Anal Bioanal Chem (2012) 403:255–263
DOI 10.1007/s00216-012-5792-2

ORIGINAL PAPER

Combined time- and space-resolved Raman spectrometer for the non-invasive depth profiling of chemical hazards

Biju Cletus · William Olds · Emad L. Izake · Shankaran Sundarajoo · Peter M. Fredericks · Esa Jaatinen

Received: 6 December 2011 / Revised: 13 January 2012 / Accepted: 25 January 2012 / Published online: 8 February 2012

Abstract A time-resolved inverse spatially offset Raman spectrometer was constructed for depth profiling of Raman-active substances under both the lab and the field environments. The system operating principles and performance are discussed along with its advantages relative to traditional continuous wave spatially offset Raman spectrometer. The developed spectrometer uses a combination of space- and time-resolved detection in order to obtain high-quality Raman spectra from substances hidden behind coloured opaque surface layers, such as plastic and garments, with a single measurement. The time-gated spatially offset Raman spectrometer was successfully used to detect concealed explosives and drug precursors under incandescent and fluorescent background light as well as under daylight. The average screening time was 50 s per measurement. The excitation energy requirements were relatively low (20 mW) which makes the probe safe for screening hazardous substances. The unit has been designed with nanosecond laser excitation and gated detection, making it of lower cost and complexity than previous picosecond-based systems, to provide a functional platform for in-line or in-field sensing of chemical substances.

B. Cletus · W. Olds · E. L. Izake (✉) · S. Sundarajoo · P. M. Fredericks
Chemistry Discipline, Faculty of Science and Technology, Queensland University of Technology, 2 George St., Brisbane, QLD 4001, Australia
e-mail: e.kiriakous@qut.edu.au

E. Jaatinen
Physics Discipline, Faculty of Science and Technology, Queensland University of Technology, 2 George St., Brisbane, QLD 4001, Australia

Keywords Time-resolved SORS · Noninvasive detection · Depth profiling · In-field screening · National security

Introduction

Raman spectroscopy is a powerful detection technique that provides detailed vibrational information on the chemical components of a sample. Raman measurements can be carried out in aqueous solutions unlike FT-IR. Detection can be done during day and night-time, without the presence of a large background signal due to ambient light. Where depth-resolved information is required, Raman spectroscopy, as a technique employing electromagnetic radiation, is an ideal candidate as photons can penetrate the sample and their interaction with different layers can be monitored [1, 2]. These key features, along with the recent technological advances in lasers and imaging technologies, have transformed depth profiling with Raman spectroscopy to become a valuable tool in real-life analytical spectroscopy [3].

A simple approach that also enables recording of Raman spectra from layers several millimetres below the sample surface is spatial offset Raman spectroscopy (SORS) [4]. In this approach, Raman photons are collected from an offset distance (ΔS) from a laser-illuminated spot on the surface of the sample. The light propagation inside the sample depends on the optical density of a material, which influences the probability of a photon to be absorbed or to be converted to a Raman photon at each step. As a consequence, when a laser beam hits a turbid sample, the photons propagate in a random walk-like fashion. Due to random scattering of the photons in the sample material, the illuminated area in the sample increases with increasing depth. On the other hand, the surface layer Raman photons experience lateral fading that increases with increasing spatial offset ΔS [5]. Therefore, the spectrum

collected at the zero offset from the illuminated spot is always rich in Raman and fluorescence photons from the surface layer while the spectrum collected from an offset distance (ΔS) will be relatively enriched with Raman photons from the sub-layer. The SORS setup indirectly reduces the contributions from the surface layer Raman photons and allows for the detection of the Raman signal from the sub-layer [4, 5]. SORS has been demonstrated for biomedical applications [6, 7], pharmaceutical analysis [8, 9] and forensic and national security investigations [10].

Another approach to selectively collect Raman photons from a deeper layer is time-resolved Raman spectroscopy [2, 11, 12]. When a double-layered system is illuminated by an excitation laser, the Raman photons emitted from the surface and shallow layers arrive earlier at the detector. However, photons emitted from deeper layers experience multiple scattering events while travelling from the bulk of the sample and consequently arrive at the detector after a time delay. This time delay can be utilised to exclude the detection of the majority of photons being emitted from the surface layer and to selectively obtain chemical information from a deeper layer within a diffusely scattering sample of several millimetres thickness [12]. On the other hand, the time-resolved photon counting by a gated intensified charged coupled device (ICCD) detector significantly reduces the influence of fluorescence on Raman measurements under pulsed excitation which facilitates a marked improvement in the Raman signal-to-fluorescence ratio [2, 17]. Matousek et al. [2] demonstrated time-resolved depth profiling using picosecond Kerr gating. However, this method is instrumentally complex and challenging [13].

