doi:10.2533/chimia.2025.46 Chimia 79 (2025) 46–51 

# Portable and Handheld Raman Instruments Open a Multitude of Applications

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*Abstract*: Fundamental science can sometimes take a long time until it is useful for practical applications, as was the case for Raman spectroscopy. For a long time, it lacked powerful excitation sources and sensitive detectors. However as technology evolved, the number of exciting applications has boomed. Modern Raman spectroscopy has significant advantages, especially in sample preparation. Handheld Raman devices can be very compact and therefore be easily taken to the sample instead of bringing the sample to the lab. Non-destructive measurements obviously are important in gemmology and mineralogy, even in space. In the field of archaeology, pigments in precious ancient paintings, scrolls or books can be identified. This application is also used to identify fraud and falsification and in studies from a medical school they have reported that Raman spectroscopy can be applied to distinguish cancerous tissue from healthy tissue.
Due to the mobility and ruggedness of the handheld hardware, Raman spectroscopy can be used for police, firefighters, and military applications for identification of explosives and illicit drugs or warfare substances. With SERS (Surface Enhanced Raman Spectroscopy), Raman spectroscopy can even be used for trace analysis. The SERS effect enhances the sensitivity of the Raman signal by a factor of up to $10^7$. This enables, for example, measuring pesticide residuals on fruit or vegetable surfaces for food safety. It can also be used to identify traces of drugs, *e.g.* in urine. However, one of the most common Raman-applications is the identity check or verification of incoming goods (RMID) in the pharma industries, directly in the warehouse. Users appreciate the ease of use and the ruggedness of the Raman hardware.

**Keywords**: Fraud detection · Handheld Raman · Raman applications · Raman on robots · RMID · SERS

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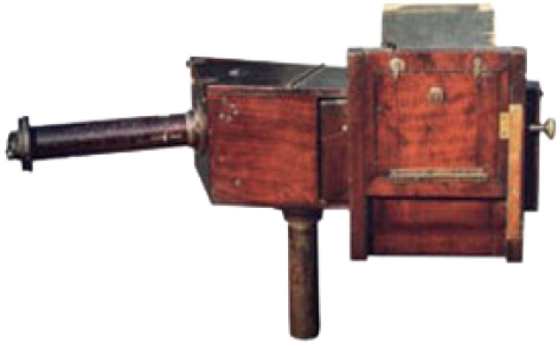

Fig. 1. C. V. Raman's instrument to confirm his hypothesis of inelastic scattering, which was later named after him: Raman spectroscopy.

## 1. Introduction

The first Raman spectrometer ever was actually 'portable'(Fig. 1). Well, it was a simple wooden box housing a Quartz Spectrograph, lacking electronic components and relying on sunlight as its excitation source. Yet, this invention earned its creator the Nobel Prize in 1930 and the honor of having the new principle of inelastic scattering named after him. This gentleman was C. V. Raman.[1]

Raman had the idea of inelastic scattering from an ocean trip when he tried to understand the color of the sea. Inspired by A. Compton's observation from 1922 of X-ray scattering and wavelength change, by inelastic collision with electrons, Raman thought something similar must be observable with visible light.

In some simple experiments, his research group looked at the scattering of light in 60 different liquids. As a light source they initially used sunlight. Using a colored filter, they separated out blue-violet light, which then was scattered off the target liquid. They used yellow-green and other colored filters to visually detect a change in color of the scattered light. The weak effect in the original setup needed improvement and they focused more sunlight for the experiment.[2] In 1928, they published a paper in *Nature*, 'A New Type of Secondary Radiation'[3] describing the observations.

The path to useable Raman spectrometers was long and the Raman principle for many decades was rather a scientific curiosity. The first commercial Raman spectrometers were monsters in size and cost. Due to the fact that Raman spectroscopy produces only a weak yield of the excitation signal (a factor of $10^{-7}$), it needs strong light sources. This started in the 1950s with 2,000 W mercury arc lamps. About 20 years later the first lasers had been considered and used, with an improvement of the signal. How-

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ever, the 5 W $AR^+$-lasers were in big devices and needed massive water cooling. None of these instruments could be described as compact, portable, or for on-site field use.

