed holding configurations are possible. It is also easy to place the device close to the object on a desk or floor and analyze it by semi-hands-free operation. Irregardless of position, the optical axis is always horizontal and the operator doesn't need to hold the spectrometer or the sample. Figure 13 shows examples of semi-hands-free operation for chemical identification of contents depending on type of bottle and amount of the contents.

2) Periscope accessory for small amount of sample

If the amount of sample in the container is too small an additional optional accessory, the periscope shown in Fig. 14 is available. The optical axis is much lower allowing scanning at a lower depth in a container. The periscope can also be rotated to compensate for any awkward scanning directions.

6. Conclusion

Handheld Raman spectrometer technology for



Fig. 13. Semi-hands-free analyses by putting any side down.



Fig. 14. Periscope adaptor for small amount at the bottom.

security applications is always improving in both function and performance. As new hazardous materials constantly appear, device manufacturers will need to work with end users to upgrade systems. At Rigaku, we will strive to provide equipment that meets the needs of this field as much as possible, under the collaboration and guidance of various research institutes.

References

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