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## Review

## Determination of chemical hazards in foods using surface-enhanced Raman spectroscopy coupled with advanced separation techniques



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## ABSTRACT

**Background:** Surface-enhanced Raman spectroscopy (SERS) has been validated as a highly accurate and specific technique for the discrimination, identification, and potential quantification of different types of chemical compounds. However, its application for the detection of potential hazardous chemical targets in foods has not yet been well developed due to interferences from the complicated food matrices, which could lead to challenges in spectral deconvolution and interpretation. The accurate separation and enrichment of the analyte from food samples are major challenges for analytical chemists and food technologists.

**Scope and approach:** Four promising “capturing” techniques (molecularly imprinted polymers, aptamer, antibody, and microfluidics) coupled with SERS were introduced in this review paper for the reliable and ultrafast determination of chemical hazards in food systems. These developed “one-step” or “two-step” SERS methods can achieve accurate and sensitive detection of trace level chemical hazards in agricultural products including foods.

**Key findings and conclusions:** Tandem SERS methods can be applied for rapid and reliable detection of trace level of chemical hazards in foods.

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## 1. Introduction

Chemical hazards are harmful compounds that can either naturally occur or be intentionally added in food products (Ellis et al., 2012). One of the recent representative examples includes the deliberate contamination of melamine into dry infant formula powder and various pet foods. Analytical chemists and food scientists have strived to design and apply various instruments and analytical methods for the accurate detection of these chemical compounds in foods. The most prevalent technologies are chromatography-based tools, especially when they are combined with mass spectrometry. Even though liquid chromatography tandem mass spectrometry and gas chromatography tandem mass spectrometry are currently the “gold standards” for the detection of chemical contaminants, these methods require highly trained personnel for instrument operations. In addition, a large amount of chemical reagents are consumed during the detection process, yet these methods still fail to realize a high-throughput screening of a large batch of foods within a short time, which could not fully satisfy

the needs for the modern food industry. Alternative methods are required to improve the efficiency of detection. Raman spectroscopy is one of the highly featured tools with unique properties such as non-destructive, label-free, and high-throughput screening of a large amount of samples in a short time period (Li-Chan, 1996). It eases the operation procedures and has high-level multiplex capabilities (Lu, Al-Qadiri, Lin, & Rasco, 2011).

## 2. Raman spectroscopy

Raman spectroscopy can observe vibrational, rotational, and other low-frequency modes in a molecule and/or a system. Among different modes of frequencies, the vibrational mode provides a major contribution to the chemical constitution of a specific analyte. The principle of Raman scattering can be referred to previous literature (Li-Chan, 1996). The cross section of Raman scattering is 14 orders lower in magnitude than that of the fluorescence spectroscopy and only one part in a million of the total intensity of incident light is Raman scattered. Thus, the intensity of Raman signal is several orders weaker than fluorescence emission (Li-Chan, 1996).

The entire platform of the confocal micro-Raman spectroscopy usually includes an illumination (excitation) laser source, a

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microscope, an optical manipulation system, a spectrometer, and a CCD (charge coupled device) detector. Laser powers with the excitation wavelengths at  $532\text{ cm}^{-1}$ ,  $633\text{ cm}^{-1}$ , and  $785\text{ cm}^{-1}$  are widely reported for the use in surface-enhanced Raman spectroscopy (SERS) (Ellis, Cowcher, Ashton, O'Hagan, & Goodacre, 2013; Hering et al., 2008; Jarvis & Goodacre, 2008). Raman microscope provides the system with unique advantages such as optical sensitivity and high spatial resolution, which are critical when determining the location for detection on a sample. In addition, the coupling of a microscope with Raman spectroscopy makes Raman imaging feasible (Lu et al., 2012). The objective lens enables great focus of the incident laser and offers a good performance of collecting heterocentric Raman scattering lights. These optical features in a confocal Raman mode altogether provide a higher signal to noise ratio (S/N) and a lower limit of detection (LOD) compared to a Raman spectrometer without a microscope (Buijtsels et al., 2008).

### 3. SERS method

Surface enhanced Raman spectroscopy (SERS) effect is the enhancement of the Raman signals of a molecule when it is adsorbed onto a roughened metal surface (Albrecht & Creighton, 1977; Fleischmann, Hendra, & McQuillan, 1974). This effect is attributed to electromagnetic and chemical enhancement (Hering et al., 2008). An electromagnetic enhancement occurs when an electromagnetic field is induced by localized surface plasmon resonance (LSPR) of the metal surface, which occurs when electrons on the metal surface are excited by photons from the incident laser source (Banholzer, Millstone, Qin, & Mirkin, 2008). When the analyte molecules are on or in close proximity to the surface of the roughened noble metallic (e.g., gold and silver) nanostructures, the number of induced dipoles increase that subsequently contributes to the formation of SERS effect, resulting in the detectable enhancement of otherwise faint Raman signals (Qian & Nie, 2008). Both silver and gold have small imaginary values for the dielectric constants, which sustain strong LSPR required for SERS effect even under different illumination conditions.

