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Detecting forensic substances using commercially available SERS substrates and handheld Raman spectrometers

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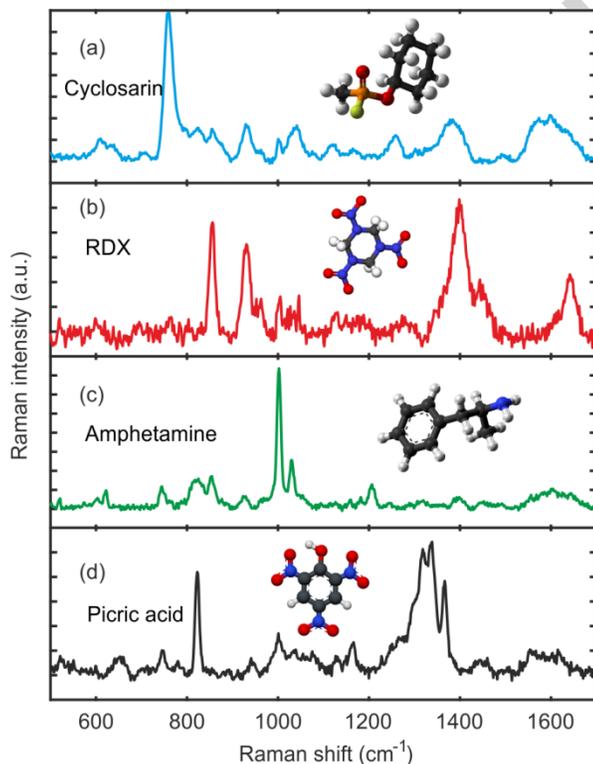
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ABSTRACT:

Ultra-sensitive in-field measurements of most forensic substances still today remain a challenge for first responders and forensic investigators. Handheld Raman spectroscopy equipment is getting more and more routinely used in the field for evidence collection, however, restricted to measurements of pure or high concentration samples. Here, surface-enhanced Raman scattering (SERS) sensing of common forensic substances with commercially available SERS substrates and handheld spectrometers, have been investigated. 3D-Finite Element Method (FEM) and Discrete Fourier Transformation (DFT) simulations were used to show the high SERS enhancement of the nanostructures and to interpret the detection of the substances. The forensic generality and high performance of the analytical method were demonstrated by explicit detection of close to unprecedented amounts, down to femtograms, of Cyclosarin, RDX, Amphetamine and Picric acid. Implications are ultra-sensitive in-field SERS detection of these substances with commercial equipment .

Graphical abstract



Keywords: SERS; Raman; forensic detection; chemical warfare agents; explosives; narcotics

One of the most promising techniques for future ultra-sensitive in-field forensic detection may be surface-enhanced Raman scattering (SERS).¹⁻¹⁰ SERS based detection displays highly attractive properties in term of sensitivity, speed, cost, multiplexing and portability.¹⁰⁻¹⁵ For in-field forensic chemical detection one of the most important parameters is the portability, preferably it should be in the form of a small and robust handheld device for convenient in-situ measurements. Handheld Raman scattering spectrometers and commercial availability of such instruments are essential for promoting and advancing in-field applications.¹³ Portable and quick on-site identification of target substances is becoming a reality with progressively better, smaller and cheaper Raman instruments. Prices for such instruments starts roughly at 10 000 US\$. Nowadays, reports utilizing commercial handheld spectrometers are becoming more and more common for various constituents such as: amino acids,¹⁶ fungicides,¹⁷ pesticides,¹⁸ food elements,^{19,20} meat quality,²¹ cannabinoids²² and viruses.²³

Fig. 1 Profile SEM image of the Ag nanopillar SERS substrates (top). The pillars are roughly 400 nm in height. Schematic picture of the structure with a droplet and water capillaries (left). SEM image of nanoparticle clusters that have been pulled together by the elasto-capillarity (middle). Cartoon demonstrating how the electromagnetic fields around two pulled together nanopillars can look like (right).

Competitive in-field detection techniques are for example FTIR, NIR, XRF, IMS, LIBS and fluorescence.²⁴⁻²⁷ However, rather than seeing these techniques as competition one could view them as complementary and as tools for cross validation directly in-situ. Ideally two or more of them could be incorporated in the same instrument.