Time-resolved spatially offset Raman spectroscopy (TR-SORS) has been recently proposed as a combined approach that allows for further reduction of the fluorescence and surface layer contributions and, therefore, offers a powerful tool for probing higher depths of sub-surface layers in highly scattering media with larger thicknesses [14]. In time-resolved SORS, a short laser pulse (picoseconds) is used as the excitation source, and delayed time-gated detection of the Raman photons reveals the different layer information of the diffuse medium. Petterson et al. compared the selectivity offered by conventional SORS and TR-SORS towards the sub-layer in a double-layered system [14]. They demonstrated that a combination of spatially offset excitation with time-resolved detection provides a greater selectivity for measuring a second layer through a diffusely scattering first layer than using either technique alone. However, the lower signal-to-noise ratio in their TR-SORS measurements was a major point for future improvements to the technique [14].

In this paper, we demonstrate an inverse spatially offset [15] system that uses nanosecond excitation coupled with nanosecond time-resolved detection for depth profiling of concealed chemical substances. For comparison, a continuous wave (CW) laser source and a conventional CCD camera were used for non-gated SORS measurements. The design of the TR-SORS probe described here is lower in cost and less complex than picosecond systems described in earlier literature [14]. The new spectrometer showed improved sensitivity when compared with CW SORS measurements, as well as superior performance under background light conditions.

Experimental

Instrumentation

Continuous wave SORS setup

Our CW SORS spectrometer has been previously described in detail elsewhere [10, 16]. The excitation source was a diode laser operating at 785 nm with a maximum output power of 450 mW. The excitation laser intensity is adjusted so as to avoid deterioration or destruction of the samples. A bandpass cleanup filter was used to provide a monochromatic excitation beam. Axicon lens mounted on a rail was used to create the required spatial offset. By moving the axicon on the rail, spot (at focal point, zero offset) and ring (offset of 7 mm) illumination patterns were created on the sample. A one-to-one imaging system consisting of two 6-cm focal length biconvex lenses constituted the light collection system, which was directly coupled at the spectrograph input slit. A notch filter was used to block the backscattered 785 nm excitation light from reaching the spectrograph. The Raman photons were detected by a PIXIS CCD camera (Princeton Instruments, USA) coupled to an Acton SP2300 spectrograph (Princeton Instruments, USA).

For CW SORS measurements under background light, reference signatures of the background light were collected while the laser excitation beam is switched off. The acquired signature was automatically subtracted from both the raw spot and ring measurements during acquisition.

Time-resolved SORS setup

For TR-SORS measurements, a VIBRANT pulsed 785 nm near infrared (NIR) excitation laser (Opotek Inc, USA) was used. The laser source had pulse energy of 2 mJ with an average excitation power of 20 mW and a pulse width of 4 ns. The return Raman light was detected by a PIMAX 1024RB ICCD camera (Princeton Instruments, USA). The ICCD camera has a minimum gate width of 500 ps. Figure 1 depicts a schematic representation of the developed TR-SORS spectrometer. The camera gate width was set to 4 ns. The laser and ICCD camera were synchronised so that

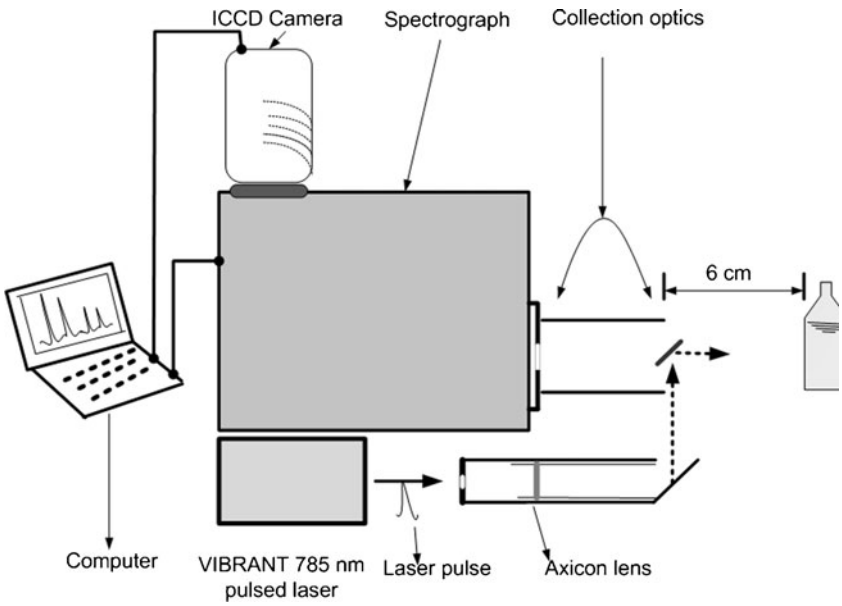


Fig. 1 Schematic diagram of the developed time-resolved spatially offset Raman spectrometer

the measurement window coincided with the maximum Raman signal, minimising the signal contributions from fluorescence and background light. To achieve this condition, the initiation of the gate opening was first set to overlap with the laser pulse and then the 4 ns gate was shifted in time using steps of 500 ps to increment the delay and thus obtain depth profiles of the concealed chemical substances.