Portable instruments allowed measurements at sites where you could not go with a large benchtop instrument: archeologic sites (identification of dyes and pigments of wall paintings),[4,5] museums with extremely precious objects (gemology),[6] space research,[7] warfare (identification of dangerous material), crime scenes (identification of illicit chemicals,[8] falsification, fraud), sites with environmental issues (identification of chemicals), and even research hospitals in surgery rooms (rapidly distinguishing healthy from cancerous tissue[9,10]) to mention just a few. When the first Metrohm handheld Raman spectrometers were introduced in 2016, battery driven 'pocket' devices made the usage more flexible.[11] Now it is possible to mount them on drones or robots (Fig. 2)[12] to enter danger zones and identify hazardous substances, mitigating the risk for the operators. In less extreme applications, operators in a warehouse simply carry them to the samples for identification with low effort.

Fig. 2. Handheld Raman (MIRA XTR) mounted on a robotic device to enter a danger zone. A zoom lens allows for sample identification from a 2 m distance to the instrument. Handheld Raman devices can also be mounted on flying drones for chemical identification.

With evolving technology during the telecommunication boom of the late 1990s, lasers became smaller and detectors and optics more compact. With these developments the first portable Raman spectrometers[13] were launched. The market for portable Raman instruments observed an increasing interest after the 9/11 terror attacks in 2001, caused by the desire for fast and easy identification of explosives.

## 2. SERS

Raman spectroscopy was used to measure main components, rather than traces of impurities. This changed when SERS (**S**urface **E**nhanced **R**aman **S**pectroscopy) was accidentally discovered and published in 1973 by Martin Fleischmann.[14] Nanostructures on metals (Au, Ag …) as a substrate can enhance the Raman signal by a factor of $10^7$. This allows the measurement of drug metabolites in urine, pesticide residuals on fruits and vegetables, traces for cleaning validation, and many other applications. SERS applications are not as easy as direct Raman spectroscopy. Methods must be developed to find the proper substrate and solvent, as well as LOD/LOQ (level of detection/level of quantification), *etc*. pH also has a large impact.

SERS can help mitigate fluorescence problems because the SERS signal can be much stronger than the fluorescence signal. SERS experiments can be carried out with handheld devices, which makes them very well suited for routine use even in a small or portable lab.

## 3. Advantages of Raman Spectroscopy

A major advantage of Raman spectroscopy over other techniques is its ease of use. This is mainly because Raman results are not as sensitive to water or $CO_2$ as in mid-IR spectroscopy, and glass optics can be used in the devices. Peaks can be sharp and well-defined for secure 'fingerprint identification', comparable to mid-infrared spectra but without the influence of water, $CO_2$, and optical components, such as KBr or toxic window material.

Challenges arise when fluorescence overwhelms the spectral signal. In these cases, we often see a wobbly line only, caused by saturation due to fluorescence, this is sometimes mistaken as a Raman spectrum. As long as the spectrum is not saturated and fluorescence is not too strong, the Raman signal can be extracted by electronic signal enhancement (XTR). XTR is a combined algorithmic approach used to differentiate Raman scattering and fluorescence signals. It is a Raman eXTRaction method that wasdeveloped for the MIRA (Metrohm Instant Raman Analyzer) systems. Like Sequentially Shifted Excitation (SSE),[15,16] XTR uses multiple shifted spectra generated by internal algorithms during the experiment to distinguish the Raman shift from fixed fluorescence, permitting the fluorescence component to be isolated and extracted. In a secondary automated process in real-time, the Raman data is optimized through an iterative process similar to that employed by Cooper.[17] After identification and elimination of the fluorescence component, only a pure, unobstructed Raman spectrum remains,[18] by using a higher excitation laser (*e.g.* > 785 nm), or enhancing the signal with SERS.

## 4. Excitation Laser Frequencies

In modern Raman spectroscopy, light from a single wavelength is used to excite a sample, causing elastic scattering (strong Rayleigh-scattering signal) and, a small portion of inelastic scattering (Raman). The inelastic scattering is caused by the excitation of a molecule into a virtual state. When the molecule returns to a different vibrational level in the ground state, the energy of the scattered photon is lower than that of the incident photon. The difference in energy between the incident and scattered photons, which corresponds to the vibrational energy, appears as characteristic fingerprint peaks in the Raman spectrum.