Figure 1 illustrates the SERS substrates used in this study. These, recently commercially available (Silmeco™), Au and Ag nanopillar substrates have been developed, optimized and characterized over the last few years.^{28,29} A guiding average price per sample is 10 US\$, when 4 – 5 sample droplets are analysed on each substrate, which could be even further reduced by optimized sample droplet management. Results on these substrates have demonstrated remarkable characteristics and performance, to mention a few highlights; flexibility for hot-spots,^{28,29} superhydrophobicity,³⁰ high adhesion,³⁰ elasto-capillarity³¹ and record detection of threat molecules VX, Tabun and Picric acid.^{30,31}

Fig. 2 3D FEM simulation of Ag capped Si nanopillar clusters; (a) cross-sectional field distribution of a nanopillar dimer, (b) and (c) side-view and top-view field distribution on the surface of a nanopillar trimer; scale bar: 50 nm; the minimum gap distance between adjacent nanopillars is ~3 nm; the excitation wavelength is 780 nm. More details in supporting information.

Some of the properties are really essential for the superior SERS functionality of the substrates, for example the flexibility and potential to generate SERS hot-spots.²⁸ Also, the high adhesion and elasto-capillarity are crucial as they make it possible for the analyte molecules to end up in the hot-spots.³¹

To demonstrate the high enhancement of the nanopillar substrate and to illustrate its SERS hot spots, electrical field enhancements near a dimer and a trimer of nanopillars are 3D FEM simulated, see Figure 2. The simulation reveals that under a 780 nm excitation the nanopillar structures efficiently support the following localized surface plasmon resonance modes: (i) the hybrid gap mode,³² which generates electromagnetic hot spots in the gap junctions between adjacent Ag caps, and (ii) the cavity mode, which generates electromagnetic hot spots near the bottom of the Ag caps. The simulation also reveals that the maximum field enhancement occurs in the gap junctions between adjacent Ag caps. The calculated maximum electromagnetic SERS enhancement factor is 1.7×10^{10} and 1.0×10^{10} for a nanopillar dimer and trimer, respectively. Other studies have shown that maximum SERS enhancement factors are of the order of 10^{10} in typical SERS conditions and are at most of the order of 10^{12} in the best possible conditions.³³⁻³⁵ To achieve single molecule detection, a SERS enhancement factor above 10^9 is necessary.³⁶ The experimentally measured average SERS enhancement factor for the utilized nanopillar substrate is $> 10^8$,²⁹ which is among the best across all the state-of-the-art SERS substrates whose average SERS enhancement factors fall typically in the range of $10^6 - 10^8$.³⁷⁻³⁹

To further promote these structures as general forensic SERS substrates for portable in-situ measurements, low level measurements of four substances were made on the handheld First Defender RMX. However, not in the truly handheld mode but rather semi-fixed as previously utilized and described.^{30,35}

The new substances were Cyclosarin (GF), RDX and Amphetamine, also Picric acid is shown which previously was demonstrated on the Serstech 100 Indicator. Where

Fig. 3 Portable First defender SERS spectrum of a) Cyclosarin (2 μ L, 20 μ g/mL). b) RDX (2 μ L, 2 ng/mL). c) Amphetamine (2 μ L, 2 ng/mL). d) Picric acid (2 μ L, 0.4 ng/mL). All on Silmeco™ Ag substrates. Experimental details can be found in the supporting information.

Cyclosarin represents nerve gases or chemical warfare agents. Nerve gases are generally difficult to measure with SERS and very little is published.^{13,30} RDX is another high nitro explosive, however, lacking conjugated system which leads to a much smaller Raman cross-section. Also, common “street drug” and *Breaking bad* drug relative Amphetamine was tested.

For Cyclosarin we found no comparative SERS studies which are comprehensible due to its difficult structure as well as highly restricted use and accessibility. Figure 3a shows a SERS spectrum from a 2 μL droplet of 20 $\mu\text{g}/\text{mL}$ GF (total amount 40 ng). The major peak at 760 cm^{-1} corresponds well with major normal Raman peak at 752 cm^{-1} published by Christesen et al., and the peak assignment was P-C stretch vibration.⁴⁰ Additional nearby and likely corresponding peaks in the experimental spectrum (Fig. 3a) are at 825 and 856 cm^{-1} (830 and 858 in Christesen et al.) assigned to PO_2 stretch and P-F stretch, respectively.⁴⁰ Further, corresponding are a P=O assigned peak at 1260 (1265) cm^{-1} , and an unassigned group of peaks at 1000 - 1120 cm^{-1} .⁴⁰

In figure 3b SERS spectrum from an evaporated 2 μL 2 ng/mL (total amount of 18 fmol or 4 pg) droplet of RDX is displayed. Record RDX detection according to a recent review,¹³ is 0.5 pM ⁴¹ in concentration and 20 pg ⁴² in amount. The study by Kanchanapally et al.⁴¹ demonstrated a major RDX peak at 870 cm^{-1} with peak assignment to C-N-C ring breathing, which correlates to our 855 peak. That study also showed a major peak at 930 cm^{-1} , closely related to our 932 peak, assigned to ring stretching and N-O deformation. Remaining major bands in Fig. 4b 1400 and 1642 may be related to red-shifted NO_2 symmetric and asymmetric stretch vibration, respectively.

