



## Review

## Recent progress and perspective of trace antibiotics detection in aquatic environment by surface-enhanced Raman spectroscopy



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## ARTICLE INFO

## Keywords:

Surface-enhanced Raman spectroscopy

Antibiotics

Trace detection

On-site

## ABSTRACT

The abused antibiotic residue either in natural environment or food is a serious issue for both public health and ecological environment. Therefore, various techniques have been developed for the qualitative and quantitative of trace antibiotics in food, drinking water and human body fluid. Among them, Surface-enhanced Raman spectroscopy (SERS) is a developing technique, which outstands itself with high sensitivity and selectivity. Our presentation takes especially great care to highlight the main progresses and challenges of SERS in the trace antibiotic detection in aquatic, biosystem and food science to illustrate key aspects of this technology. Even though many advances have already been made in this area, there are many hurdles, such as the sensitivity, selectivity, stability and reproducibility, need to be overcome to bring this technology up to the level of the on-site practical application in aquatic environment. This review is written for specialists in the field and a general environment–ecosystem–chemistry readership.

## 1. Introduction

With the discovery of penicillium, the first natural antibiotic used for human therapy, by Sir Fleming in 1928, a variety of antibiotics (natural and synthesized), have helped to eliminate various human diseases including tuberculosis and anthrax and are still playing important role in medical therapy. Meanwhile, it is also extensively and effectively used as veterinary medicines or food additive to increase the productivity of livestock and aquatic products. However, each coin has two sides. Until 1990s after antibiotics have been used in large quantities and released in natural ecosystem for some decades, did the negative effect and risk of antibiotics on the ecosystem and human health receive increasing concern and become a hot research topic worldwide.

Antibiotics are excreted unchanged typically via municipal, agricultural, and industrial wastewater into the aqueous environment, where the process of emergence, transport, and dissemination of antibiotics was done. Besides chemical pollution brought by the abused antibiotics, the environmentally derived antibiotic-resistant bacteria/genes may also be significantly changed and shade health risks directly or indirectly to humans. It has been demonstrated that the abused antibiotics reduced the therapeutic potential against human and animal pathogens [1–8].

Since 1950 to the present, antibiotics related review articles are almost 9000. From the global perspective, three aspects have been investigated and discussed in detail, including: 1) the nature, action,

biochemistry, physicochemistry, pharmacology and toxicology of antibiotics; 2) the occurrence, transportation, degradation, removal, fate, and risks of trace antibiotics in various ecosystems; and 3) the emergence and development of antibiotic-resistant bacteria/gene.

To improve the knowledge of the above aspects, the state of the art detection of antibiotics is the first and fundamental step, where great efforts have been made to develop a plethora of analytical methods for the qualitative/quantitative determination of antibiotics either in food or aqueous environment. Most of these methods can be grouped into three categories [9–11].

- 1) Chromatographic methods, mainly including high performance liquid chromatography (HPLC), mass spectrometry (MS), capillary electrophoresis (CE), gas chromatography combined with mass spectrometry (GC–MS), gas chromatography coupled with electron capture (GC–EC), and liquid chromatography–electrospray–tandem mass spectrometry analysis (LC–ESI–MS/MS). Those methods are the most traditional and standard ones for the qualitative/quantitative determination of antibiotics in various environment. Nevertheless, the expensive facility and tedious operation limited this method towards the rapid on-site analysis application.
- 2) Microbiological screening assay based on the bacterial growth inhibition dependent antibiotic concentration. This method is inexpensive and simply operated for the routine quality control. However, it is time consuming and poor stability.

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3) Biosensors, including immunochemical techniques, performed high selectivity for the antibiotics even in a complicated matrix. Such characteristic is originated from the high specific and precise bioreceptor interaction, which is typically involving antibody/antigen, enzymes/ligands, nucleic acids/DNA, cellular structures/cells, or biomimetic materials. Recently, the introduction of nanomaterials endowed biosensors the ultrasensitivity and label-free strategies in antibiotics detection, where optical signals such as fluorescence, colorimetry, chemiluminescence, or surface plasmon resonance, were used according to different transduction mechanism. However, the output signal is normally not from antibiotics itself.

In general, developing a high sensitive, selective, convenient, robust, and rapid on-site method towards trace antibiotic detection in complicated matrix is still highly demanded, while laboratory methods are well established using chromatography and technology of tandem.

With the well-known inhibitory and bactericidal effects, silver nanomaterial has been widely used in daily-life as an excellent antibacterial agent, which has the synergic antibacterial activity in the presence of various antibiotic chemicals [12–14]. In order to reach the best antibacterial effect, exploring the synergic mechanism between antibiotics and Ag nanomaterial is crucial. Outstanding by the selectivity with the fingerprint spectral resolution and the sensitivity at the single molecular level, Surface-enhanced Raman spectroscopy (SERS) has been widely applied to characterize the interaction between molecules and metal nanomaterials qualitatively, and detect various trace targets quantitatively, including antibiotics in food, biosystem and water environment.

In the present review, after giving brief introduction of SERS, we will review the current advances of SERS application in the trace antibiotic detection various conditions, and give perspective of the related challenges to develop SERS method to a routine onsite analysis technique in aquatic environment, where the detected concentrations generally range from  $\text{ng L}^{-1}$  to  $\mu\text{g L}^{-1}$  [8,9,11,15–21].