Nowadays, the Raman signals in portable and handheld Raman instruments are mainly from excitation at 785 nm or 1064 nm. In standard benchtop Raman microscopes, 532 nm, 633 nm, and 785 nm excitation lasers are the most commonly used. The signal intensity is typically less than 500 mW to avoid safety issues with a higher laser class, which would lead to more strict safety precautions and even a higher risk of burning the sample.

785 nm excitation is the best compromise for signal-to-noise and detector compactness. Due to the higher energy of the laser photons, 785 nm handheld Raman spectrometers can be operated with a laser energy of 50-100 mW, which reduces potential operating risks for the user and burning the sample.

For biological material that may show fluorescence at 785 nm excitation, the alternative is to use an excitation laser at 1064 nm, which is in the NIR region and invisible. This requires Peltier temperature-controlled InGaAs detectors, which means heavier electronics and higher power consumption for the handheld device.

In rare cases, 532 nm (green) excitation can be considered when certain inorganics must be measured, or single-cell Raman spectroscopy, where users need to collect spectra from a microscopic sample without sacrificing resolution and intensity. This is often used in gemology, medical applications, and carbon nanomaterial manufacturing.

## 5. Laser Safety

Modern handheld Raman instruments are equipped with class 3B lasers. This applies to all wavelengths, which are limited to

500 mW maximum. As the accuracy of the laser power has an uncertainty of ± 1%, they are typically specified with 495 mW. 'Class 3B' recommends no direct exposure to the eye, not even for a short time or through an optical instrument. Diffuse reflectance poses a minor hazard for the eye and no risk for the skin. Direct exposure to the skin also comprises a minor risk.

Proper colored safety goggles (Fig. 3) are recommended to protect the eyes. The color of the glass should be suitable for the excitation wavelength.


Fig. 3. OTG safety glasses suitable for a 785 nm Laser.

An important value for the risk assessment is the NOHD (Nominal Ocular Hazard Distance). For example, for Metrohm handheld devices, the conservative NOHD specification is around 30 cm and 40 cm.

## 6. Examples of Popular Raman Applications

The following examples show the versatility of modern Raman spectroscopy.

### 6.1 *RMID (Raw Material Identification)*

Today one of the most applied usages of handheld Raman spectroscopy is raw material identification (RMID) of incoming goods. This can sometimes be done through packaging material without opening the bag or bottle. Packaging material can be plastic, transparent, or brown glass bottles. Raman does not work through metal or metal-coated packaging. Rough identification through paper packaging is possible but not recommended for raw material identification. In addition to a poor spectrum, there is the risk of burning a hole in the paper bag. With large noise in the spectrum, there is the risk of false negatives. For cGMP (regulated pharma production), this would result in extra documentation work and justification.

When incoming goods of the same material come in multiple bags, bottles, or barrels, most industries may only sample a few packages (Fig. 4) to confirm the identity and quality of the whole delivery. In regulated pharma companies, it is becoming an industry standard to test 100% of the incoming packages. For example, 50 bottles of the same material need 50 measurements and confirmation of identity. Opening a package involves much effort and cleaning measurement devices to avoid cross-contamination. It has to be documented, preferably with electronic records, in compliance with 21 CFR Part 11.

If the packing material is transparent to Raman (PE or PP with no metal layer), the measurement is easily achievable through the plastic barrier. For more critical packaging, such as a double-


Fig. 4. Sample identification with a handheld Raman spectrometer. In this case, the identification of a liquid is done through packaging material.

layered brown paper bag, it must be opened for direct access to the content. An immersion probe attached to the handheld Raman can be protected with a disposable plastic sheath to avoid cross-contamination. This is not as easy as measuring directly through the package material, but it is still advantageous over most alternative methods. It can be applied to verify and identify solid and liquid material.

### 6.2 *Gemology*

Precious gemstones do not travel well. Depending on their value, they should be kept in a highly secure environment for safety reasons. Museums that require testing would like to minimize the risk to rare and precious gemstones during transportation. With a handheld instrument, Raman measurements can be carried out at the museum instead of bringing the stone to the Lab.

Gemstone falsification and fraud are significant issues in the market. The difference between a diamond and a cubic zirconia (Fig. 5) can only be identified by experts. With Raman, it is easy to tell the difference between diamonds and cubic zirconia ($ZrO_2$) or zircon ($ZrSiO_4$). However, technology has evolved, and carbon-based synthetic 'lab-grown diamonds' are much easier to make and are becoming cheaper. As they are chemically almost identical to natural diamonds, the differentiation with Raman spectroscopy becomes more of a challenge.