Amphetamine SERS spectrum can be seen in Fig. 3c. Main peak is at 1002 cm^{-1} , i.e. near 1000 cm^{-1} as frequently shown.⁴³⁻⁴⁵ Though, many peaks are present despite the low concentration/amount (2 ng/mL, 2 μL), of which many peaks corresponds to literature, e.g. 604 , 622 , 745 , 820 , 854 , 927 , 1002 , 1030 , 1159 , 1182 and 1207 cm^{-1} are all near Faulds et al’s peaks.⁴³ Further, for some peak assignments the major 1002 peak is assigned to aromatic ring breathing. The 622 cm^{-1} peak comes from in plane aromatic ring deformation, 1033 from in plane C-H deformation, and 1207 relates to C_6H_5 -C vibration.⁴⁵ Equally low SERS detection of amphetamine as in the present study (2 ng/mL, 2 μL) could not be found within present literature, for example in the above mentioned article ($135\text{ }\mu\text{g}/\text{mL}$, 25 μL) was used.⁴³

Picric acid is a high explosive that has had a revival as an interesting analyte over the last few years.⁴⁶⁻⁴⁸ The SERS spectrum of low amount Picric acid in Fig. 3d clearly displays previously shown Raman signature, with major single peak at 823 cm^{-1} , as earlier demonstrated and used for quantification.³¹ A group of large peaks are located at 1300 cm^{-1} and just above.³¹ Major peaks maxima’s at 820 and 1332 cm^{-1} was assigned to vibrational modes of the NO_2 -group.³¹ A record calculated SERS detection limit of $0.02\text{ ng}/\text{mL}$ picric acid has been demonstrated.³¹ This is a calculated detection limit that is below our explicitly detected $0.4\text{ ng}/\text{mL}$, however, at this higher concentration the signal to noise ratio was on the same order of magnitude ($\text{S}/\text{N} = 100$) indicating that similar detection is possible. The detection capabilities for the four analytes are summarized in Table 1.

DFT simulations of the Raman spectra of these forensic molecules demonstrate many similarities, but also in some cases differences (Fig. 4). Peak assignment tables and detailed correlations with the experimental data can be found in supporting information tables S1 – S4. Also, other simulation and experimental details can be found in the supporting information.

Fig. 4 DFT simulated spectras of Cyclosarin, RDX, Amphetamine and Picric acid. Insets show the modelled molecular structures. More details in supporting information.

Table 1. SERS detection limits* found in literature compared with present study.

Analyte	Literature	Present study
Cyclosarin	- **	40 ng
RDX	20 pg ⁴²	4 pg
Amphetamine	$3\text{ }\mu\text{g}$ ⁴³	4 pg
Picric acid	0.04 pg ³¹	0.8 pg

*Calculated detection limits or explicitly shown detection.

** No SERS detection found in literature up to date.

Conclusions

Within this study, portable surface-enhanced Raman scattering (SERS) sensing of common forensic substances on commercially available SERS substrates with commercial handheld spectrometers, have been demonstrated. Forensic generality and high performance of the substrates and high applicability of the analytical method are demonstrated by explicit detection of close to unprecedented amounts, down to femtograms, of Cyclosarin, RDX, Amphetamine and Picric acid. In addition, new 3-D FEM and DFT simulations have been used to explain and understand the photonics of the system leading to vast SERS enhancements. Implications from this study may be the possibility of ultra-sensitive in-field SERS detection of forensic substances with commercial equipment.