Measurements and data treatments

The various SORS measurements were carried out under incandescent and fluorescent light as well as under daylight while placing the sample at 6 cm from the illumination and collection optics. An average acquisition time of 50 s (100 pulses, five acquisitions) was used for the measurements. Opaque high-density polyethylene (HDPE) containers (with a wall thickness of ~2 mm) of different colours were used to conceal chemical substances under investigation. A transparent plastic clip seal bag was used to contain powders hidden behind blue fabric garment. The HDPE polymer or fabric material represented the surface layer of a double-layered system while the concealed chemical substance represented the sub-layer. Reference spectra of the chemical substances were obtained by screening the pure standards using the SORS spectrometer at zero offset.

The CW SORS spectra were imported into Matlab R11 (the Mathworks Inc., USA) and processed with locally written scripts. In practice, unknown substances would be identified by matching the obtained SORS spectrum with the unique Raman spectrum from a spectral library of target substances. For TR-SORS measurements, clean Raman spectra of the concealed chemical substances were directly obtained by single measurements at 7 mm offset.

Chemicals and reagents

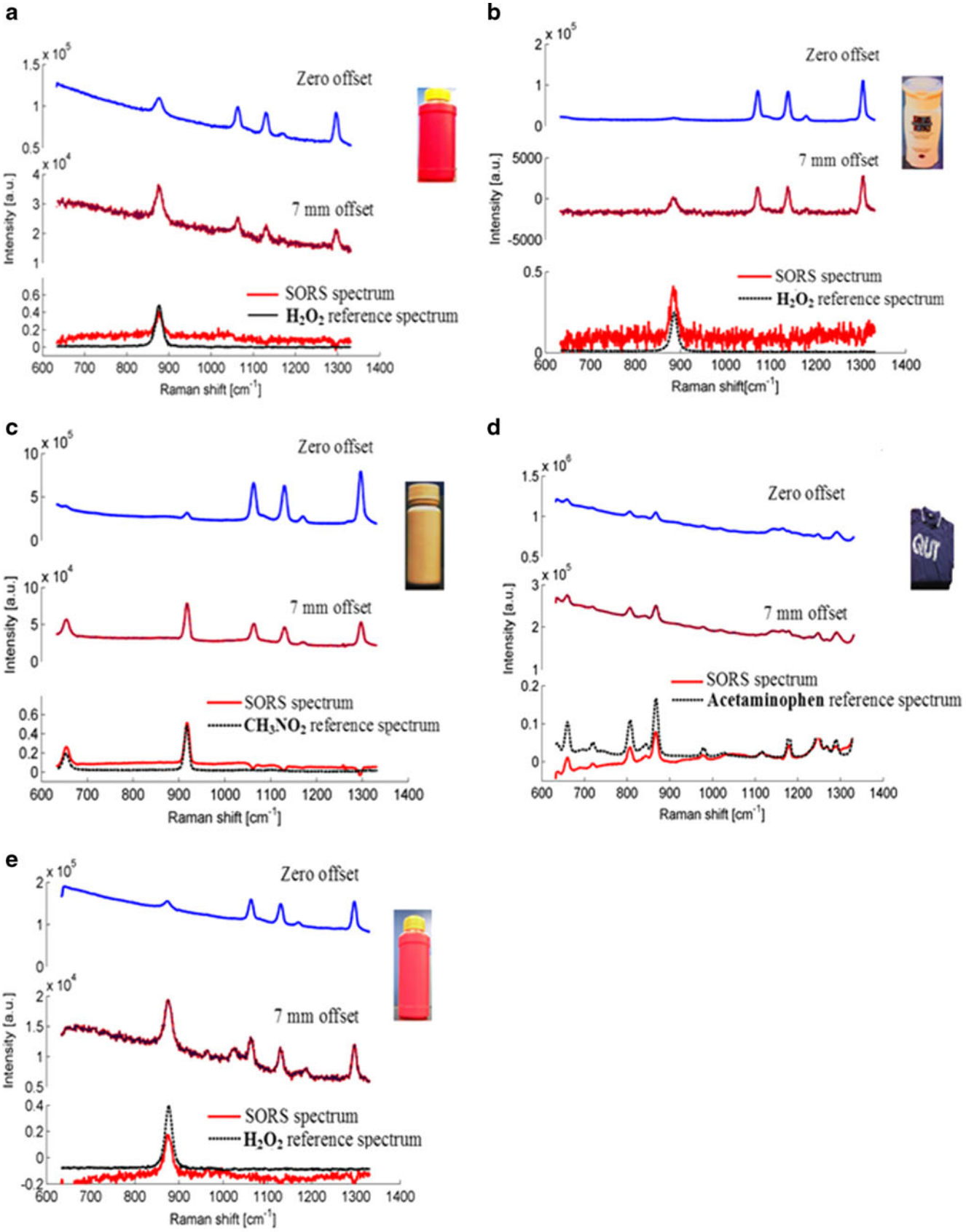
Ammonium nitrate (NH_4NO_3 ≥98%), Barium sulphate ($BaSO_4$ ≥99.9%), hydrogen peroxide (H_2O_2 30% *w/v*), nitromethane (CH_3NO_2 ≥99%), 2,4-dinitrotoluene ($CH_3C_6H_3(NO_2)_2$ ≥97%), and acetaminophen ($CH_3CONHC_6H_4OH$ ≥99%) from Sigma were screened by the SORS unit under both of the continuous wave and pulsed laser excitation modes.