Garnets are a class of silicate minerals that include several varieties with the general form $X_3Y_2(SiO_4)_3$. Raman spectroscopy's high selectivity and sensitivity to the crystalline structure allows for the differentiation of garnet varieties (Fig. 6). Andradite and grossular fall into the ugrandite group of garnets (calcium in the X

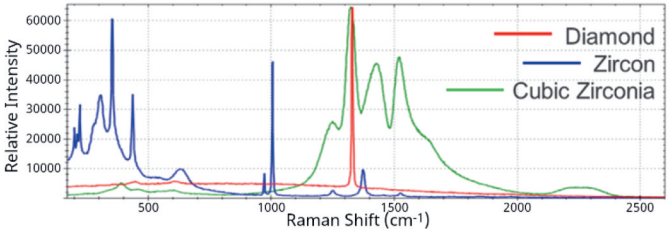


Fig. 5. Real diamond or fake zircon or cubic zirconia: All three are easy to identify.

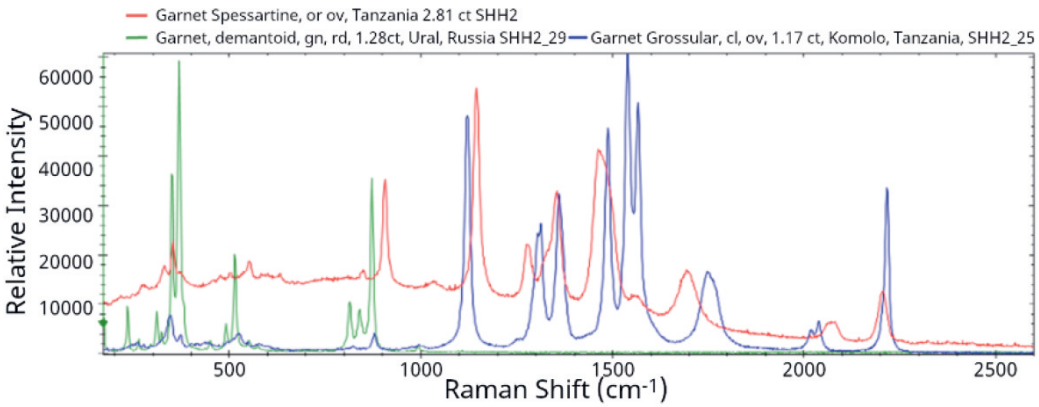


Fig. 6. Spectra of various garnets. The different types are easy to distinguish and identify.

site), while spessartine falls into the pyralspite group (aluminum in the Y site).

### 6.3 *Forensics: Illicit Drugs and Explosives*

Police, military, firefighters, and customs personnel need to rapidly identify materials for a quick decision in a situation where an unidentified material is found in a conspicuous scene. They must decide what to do next based on scientific identification of the material. Arrest a person, evacuate a building, collect water to extinguish a fire in a safe container, *etc.* For those professionals, it is very helpful to have a small handheld device at hand to make quick and profound evaluations.

When an illegal drug lab is found, *e.g.* to make methamphetamine, all synthetic steps can be measured with a handheld Raman spectrometer to understand the scene.[8]

### 6.4 *Art and Archeology*

Historical sites with precious and old wall paintings can only be measured with portable devices. For example, wall paintings at the Alhambra in Spain have been measured to identify pigments and their alteration over time (Fig. 7). This type of knowledge helps understand what chemicals were used, identify possible precautions to protect the paintings or even restore them, and distinguish ancient (original) from restored parts. One may identify falsifications or later additions to fragments and learn the historical context.[20]

At the Pompei site (Italy), Raman spectroscopy was used to identify efflorescence at walls exposed to rain, revealing the nature of the material extracted from the walls. This helped identify risks and actions to preserve the historical ruins.[5]

### 6.5 *Biomedical Applications: Cancer Surgery*

During a cancer surgery, it is very important to be able to distinguish between healthy and tumorous tissue.[9,10] It is necessary to avoid removing too much tissue to make the damage minimal whilst removing all malignant cells. Although the application of Raman spectroscopy is still being studied for feasibility, the results look promising. Research hospitals have successfully made this distinction. Potentially, one day, the determination can be done close to the surgery and within seconds (Fig. 8).

