



# Identification and analysis of Triphenyltin chloride with surface enhanced Raman scattering spectroscopy



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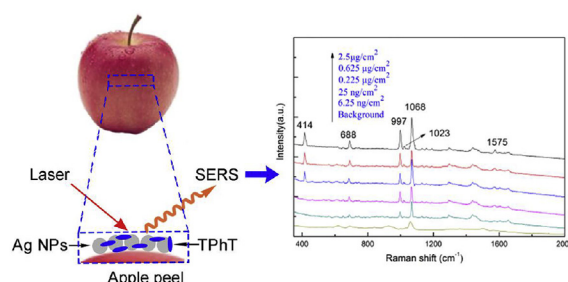
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## HIGHLIGHTS

- The complete Raman spectra vibrational characterization of TPhT along with the IR spectroscopy is reported.
- The optimal pH value in TPhT solutions detection using Raman spectroscopy is selected.
- TPhT on apple peels could be detected by using AgNPs SERS substrate at as low as 6.25 ng/cm<sup>2</sup>.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Triphenyltin (TPhT) is a kind of organotin compounds which have been used ubiquitously as herbicide, pesticide, and fungicide in agriculture. The present study provides the possibility to detect and monitor TPhT with normal Raman spectroscopy and surface enhanced Raman scattering (SERS) spectroscopy. Firstly, the complete vibrational Raman spectra characterization of TPhT along with the IR spectroscopy were reported for the first time. Then a wide range of pH values were carried out to choose the optimal pH value in TPhT detection by using Raman spectroscopy. Afterwards, Raman spectra of various TPhT solutions were collected and analyzed. The results indicate that the optimal pH value for TPhT detection by Raman spectroscopy is 5.5, and with silver nanoparticles (Ag NPs) as SERS substrate is an effective technique for trace TPhT detection with an enhancement by 5 orders of magnitude and the detection limit can be as low as 0.6 ng/L within less than 30 s. Finally, in this study, the residual of TPhT on apple peel was investigated by casting different concentrations of TPhT on apple peel under the current optimized condition. The result demonstrates that TPhT could be detected based on its SERS spectra at 6.25 ng/cm<sup>2</sup> in standard solutions.

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## 1. Introduction

Triphenyltin derivatives, especially Triphenyltin chloride (TPhT), have been proved to be a non-substitutable pesticide and widely used as agricultural chemicals, such as herbicide, pesticide, and

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fungicide as well as in marine antifouling paints for ship hulls and fish nets (Grote et al., 2007), although they have toxic effects on microorganisms, insects, seaweeds and even mammals (Ohhira and Matsui, 1996). TPhT can be released into the environment through several routes. For example, TPhT in sediments and flakes of anti-fouling paints may serve as reservoirs so as to cause the locally high concentrations of TPhT. TPhT can also be input via its use as pesticides in agriculture (de Carvalho and Santelli, 2010). The impact of TPhT on aquatic organisms is significant because some aquatic organisms have a strong ability in accumulation of TPhT. Even at very low concentrations, TPhT can lead to the toxic effect or reproductive adverse changes, which could cause the degeneration of female animals in marine and reproductive toxicity (Negri and Marshall, 2009). TPhT is also known as a kind of hormone disruptors which are capable of activating or blocking hormone receptors especially estrogen or androgen receptors, and then inhibit a variety of enzymes which are responsible for the production of sex steroid hormones in male and female organisms (Dagmar and Doering, 2002). In vitro exposure to TPhT in human choriocarcinoma cell lines decreases DNA and protein synthesis (Graceli et al., 2013). TPhT can enter the body through the respiratory tract, gastrointestinal tract, skin and mucous membrane to interfere with in vivo hormone secretion and transportation. And these may increase the risk of cancer and viral infections. Research indicates that nominal concentrations of 100 ng TPhT/L could cause the significant spermatogenesis in ovaries of exposed females organisms (Horiguchi et al., 2002). In addition, exposure to 1–100 nM of TPhT can promote the expression of genes related to male hormones and the proliferation of prostate cancer cells (Yamabe et al., 2000).