Results and discussion

Continuous wave (CW) SORS measurements

Acetaminophen, hydrogen peroxide, and nitromethane were screened in different coloured containers and behind coloured garment using NIR excitation and the non-gated CCD camera. The SORS spectra collected under incandescent, fluorescent, and daylight backgrounds are shown in Fig. 2a–e.

The measurements show observable differences in the relative contributions from the surface and sub-layer within the Raman spectra collected at zero and 7 mm offsets. The return light collected from the offset point shows high contributions of the Raman photons from the sub-layer. These photons emerge from the bulk of the sample to the surface after experiencing several scattering events that make their pathway longer than photons generated from the surface layer. Meanwhile, Raman photons from the excited spot, on the surface layer, start to experience lateral fading [15]. Since the light collection optical elements are offset from the excited spot by 7 mm, the Raman and fluorescence photons from the surface layer are collected in a significantly lower


a
Zero offset
7 mm offset
SORS spectrum
H_2O_2 reference spectrum
Intensity [a.u.]
Raman shift [cm^{-1}]
b
Zero offset
7 mm offset
SORS spectrum
H_2O_2 reference spectrum
Intensity [a.u.]
Raman shift[cm^{-1}]
c
Zero offset
7 mm offset
SORS spectrum
CH_3NO_2 reference spectrum
Intensity [a.u.]
Raman shift [cm^{-1}]
d
Zero offset
7 mm offset
SORS spectrum
Acetaminophen reference spectrum
Intensity [a.u.]
Raman shift [cm^{-1}]
e
Zero offset
7 mm offset
SORS spectrum
H_2O_2 reference spectrum
Intensity [a.u.]
Raman shift [cm^{-1}]

population than that in the case of zero offset measurements [17]. On the other hand, the spectra collected at zero offset are highly contaminated with Raman and fluorescence photons from the surface layer. By subtracting the zero offset spectrum from the spatially offset spectrum, after appropriate scaling, a pure spectrum of the concealed substance is produced (Fig. 2). Therefore, the collection of both the zero offset and spatially offset Raman spectra is necessary to enable the identification of the concealed substance by CW SORS.

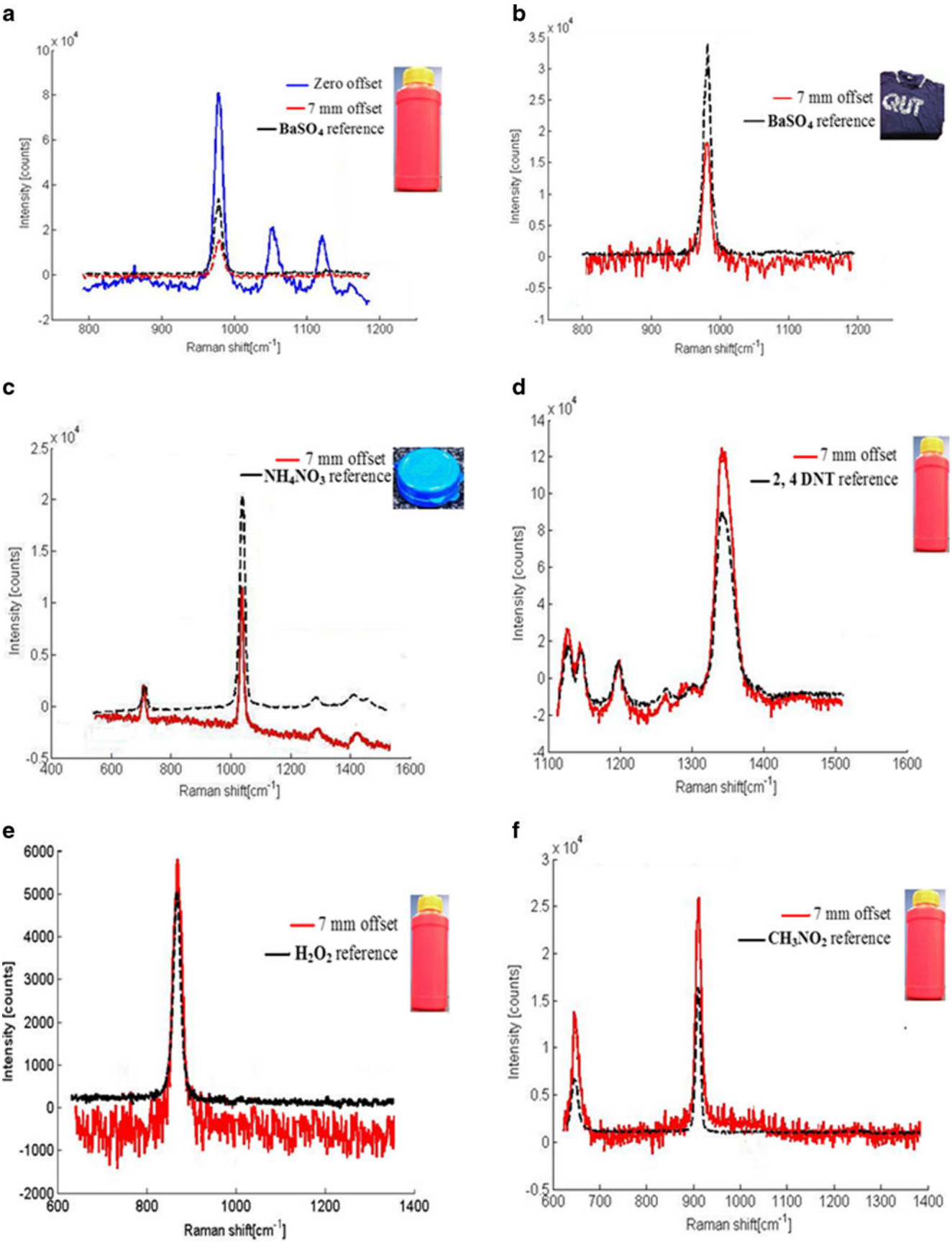
As indicated by the figures, the background noise from different light sources did not prevent the identification of the interrogated chemical substances within relatively short time periods. This can be attributed to the efficient direct coupling of the collection optics that allows for the backscattered photons to be collected into the slit of the spectrograph with minimum losses [16]. However, the signal-to-noise ratio (SNR) in CW SORS measurements is relatively poor in many cases. This is due to the inability of the non-gated CCD detector to reject background light. Thus, the noise and light fluctuations occurring in the background light (particularly from the incandescent light and sunlight) were impressed upon the SORS spectra, resulting in a relatively high level of noise in these spectra.