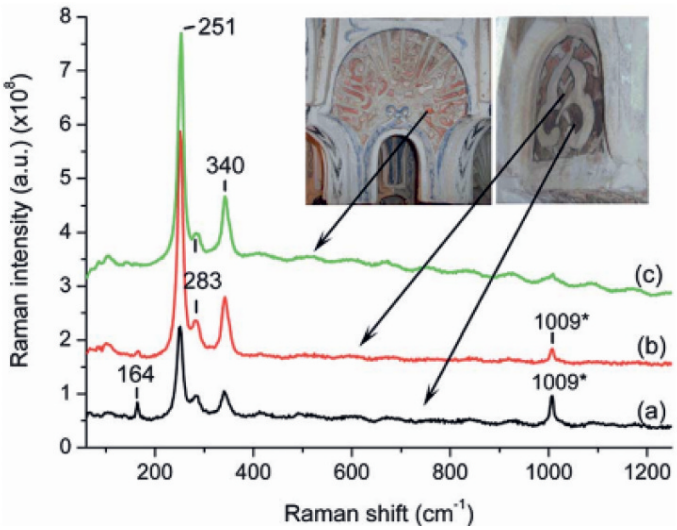


Fig. 7. Pigments of wall paintings in the Alhambra: Cinnabar alteration to calomel. Photographs represent red-colored cinnabar decoration (c), which is in a good state of conservation (b), and completely degraded to calomel, where the red color is only a remnant (a). Calomel peak at 164 $cm^{-1}$, the peak at 1009 $cm^{-1}$ indicates gypsum. A portable Raman spectrometer is used for identification of pigments.[4]

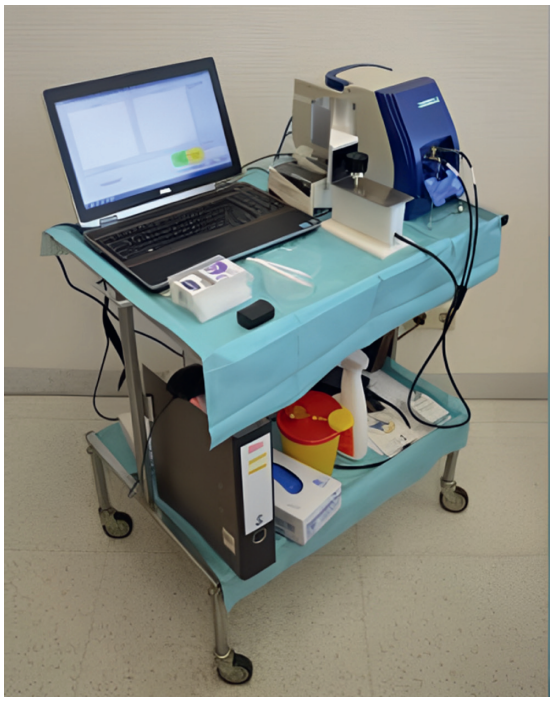

Fig. 8. Raman table in the surgery room for tissue evaluation.

## 7. SERS Applications

While classic Raman is not suitable for low-concentration trace analysis, due to the enhanced signal, this can be achieved with SERS. The routine application is relatively easy: you can

either apply a solution on a 'SERS Strip', which is basically filter paper with a printed nano-metal structure, or you can apply a colloid nanoparticle metal solution to a liquid, mix it and measure directly in a small cuvette holder attached to the Raman instrument.

### 7.1 *Explosives Residuals for Forensics*

For many obvious reasons, even traces of explosives must be identified for forensics research or investigation.

Traces as low as a tenth of pg of various nitro-based explosives can be identified with SERS, such as pentaerythritol tetranitrate (PETN), ethylene glycol dinitrate (EGDN), cyclotrimethylenetrinitramine (RDX), and trinitrotoluene (TNT), using commercially available substrates. High-quality spectra were achieved within 10 seconds with a compact Raman spectrometer.[19]

### 7.2 *Pharma: Cleaning Validation, Cleaning Verification*

Uptime is an important cost factor for pharmaceutical production. Batch production requires thoroughly cleaning the equipment between batches, which must be verified before the new batch can be started. Reducing the cleaning time requires fast determination of the rinsing solution. In this matter, 'time is money'. SERS can be a relatively quick method to measure the rinsing solution for traces of product. This reduces traditional testing time, therefore decreasing the total time during the cleaning regime.