Although the use of TPhT has been banned as a biocide in the EU due to the serious concerns about operator safety and undesired effects on non-target organisms (Verhaegen et al., 2012), its environmental impact still exist. And now in China (Gao et al., 2013), the pollution of TPhT especially in coastal areas is also a challenging problem (Ho and Leung, 2014). Because of the environmental hazard of TPhT, the analysis methods of organotin have attracted great interest of scientists in the last few decades. Those detection methods commonly include gas chromatography (GC) coupled with mass spectrometry (MS) (Ikonomou et al., 2002; Kulkarni et al., 2013), atomic emission detection (AED) (Santosa et al., 2009), pulsed flame photometric detector (PFPD) (Sant'Anna et al., 2012), mass spectrometry equipped with flame photometric detector (FPD) (Tang and Wang, 2007), stir bar sorptive extraction (SBSE) followed by solvent desorption and liquid chromatography tandem mass spectrometry (SD–LC–MS/MS) analysis (Camino-Sanchez et al., 2012), etc. Although above methods can be used to detect trace amount of TPhT with good sensitivity and low detection limit, they are normally complicated, tedious, time-consuming, labor-intensive with elaborative special sample preparations. In addition, it is not easy to apply these techniques for fast, field and nondestructive detection of TPhT.

Raman spectroscopy is a spectroscopic technique which has been used to investigate the transition modes of functional groups in materials. The Raman fingerprint spectra can provide overall and the specific information of various chemical as well as biological materials compositions. In recent few years, Raman technology has demonstrated its important application for detection of pesticide contents in fruits (Yi et al., 2012; Dhakal et al., 2014; Fan et al., 2014; He et al., 2014; Fang et al., 2015). In order to improve the analytical sensitivity and detection limit, surface enhanced Raman scattering (SERS) is becoming a hot research field. As for SERS, when the target molecules attach to metallic nanostructures (typically, Au, Ag and Cu), the Raman signals can obtain a significant enhancement by millions of times at active sites of these structures due to electromagnetic field enhancement and chemical enhancement. SERS is a

highly effective technique for detection of molecular vibrations in substance at trace amount even to the single molecular detection level (Dhakal et al., 2014). SERS has been widely used in pesticide residue analysis, especially in trace amount analysis with high sensitivity. Wang and coworkers (Wang et al., 2014) reported in-situ detection of phosmet and disulfoton residues on oranges with surface-enhanced Raman spectroscopy by using Au nanoparticles (AuNPs) decorated with glycidyl methacrylate-ethylene dimethacrylate powder materials for the solid-phase extraction. Similarly, Fan and coworkers (Fan et al., 2014) reported the detection of phosmet residues in apples with surface-enhanced Raman Spectroscopy with gold-coated substrates for Raman signal enhancement. However, the application of Normal Raman or SERS spectroscopy in TPhT detection has not been reported so far.

In this paper, the possibility of quantitative analysis of TPhT with Raman spectroscopy were demonstrated with linear relationships between the concentrations of TPhT and the corresponding intensities of major characteristic peaks of Raman spectra. The purpose of this study is to investigate the Raman characteristic peaks of TPhT, and to explore the feasibility of detecting TPhT with normal Raman and SERS spectroscopy with silver nanoparticles SERS substrate. The proposed method could be used as a rapid, highly sensitive, and reliable analytical tool for the further study of SERS combined with chemometrics method in TPhT detection for their potential detection of environmental pollutants.

## 2. Material and methods

### 2.1. Materials and reagents

Triphenyltin chloride (TPhT, 95%) were purchased from German, Dr. Ehrenstorfe. Methanol, Hydrochloric acid (HCl, AR) and Sodium hydroxide (NaOH, AR) were purchased from J.T. Baker (Phillipsburg, NJ). Silver (99.999%) and titanium (99.995%) pellets were purchased from Kurt J. Lesker (Clairton, PA). Aluminum sheet were purchased from a Chinese industry (Advanced pure, 99.99%). All the chemical, solvent and materials were used without further purification. Water was purified by using Milli-Q water system (18.2 M $\Omega$  cm).

### 2.2. Preparation of SERS substrate

SERS active substrate with silver nanoparticles was prepared based on chemically reduction of silver nitrate (AgNO<sub>3</sub>) with trisodium citrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>). Briefly, 1.0 mM of AgNO<sub>3</sub> was prepared by dissolving 40.00 mg silver nitrate in 250 mL of ultra pure water. The solution was kept boiling with continuous stirring. Then about 8 mL of 1% Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> solution was added to the boiling solution drop wisely. The mixture was kept boiling for about 30 min until the solution turns gray green.

### 2.3. IR spectrum of TPhT

In order to study the corresponding vibrational modes of the characteristic Raman peaks, the IR spectrum of TPhT was collected in this experiment. The combination of Raman and IR spectra for TPhT were analyzed to attribute their characteristic peaks. The fourier transform infrared spectrometer is set in the range of 100–2000 cm<sup>-1</sup> to collect TPhT standard powders.

### 2.4. Normal Raman and SERS measurements

All the measurements were performed on Renishaw (The UK) in Via micro-Raman spectroscopy system with 785 nm provided by a near-infrared diode laser with a cooled charge-coupled device

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