Time-resolved SORS measurements

In order to acquire an enhanced SORS spectrum with improved SNR, rejection of Raman and fluorescence photons from the surface layer must be maximised and background light contributions should also be minimised. To meet this requirement, we considered combining time-resolved Raman spectroscopy to SORS. Time-resolved Raman spectroscopy is an alternative approach for depth profiling [11]. In time-resolved Raman spectroscopy, when a double-layered system is illuminated with laser pulse, the Raman photons are generated almost spontaneously for the first layer of the system and they travel back to the detector with minimum time delay. In contrast, fluorescence occurs with a time constant on the order of 10^{-9} s from excitation. A finite amount of time must therefore transpire between incidence and absorption of the excitation photon and emission of the fluorescence photon. Thus, Raman scattering and fluorescence emissions occur in distinctly separate time frames if excited by pulsed laser. This facilitates a marked improvement in the Raman signal-to-fluorescence ratio compared with that achievable with a continuous wave excitation [18–21]. On the other hand, the Raman photons from the sub-layer of the system experience multiple scattering events due to the random walk of photons in a scattering medium. This causes the optical pathways of the sub-layer photons to be considerably longer than those of the surface layer photons. By using timed measuring gate, the opening and closing of the gated detection can be delayed after the laser pulse to correspond with the arrival of the delayed photons from the sub-layer and effectively to exclude the detection of the majority of photons being emitted from the surface layer and, ideally, those also originating from fluorescence. This means that, within the Raman measurement, there will be at a specific time domain during which the detector would receive Raman photons mainly from the sub-layer with minimum or negligible contribution from the surface layer. By using a proper gate width and gate delay, an enhanced spectrum of the concealed chemical substance can be acquired [11, 12, 14]. Finally, since the detection occurs over nanosecond timescales, the level of background light acquired is negligible. Therefore, unlike CW SORS, the measurements can be conducted under any type of background lighting, without the requirement of subtracting the background spectrum from each measurement.

Petterson et al. demonstrated time-resolved SORS using picosecond pulsed laser excitation with fast ICCD gating of 250 ps [14]. They used a narrow gate width in order to achieve good temporal resolution and suppress fluorescence and surface-layer contributions. However, picosecond TR-SORS systems tend to be complex, costly, and less portable. In addition, using a picosecond pulsed laser in combination with a very narrow gate width potentially reduces the signal intensity and therefore may preclude the detection of substances with weak Raman scattering properties (e.g. hydrogen peroxide). For our TR-SORS experiments, we modified our CW SORS unit to use nanosecond pulsed laser excitation with a gate time delay that is dependent, in part, on the refractive index and scattering properties of the concealed chemical substance. For example, when light travels to a sample depth of 50 mm through a clear liquid nitromethane sample (refractive index=1.382) it will be delayed by 230 ps on both its incoming path and its outgoing path (when the Raman photons emerge), thus amounting to a ~460 ps time delay. When it travels to a similar depth in barium sulphate, a delay will be experienced due to the refractive index (1.64) as well as the diffuse scattering of the light through the powdered medium. The speed of light in a diffuse medium, according to the work of Petterson et al., is at least an order of magnitude slower than in a transparent medium [14]. Considering a 50-mm sample depth of barium sulphate, the refractive index will contribute delays that amount to 550 ps, while diffuse scattering will increase this delay to >~5 ns. From these approximations, the expected time