In addition to electromagnetic enhancement, chemical enhancement, which is also called charge-transfer effect, is another major contributing factor to SERS effect. By providing a pathway for resonant excitation, this charge-transfer state increases the polarizability of analytes, resulting in a higher degree of Raman transition (Muehlethaler, Leona, & Lombardi, 2016). Charge-transfer effect is an effective metal-adsorbate interaction that resonance electron transition occurs between molecular orbital of adsorbate and Fermi level of substrate once the energy of incident light matches charge transfer transition energy. This will result in the change of molecular polarization and subsequently produces SERS effect (Centeno, Lopez-Tocon, Arenas, Soto, & Otero, 2006). Chemical enhancement can only enhance Raman signal for roughly 100 times while electromagnetic enhancement can improve Raman signal for  $10^6$  times (Dieringer et al., 2006).

SERS is highly sensitive, selective, and high-throughput (Hakonen, Anderson, Schmidt, Rindzevicius, & Kall, 2015). Thus, it can be used first to screen large numbers of foods to eliminate presumptive negative samples containing chemical hazards. However, challenges still exist when exploiting SERS method for the diagnosis of real food products.

#### 3.1. Challenges

Being a vibrational spectroscopy, SERS exhibits a high molecular specificity that allows the identification of compounds. Essentially, SERS is a detection method rather than a recognition/separation method. Thus, all organic fractions of food debris remained after

sample pre-treatment will inevitably contribute to SERS spectral patterns (Rodriguez-Lorenzo, Fabris, & Alvarez-Puebla, 2012). Because every SERS band is derived from a defined vibrational mode of a functional group in molecules, the interfering food debris (e.g., proteins, lipids, polysaccharides) may lead to challenge of obtaining the spectral pattern from only the target analyte (Zheng & He, 2014).

Thus, researchers perform elaborate sample pre-treatments before conducting SERS to remove undesired food components. However, it is difficult to only rely on extraction and centrifugation methods to receive reliable SERS spectral features of target analyte because some food components may contain similar chemical and physical properties to the target analyte. An alternative to the sample pre-treatment methods is the use of advanced spectral processing and machine learning to unravel any spectral interference from the remaining food components. This strategy was extensively applied in near infrared (NIR) spectroscopy for online monitoring of food quality and safety (Wang, Sun, Pu, & Cheng, 2016). However, challenges still lay ahead when using spectral processing techniques because they may fail to give satisfying spectral specificities to the target analytes for real-time applications, when considering a single complex sample matrix with several potential target analytes. For example, a food product may contain several types of antibiotic residues and/or their structural analogs, which will influence the spectral analysis due to overlapping SERS spectral patterns. To conclude, a separation method is in demand before spectral recording using SERS.

#### 3.2. Tandem SERS method

The general concept and theory of tandem SERS method is the combination of a non-conventional separation method and SERS (as the detection method) to achieve a higher detection sensitivity compared with the conventional SERS technique. Table 1 summarizes representative studies for using different advanced separation techniques coupled with SERS to determine trace level chemical hazards in foods.

#### 3.3. "Two-step" and "one-step" SERS

"Two-step" SERS method is named after the fact that the recognition/separation components and the SERS detection component are independently constructed and performed. The analytes are first identified, separated, and enriched. The resultant aliquots containing the analyte molecules are then deposited onto SERS substrate for signal recording. By conjugating the separation and detection components into a single device, a "one-step" SERS method can be developed. The most critical requirement for the "one-step" SERS method is to ensure that the analyte resides within the enhanced electromagnetic fields generated by excitation of LSPR. The size of the identification/separation component of the "one-step" SERS method is critically controlled to be  $< 10\text{ nm}$  to ensure that the target analyte is localized close to the metal surface within a few nanometers.

#### 3.4. Direct and indirect SERS

Direct SERS method directly determines Raman spectral features of the target molecule, while indirect SERS is an indirect detection method by exciting a strong Raman scattering reporter that is conjugated to the captured target molecule (Driscoll, Harpster, & Johnson, 2013). Direct SERS method is a direct way to characterize the target molecule that contains unique Raman modes. This is especially important if the target molecule is in a relatively impure matrix and/or environment. Regarding the

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