Compact handheld devices[20] (Fig. 9) allow measurements to be close to the equipment and minimize sample transportation. As the laser beam of this equipment does not leave the instrument, it can be operated even without the typical laser safety glasses.

Fig. 9. Sample preparation on a SERS Strip. A dedicated SERS instrument with an open SERS attachment is in the background.

### 7.3 *Food: Pesticide and Fungicide Residuals in Olive Oil and on Fruit*

#### 7.3.1 *Fungicide Example*

Thiram is the trade name for dimethylcarbamothioic dithioperoxyanhydride and was traditionally used in apple and wine farming. Since January 2021, sales of, and a year later, the usage of Thiram have been forbidden in the EU and Switzerland. However, in Brazil, it is still being sold and used.

The detection of Thiram with SERS is relatively straightforward. In a study, 1 ppm and 10 ppm Thiram were dissolved in ethanol and applied to apples (to simulate crop spray). Without specific sample preparation, a direct swab with a commercially available SERS strip[21] (Fig. 10) allowed the detection of Thiram by a handheld Raman spectrometer.

Fig. 10. Sample preparation with a SERS Strip for Thiram: rub the strip on the apple surface.

#### 7.3.2 *Example of an Insecticide*

Fenthion™ (*O*,*O*-dimethyl-*O*-[3-methyl-4-(methylsulfanyl) phenyl] phosphorothioate) is an organophosphate insecticide used against many biting insects and pest insects. There are concerns that it can have a negative effect on birds and can be a health hazard through contact with farmers, inspectors and other people working with treated items. The US Environmental Protection Agency has classified it as a restricted pesticide.

The detection of Fenthion™ traces in extra virgin olive oil using SERS techniques can be performed in approximately 15 minutes, including extraction and sample preparation. The determination is carried out on the extract in a sample vial with a colloidal gold solution. The final Raman measurement takes only a few seconds. Amounts as low as 0.5 µg could be determined with this method.

#### 7.3.3 *Melamine in Milk*

The determination of protein in milk is typically carried out with a Kjeldal measurement. This method only detects nitrogen content, which is sufficient if the milk is not contaminated with other chemicals containing nitrogen. In 2008, the illicit addition of melamine to milk, due to its apparent enhancement of protein content in foods, attracted worldwide attention. This practice sickened thousands of children, infants, and babies in China, with some cases leading to death. As a result, both daily intake limits and increased monitoring of melamine in dairy products were established globally.

SERS techniques can be used to detect traces of melamine in milk. The sample processing steps are relatively easy: dilution, coagulation, and application to an Ag SERS strip. Concentrations as low as 5 µg/ml[22] were detected (Fig. 11).

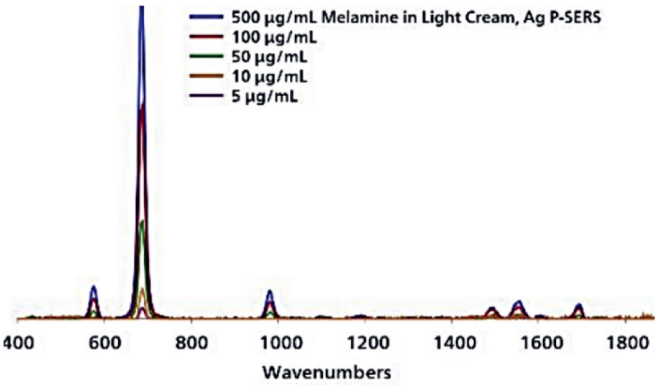


Fig. 11. Various melamine concentrations in milk, measured with SERS. Concentrations as low as 5 µg/ml still show a spectrum.

## 8. Conclusion

Portable Raman spectroscopy has recently developed into one of the most versatile analytical instrument methods, with a multitude of routine application fields. Ease of use and compactness

(portability) are major advantages. Identification and quantitative measurements are possible within a short time. With the signal enhancement of SERS, even trace analysis is feasible.

Received: October 23, 2024

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