◀ **Fig. 2** CW SORS spectra of **a** H_2O_2 in a red plastic bottle (measured under incandescent background light, SNR=4); **b** H_2O_2 in an orange shampoo plastic bottle (measured under incandescent background light, SNR=2); **c** CH_3NO_2 in an off-white plastic bottle (measured under fluorescent light, SNR=10); **d** acetaminophen behind a blue fabric garment (measured under fluorescent background light, SNR=10); **e** H_2O_2 in a red plastic bottle (measured under daylight, SNR=5)


a
x 10^4
Intensity [counts]
Raman shift[cm^-1]
Zero offset
7 mm offset
BaSO4 reference
b
x 10^4
Intensity [counts]
Raman shift[cm^-1]
7 mm offset
BaSO4 reference
QUT
c
x 10^4
Intensity [counts]
Raman shift[cm^-1]
7 mm offset
NH4NO3 reference
d
x 10^4
Intensity [counts]
Raman shift[cm^-1]
7 mm offset
2, 4 DNT reference
e
Intensity [counts]
Raman shift[cm^-1]
7 mm offset
H2O2 reference
f
x 10^4
Intensity [counts]
Raman shift[cm^-1]
7 mm offset
CH3NO2 reference

delays are on the order of the increment with which the gate delay was shifted (500 ps). This confirms that, for both transparent liquid samples and diffusely scattering solids, a nanosecond system is suitable for the interrogation of concealed samples. In all TR-SORS measurements, we used a gate width of 4 ns, and this provided efficient collection of the delayed Raman light from the concealed chemical substance.

Ammonium nitrate, acetaminophen, barium sulphate, 2,4-dinitrotoluene and hydrogen peroxide were screened in different coloured containers and behind a coloured garment. The results are shown in Fig. 3a–f. As indicated by the figures, the TR-SORS measurements showed better SNR when compared with those from the non-gated CW SORS. Moreover, TR-SORS enabled Raman spectra representing the concealed substances to be obtained with a single measurement. Using the ring illumination with spatial offset of 7 mm, we were able to acquire a clean spectrum of barium sulphate within the red plastic container showing that the Raman bands due to the container are greatly suppressed by the combined time- and space-resolved Raman spectroscopy (Fig. 3a). Therefore, time-resolved SORS detection mode enables the identification of concealed substances with one measurement (Fig. 3) and eliminates the need for collecting spot and ring Raman spectra which is necessary in the case of CW SORS detection as explained in "Continuous wave (CW) SORS measurements" section.

The critical effect of gate delay, in time-resolved SORS measurements, on developing a clean Raman spectrum from the sub-layer can be realised from Fig. 4. At zero time delay of the detector gate and 7 mm spatial offset, the acquired TR-SORS spectrum of the barium sulphate sample was still contaminated with Raman signals from the surface layer along with a high background level of fluorescence originating from the container wall material. By introducing a time delay to the detector gate, the Raman and fluorescence photons from the surface layer were progressively rejected and a clean Raman spectrum from the sub-layer was obtained at 82 ns gate delay. The gate delay was established by shifting the detector gate in time with steps of 500 ps from its synchronised original position. At the original position of the detector gate, the developed spectrometer has an inherent detection delay of 76 ns between the triggering of the laser and the actual detection of the return light. This inherent delay is due, in part, to the non-spontaneous responses of the electronics of the different units within the system as well as the travel time which the return photons take to arrive back to the detector. Therefore, the efficient gate delay at which maximum rejection of fluorescence occurred was 6 ns. Figure 5 shows the genesis of the barium sulphate (sub-layer) signal and the increase in its intensity with the change in the detector gate delay. As confirmed by the results, TR-SORS allowed for depth profiling of chemical substances within coloured containers, under real-life conditions of background illumination, by means of a single measurement. On the other hand, TR-SORS required a laser excitation average power of only 20 mW which is significantly lower than the overwhelming excitation power of 450 mW that was required for CW SORS. The reduced power density greatly improves the safety measures of this laser-based screening technique especially when used to interrogate hazardous samples like explosives precursors [12, 13].