Conflicts of interest

T. Rindzevicius, A. Boisen and M. S. Schmidt are co-founders of the Silmecco ApS company.

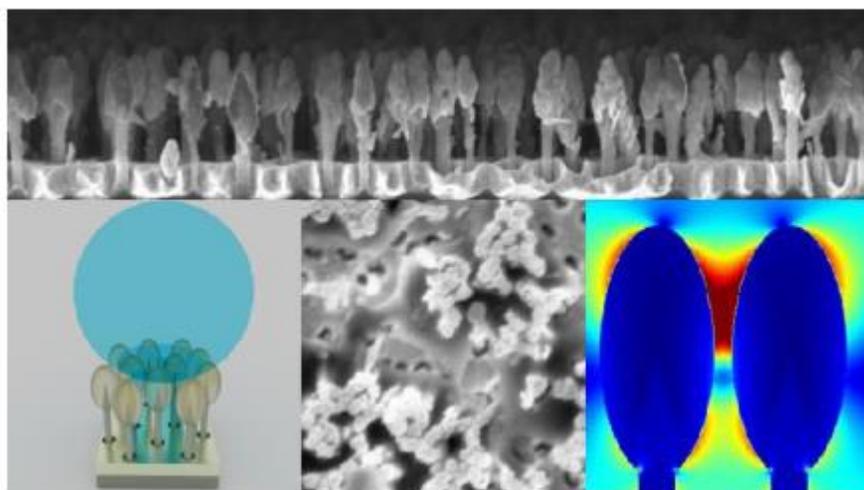
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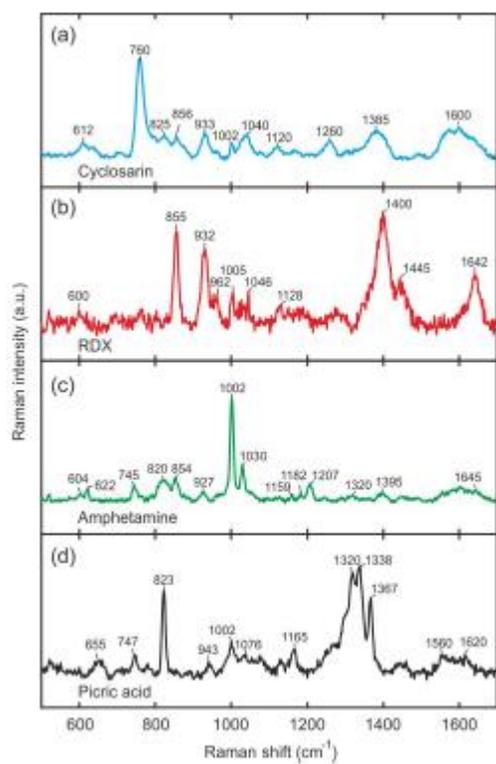
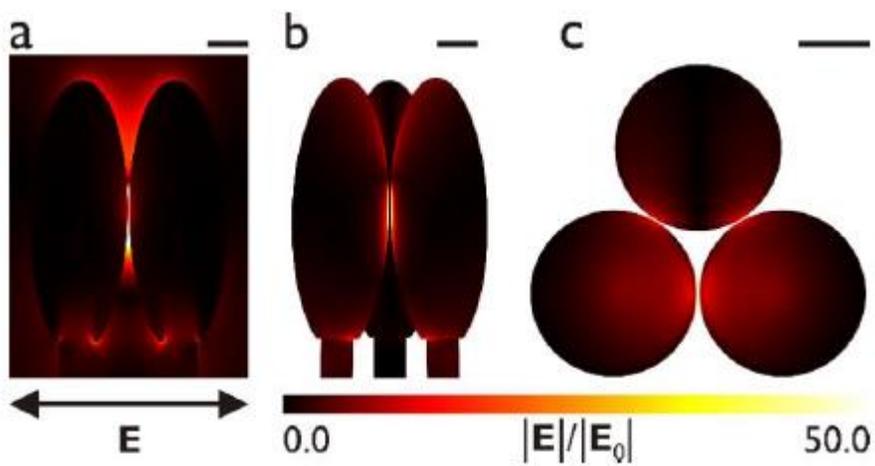
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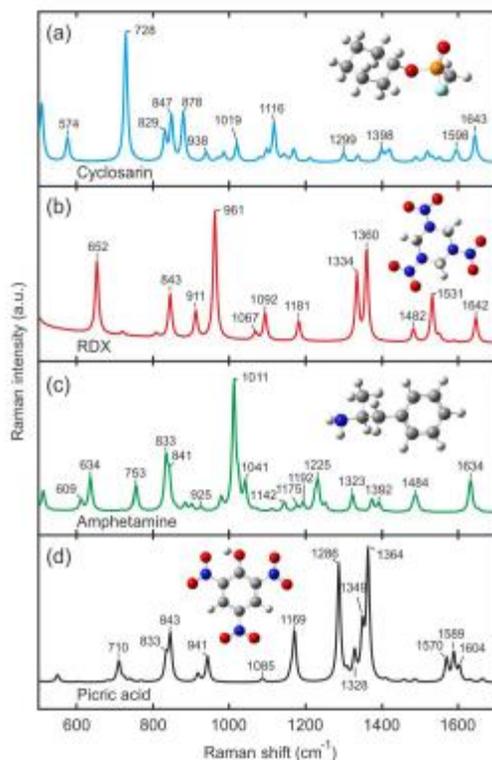
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Highlights

- Close to unprecedented detection of nerve gases, explosives and narcotics are presented
- Simulations are performed to support and interpret results
- Comprehensive peak-assignment tables are included in the supplementary material
- Implications are ultra-sensitive in-field SERS detection of these substances with commercial equipment