## 2. Brief introduction of Raman & surface-enhanced Raman spectroscopy

Raman scattering is a kind of inelastic scattering discovered by C. V. Raman in 1928, and the Jablonski diagram of Raman process was shown in Scheme 1. The obtained Raman spectroscopy provides the structural fingerprint information to identify molecules on the basis of the energy difference between the incident light and the Raman scattering, which reflects the vibrational, rotational, and other low-frequency modes of the molecule and is specific to the chemical bonds and symmetry of certain molecule structure. The fingerprint identification ability and the non-destructive detection qualify Raman spectroscopy to be one of the most important tool for qualitative and quantitative analysis widely applied in chemistry, physics, biology, bio-pharmaceutical, nanotechnology, art and aerospace science etc. However, The fingerprint level high energy resolution is accompanied by the inherently low sensitivity induced by the weak Raman scattering cross-section ( $\sim 10^{-30} \text{ cm}^2/\text{molecule}$ ), a value 10 orders lower than that of

Infrared or fluorescence spectroscopy, which makes Raman spectroscopy being restricted in the routine macro-analysis with bulk or concentrated ( $> 0.01 \text{ M}$ ) sample.

When the energy of the incident laser is close to an electronic transition of the molecule, the frequency resonance can lead to greatly enhanced intensity of the Raman scattering as much as a factor of  $10^6$ . This phenomenon is named as Resonance Raman (shown in Scheme 1), which facilitates the study of molecules at low concentrations down to  $10^{-8} \text{ M}$ . However, the companion fluorescence and photodegradation of the sample is the major disadvantage [22].

A new prospect was open with the discovery of Surface-enhanced Raman scattering/spectroscopy (SERS), which was observed by Fleischman et al. first in 1974 [23], and then confirmed by Van Duyne et al. [24]. and Creighton et al. [25]. to be an extraordinary surface enhancement phenomenon three years later. The sensitivity of Raman spectroscopy was improved up to 6 orders or even to single molecule level by SERS [26–28].

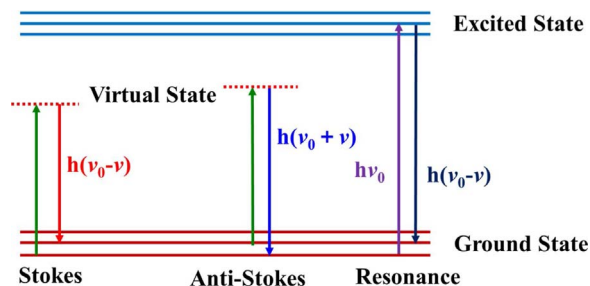
After forty years' development, SERS obtained profound improvement both theoretically and experimentally. Up to now, the enhancement mechanism is still an open question and a combination of electromagnetic enhancement (EM) and chemical enhancement (CT) [29–31]. EM enhancement originates from the coupling of the incident and Raman EM fields on nanomaterial surfaces with localized surface-plasmon resonance (LSPR). The induced resonance involves the plasmon frequency, the frequency of the incident and scattered radiations, and leads to a resonant plasmon transition responsible for the giant electric field on the nanoparticle surface. EM enhancement is widely accepted to be the main contribution in the SERS enhancement, whose local enhancement at certain highly localized electromagnetic "hot spots" is in the order of  $10^{11}$  [32]. CT enhancement is from the formation of charge transfer complexes between the nanomaterial and the adsorbed target molecule, whose contribution is a minor, but plays key role for the surface plasmon-enhanced photochemical reactions [33]. It should be noted that more than 200 reviews have been published related to the mechanism & applications of SERS, readers are encouraged to read more related reviews for a better understanding of SERS theoretically and experimentally. For example, the recently published special issue related to SERS in Chemical Society Reviews [34].

Although the mechanism is not in a conclusive state yet, the application of SERS has been explored widely. With the trace detection ability, SERS enabled researchers to investigate various interfacial dynamic behaviors (adsorption/desorption, reaction, catalysis and so on) of the mono-/sub mono-layer target molecule fundamentally and to realize the trace detection of target molecule in various environments practically.

## 3. Trace antibiotic detection by SERS

Since Raman spectroscopy was demonstrated to successfully analyze the impurity in Polyene Antibiotics [35], it has been widely used as a powerful tool in antibiotics related researches non-destructively and free-labeling. From the pharmaceutical applicability point, the sorption mechanisms on various surfaces [36], the aggregation and cocrystallization of antibiotics with other mediums have been explored [37–39]. The detection of the eye antibiotics in the aqueous humor in early pathological levels paved a way for the potential application in pharmacokinetics and on-time diagnosis of intraocular diseases [40]. The ability of exploring the interaction mechanism between bacteria and antibiotics on the single cell level [41–44] gives the opportunities for the screening of new antibiotics [44], monitoring produced antibiotics by bacteria [43] and the identification of diverse antibiotics treated bacteria [42].

Furthermore, the feasibility of antibiotics residue detection in food, drinking water and biosystems by SERS was explored from sulfonamides to quinolones, penicillins and tetracyclines etc., a variety of antibiotics commonly used in human society [6,35–40,45–60]. For a



Scheme 1. Jablonski Diagram of Raman Process.

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