To explain how the use of nanosecond pulsed laser excitation is employed to improve depth profiling in the presence of a strongly fluorescing surface layer (coloured container wall), the arrival and resulting return signal from a nanosecond pulse of photons should be considered. This process can be divided into the following steps:

1. A subset of incident photons from the leading edge of the pulse arrives at the surface layer of the sample and generates Raman photons from the surface material. Some of the incident photons will begin to propagate (by diffusely scattering through the container wall) into the concealed sample.
2. A subsequent set of incident photons (still arriving from the long nanosecond laser pulse) will continue to be scattered (elastically and inelastically) while fluorescence begins to develop (after ~10^{-9} ns) but still remains at low levels.
3. The "trailing edge" of the long laser pulse is still arriving at the sample and Raman scattering is still occurring, but fluorescence from the surface layer is now also occurring at high levels. However, the Raman photons from the bulk (sub-layer) are still undergoing scattering inside the concealed contents and are travelling towards the surface.
4. At the end of the pulse, fluorescence from the surface layer is starting to fade out while the Raman photons from the sub-layer emerge from the bulk of the sample and travel towards the detector. Therefore, at this point in time, the Raman light is enriched with contributions from the sub-layer (chemical content). With a sufficient number of laser pulses, a significant Raman signal is collected to build up the SNR and develop a Raman signature for the sub-layer [22].

Therefore, when a suitable time delay is established between triggering the laser pulse and activating the detector gate, a significant reduction in fluorescence background

◀ **Fig. 3** TR-SORS spectra of **a** $BaSO_4$ in a red plastic bottle (SNR=10); **b** $BaSO_4$ behind a blue fabric garment (SNR=16); **c** NH_4NO_3 in a blue plastic container measured under fluorescent light (SNR=19), **d** 2,4-DNT in a red plastic bottle; **e** H_2O_2 in a red plastic bottle (SNR=9); **f** CH_3NO_2 in a red plastic bottle (SNR=17). All spectra measured under fluorescent background light

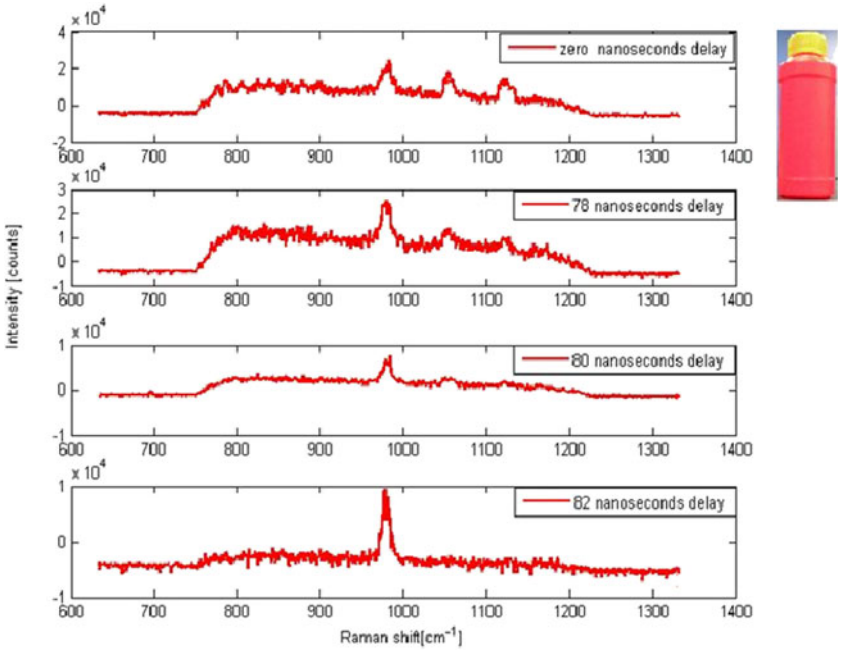


Fig. 4 TR-SORS spectra of $BaSO_4$ at different gate delays. As the delay between the laser trigger and the detector gating is progressed, the contributions from the surface layer into the SORS spectrum decrease while those of the sub-layer ($BaSO_4$) increase. At a gate delay of 82 ns, the background noise is also significantly reduced and a clean Raman spectrum of $BaSO_4$ is acquired

noise is also achieved (since much of the fluorescence is rejected while the detector gate is closed) and a Raman spectrum that represents the concealed substance is acquired.

Conclusions

A time-resolved spatially offset Raman spectrometer which uses pulsed laser excitation on the nanosecond timescale has been constructed and tested. The new spectrometer has superior selectivity towards Raman photons from deeper sample layers through diffusely scattering surface layers when compared with the conventional non-gated CW SORS spectrometer. The new TR-SORS spectrometer has improved ability to reject fluorescence and contributions from background light which makes it capable of acquiring high-resolution spectra, under real life background illuminations, from buried layers within coloured containers by means of a single measurement. The new TR-SORS unit uses low-power nanosecond pulsed laser excitation, making it safe for use in probing hazardous substances. The new unit has powerful potential for national security and forensic applications.

