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Review

Explosive and chemical threat detection by surface-enhanced Raman scattering: A review

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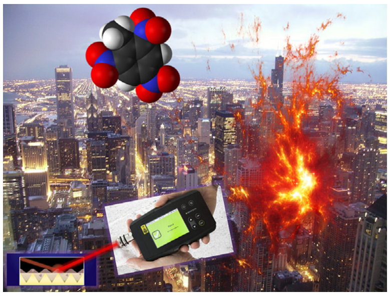
HIGHLIGHTS

- Benchmarking SERS as potentially the major in-field technique for explosives and nerve gas detection.
- Recognition of several SERS studies showing attomolar sensitivities for TNT and DNT.
- Properties of a selection of handheld Raman spectrometers are tabulated.
- Comprehensive table over SERS substrates used for explosives detection.

GRAPHICAL ABSTRACT



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ABSTRACT

Acts of terror and warfare threats are challenging tasks for defense agencies around the world and of growing importance to security conscious policy makers and the general public. Explosives and chemical warfare agents are two of the major concerns in this context, as illustrated by the recent Boston Marathon bombing and nerve gas attacks on civilians in the Middle East. To prevent such tragic disasters, security personnel must be able to find, identify and deactivate the threats at multiple locations and levels. This involves major technical and practical challenges, such as detection of ultra-low quantities of hazardous compounds at remote locations for anti-terror purposes and monitoring of environmental sanitation of dumped or left behind toxic substances and explosives. Surface-enhanced Raman scattering (SERS) is one of todays most interesting and rapidly developing methods for label-free ultrasensitive vibrational "fingerprinting" of a variety of molecular compounds. Performance highlights include attomolar detection of TNT and DNT explosives, a sensitivity that few, if any, other technique can compete with. Moreover, instrumentation needed for SERS analysis are becoming progressively better, smaller and cheaper, and can today be acquired for a retail price close to 10,000 US$. This contribution aims to give a comprehensive overview of SERS as a technique for detection of explosives and chemical threats. We discuss the prospects of SERS becoming a major tool for convenient in-situ threat identification and we summarize existing SERS detection methods and substrates with particular focus on ultra-sensitive real-time detection. General concepts, detection capabilities and perspectives are discussed in order to guide potential users of the technique for homeland security and anti-warfare purposes.

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Contents

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1. Introduction

Homeland security and effective early stage “left of boom” threat detection are a contemporary subject of increasing interest and impact. Two of the major threats used in terrorist and warfare attacks are explosives and chemical warfare agents. The 2013 Nobel peace prize to the Organization for the Prohibition of Chemical Weapons (OPCW) “for its extensive efforts to eliminate chemical weapons” puts the spotlight on these urgent matters and the Boston Marathon bombing and nerve gas attacks on civilians in Syria are recent (2013) and representative examples of the reality of today’s world threat spectrum.

Numerous analytical methods have been utilized to achieve sensitive detection of various explosives and chemical threats, including their precursors and breakdown products in air, water and soil, over the years. In many cases one have utilized combinations of analytical techniques, such as extraction procedures, liquid chromatography, electrochemistry and fluorescence spectroscopy [1–16], because different requirements are difficult to combine into a single convenient detection and analysis methodology. Several recent reports [17–26] indicate that surface-enhanced Raman scattering (SERS) could be a key technique for tomorrows threat detection devices because it combines several attractive properties, such as ultrasensitivity, high speed, comparatively low cost, multiplexing ability and portability [26–28]. However, despite a rapidly growing number of reports, there is, to the best of our knowledge, no up-to-date review on SERS detection of explosives and chemical warfare agents, although several reviews on related subjects, such as handheld optosensing [29], SERS substrates [30], various environmental applications of SERS [31–33] and vibrational spectroscopy of explosives [34,35], have appeared in the literature. This contribution aims to fill this gap by summarizing historical as well as the most recent advances in the field. After a basic introduction to the SERS phenomenon (Section 2) and a discussion of some of the general requirements of the technique (Section 3.1), we give a comprehensive overview of reported SERS performance and characteristics for detection of chemical threats (Section 3.2) and explosives (Section 3.3). We then discuss two specific recent trends, namely hybrid techniques (Section 4.1) and surface modifications (Section 4.2). All in all, we hope that this review will guide and inspire defense research agencies and researchers alike towards further development of SERS into a competent methodology for improved homeland security.

2. Surface-enhanced Raman scattering

Raman scattering is named after C.V. Raman, who made one of the first observations of the effect in the early 1920s, a discovery for which he later received the Nobel Price in Physics [36]. The Raman scattering process involves inelastic scattering of light caused by interaction with low frequency excitations, typically molecular vibrations, in gases, liquids or solids. Since the composition, structure and interatomic forces of a compound uniquely determines its vibrational excitations, Raman spectra can be used for precise identification and analysis of a huge variety of species based on their vibrational “fingerprints” [37–45]. A large number of books and reviews of Raman spectroscopy has been published over the years and we refer the reader to these general references for further reading, e.g. [46–50].

The major problem with Raman scattering, from the point-of-view of chemical analysis, is that it is a weak process, that is, only a miniscule fraction the photons (of the order 0.1% or less) incident on a sample are Raman shifted in wavelength while the rest are elastically (or Rayleigh) scattered [51]. To sort out this small fraction is technically challenging and this has, until recently, severely limited the practical applicability of the method. The light scattering intensity can be significantly enhanced if the laser wavelength used for Raman excitation is tuned in to an absorption band of the sample, an effect known as resonance Raman scattering, but often at the expense of an intense fluorescence background that overlap with the (still) weak Raman lines. Surface-enhanced Raman scattering is related to resonance Raman scattering in the sense that both enhancement effects are caused by electronic resonances, but, as the name suggest, SERS is caused by surface-induced resonance(s) rather than electronic transitions intrinsic to the molecule.

SERS was discovered in 1973 by Fleischmann, Hendra and McQuillan, who observed that the Raman intensity from pyridine molecules adsorbed to an electrochemically roughened silver surface was orders-of-magnitude stronger than expected [52]. However, the full impact of the observation was not realized until the work of Jeanmaire & Van Duyne [53] and Albrecht & Creighton a few years later [54]. The “modern” era of SERS begun in the late 1990s with experimental reports demonstrating that the surface-enhancement effect can in some cases be so strong that vibrational spectra of single molecules can be recorded [55,56]. Together with the growth of the nanooptics and “plasmonics” fields, driven by both conceptual developments and rapid advancement in nanofabrication, computational electromagnetics and measurement techniques, these findings rejuvenated the field and triggered

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