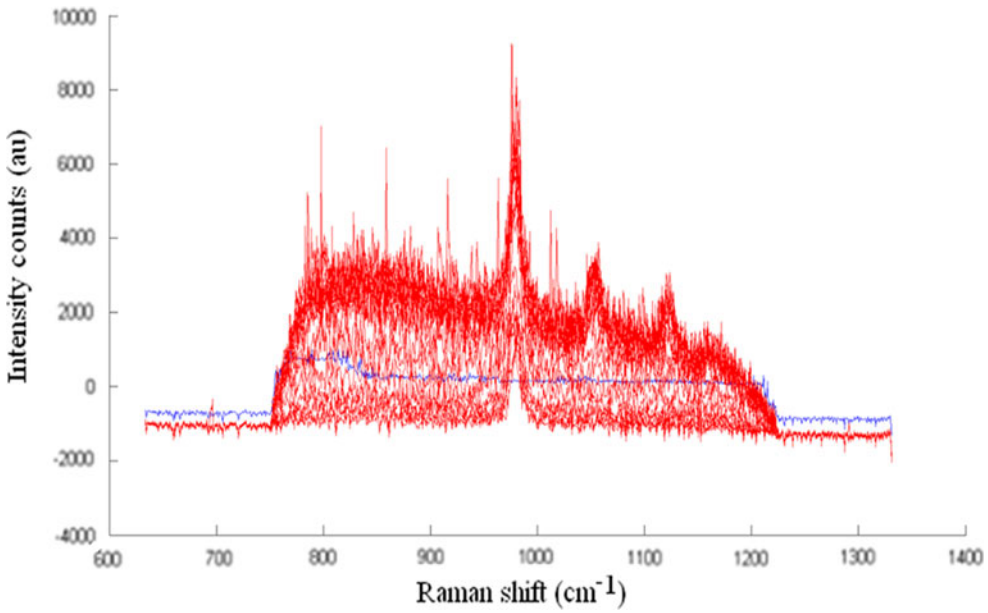


Fig. 5 Raw data of the TR-SORS measurement of $BaSO_4$ at different gate delays

Acknowledgements This work is supported by the National Security Science and Technology scheme (Department of the Prime Minister and Cabinet, Australian Government), the Queensland Government (National and International Research Alliance Partnerships scheme), Australian Future Forensics Innovation Network (AFFIN), Queensland health forensic scientific services and the Australian Federal Police.

References

1. Bonner RF, Nossal R, Havlin S, Weiss GH (1987) J Opt Soc Am 4:423
2. Matousek P, Everall N, Towrie M, Parker AW (2005) Appl Spectrosc 59:200
3. Izake EL (2010) Forensic Sci Int 202:1
4. Matousek P, Clark IP, Draper ERC, Morris MD, Goodship AE, Everall N, Towrie M, Finney WF, Parker AW (2005) Appl Spectrosc 59:393
5. Macleod NA, Goodship A, Parker AW, Matousek P (2008) Anal Chem 80:8146
6. Utzinger U, Richards-Kortum RR (2003) J Biomed Opt 8:121
7. Keller MD, Vargis E, Granja ND, Wilson RH, Mycek M, Kelley MC, Mahadevan-Jansena A (2011) J Biomed Opt 16:1
8. Ricci C, Eliasson C, Macleod NA, Newton PN, Matousek P, Kazarian SG (2007) Anal Bioanal Chem 389:1525
9. Macleod N, Matousek P (2008) Pharm Res 25:2205
10. Olds W, Jaatinen E, Fredericks P, Cletus B, Panayiotou H, Izake EL (2011) Forensic Sci Int 212:69
11. Ariese F, Meuzelaar H, Kerssens MM, Buijs JB, Gooijer C (2009) Analyst 134:1192
12. Petterson EI, Lopez-Lopez M, Garcia-Ruiz C, Gooijer C, Buijs JB, Ariese F (2011) Anal Chem 83:8517
13. Zachhuber B, Gasser C, Chrysostom E, Lendl B (2011) Anal Chem 83:9438
14. Petterson IE, Dvořàk P, Buijs JB, Gooijer C, Ariese F (2010) Analyst 135:3255
15. Matousek P (2006) Appl Spectrosc 60:1341
16. Cletus B, Olds W, Izake EL, Fredericks P, Panayiotou H, Jaatinen E (2011) Proc SPIE 8032:1
17. Matousek P (2007) Chem Soc Rev 36:1292
18. Martyshkin DV, Ahuja RC, Kudriavtsev A, Mirov SB (2004) Rev Sci Instrum 75:630
19. Efremov EV, Buijs JB, Gooijer C, Ariese F (2007) Appl Spectrosc 61:571
20. Everall N, Hahn T, Matousek P, Parker AW, Towrie M (2001) Appl Spectrosc 55:1701
21. Matousek P, Towrie M, Ma C, Kwok WM, Phillips D, Toner WT, Parker AW (2001) J Raman Spectrosc 32:983
22. Sinfield JV, Collic O, Fagerman D, Monwuba C (2010) Appl Spectrosc 64:201