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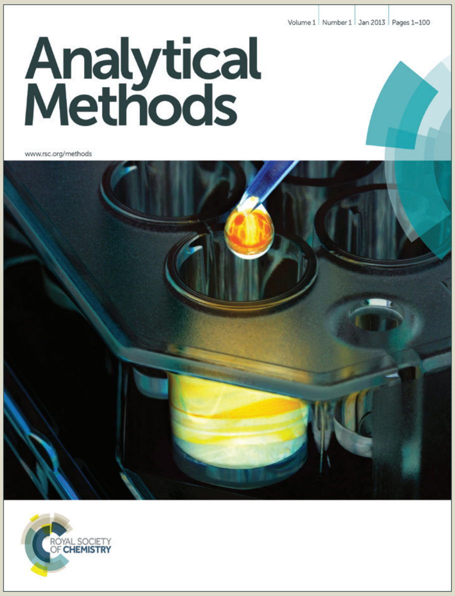

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Single wall carbon nanotubes-oxide test strip for one-step solid phase extraction of simetryn and fast detection using surface enhanced Raman spectroscopy

Zhuo Deng[a], Haihong Liu[a], Yiru Wang[a]*, Xi Chen[a,b]**

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A novel technique combined with solid-phase extraction and surface-enhanced Raman spectroscopy has been developed using a home-made test strip as the solid phase apparatus and detecting platform for surface-enhanced Raman spectroscopy. Single wall carbon nanotubes (SWCNTs) were functionalized with oxidizing acid and deposited on a filter membrane to fabricate the SWCNTs-oxide test strip for one-step solid-phase extraction. After spraying the surface of the SWCNTs-oxide test strip with gold colloids, surface-enhanced Raman scattering signals were greatly increased owing to the clean detection background of the matrix and the concentrated target molecules in the probed volume. A facile approach was recommended here to fast monitor simetryn residues in lake water samples using one-step solid-phase extraction with the SWCNTs-oxide test strip and subsequent direct detection on a portable inspector Raman. The detection limit of this method was found to be 2 μg L^{-1}, and the recovery was between 70 and 80%. In addition, the linearity was in the range 10 to 300 μg L^{-1} with a correlation coefficient of 0.9878. The method provides a promising approach for the fast analysis of triazine compounds in complex matrix samples.

Introduction

Triazines and their metabolites, which are used as important herbicides for weed control, have caused great concern as human carcinogens[1]. Water resource zones near railways, roadsides, golf courses and industrial areas or cropland are usually under the ubiquitous pollution risk of triazine due to its high mobility and solubility in water and strong absorbability in soil. Thus, the European Union legislation has set a maximum allowable herbicide residue level in drinking water[2].

In order to detect trace triazines in a complex sample, a pretreatment process is demanded. Liquid-liquid extraction, solid-phase extraction (SPE) [3], supercritical fluid extraction, solid-phase microextraction[4] and liquid-phase microextraction[5] are reported as effective sample preparation techniques to extract target compounds from environmental samples. Generally, large scale instruments such as those used in high performance liquid chromatography (HPLC)[4], gas chromatography (GC)[6], and GC-mass spectrometry[5] are adopted for their later detection. These analytical methods are sensitive but time-consuming and high cost. For on-site ultrafast detection, simple sample preparation and measurement procedure are urgently required.

The portable Raman spectrometer shows great potential for on-site ultrafast monitoring because it may provide information about molecular vibrations that can be used to quickly identify and quantify substances. Since surface-enhanced Raman scattering (SERS), a surface-sensitive technique, was developed in 1974[7], it has been widely applied in many fields such as surface studies[8], environmental analysis[9], and the biological sciences[10]with its high sensitivity and rapid identification. In general, Au, Ag, and Cu nanoparticles (spheres, rods, cubes or triangles, enabling hot spots via interparticle geometry) are commonly used as highly sensitive SERS substrates[11]. However, the SERS enhancement effect is limited mainly when the adsorbed molecules are monolayer on the supporter surface, or out of the hot spot zone induced between nanoparticles. Therefore, a low concentration of target compounds and an associated strong matrix background severely limit the practical applications of this technique.

Single wall carbon nanotubes (SWCNTs) are formed by seamless roll up of single layers of graphene sheet. With a unique one-dimensional structure and exceptional surface areas (150 to 1500 m^2/g), they can be easily covalently or non-covalently functionalized to provide selective interaction with analytes[12-14]. Using functionalized SWCNTs as adsorbent in the sample preparation, the target compounds are selectively separated from the strong sample matrix and focused on the functionalized SWCNTs, resulting in the decreasing of background interference and the increasing of the number of target molecules in the volume probed using the Raman spectrometer.

In this work, we report a new approach to analyze simetryn in aqueous samples, which is one kind of the triazines. One step SPE with a test strip was used to separate the target from complex matrix samples, and a portable Raman spectrometer was used to obtain the surface-enhanced Raman scattering of the simetryn. This showed the great potential application prospects of the SPE-SERS combination technique for on-site -fast detection.

Experimental

Reagents and materials

SWCNTs powders with 90% purity and typical lengths of 5 to 15 µm were obtained from the Shenzhen Nanotech Port Co. Ltd. (Shenzhen, China). Porous nylon membrane (200 nm pore size, 50 mm diameter) was purchased from the Tianjin Jinteng Experiment Equipment Co., Ltd. (Tianjing, China). Triazines (simetryn, ametryn, prometryn, dipropetryn, desmetryn, terbutryn, cyanazine, metribuzin, terbuthylazine, atraton, prometon and terbumeton) and acetyl cellulose were purchased from the Sigma-Aldrich Trading Co., Ltd. (Shanghai, China). Hydrogen peroxide (H_2O_2, 35%), hydrochloric acid (HCl, 36-38%), and N,N-dimethyl-formaldehyde (DMF, 99.9%) were provided by the Sinopharm Chemical Reagent Beijing Co., Ltd. Methanol, of HPLC grade, was obtained from the TEDIA Co. Inc. (Fairfield, OH, USA). The stock solutions of triazines were prepared to 1000 mg L^{-1} in methanol. The ultrapure water (18.2 MΩ cm) used in the experiments was produced using a Simplicity Water Purification System (Millipore, Molsheim, France).

Instrumentation

All SERS spectra were collected on an Inspector Raman (DeltaNu Inc.) equipped with a 785 nm laser excitation source and NuSpec^{TM} software. Spectral libraries were developed using DeltaNu's library management software for the identification of unknown substances. A laser Raman microscope, RAMAN-11 (Nanophoton Corp.), was employed to compare the characteristics of oxide SWCNT samples. A Spectrafuge Mini Centrifuge (C1301-230V, Labnet Corp.) was used for centrifugation of the prepared gold colloid.

Preparation of gold colloid

Citrated-reduced gold colloid was prepared based on the Lee and Meisel method[15], qualified by the scanning electron microscopy and UV-Vis absorbance spectra (shown in Fig. S1). The concentration of gold colloid was 0.1% (w/v) and the gold nanoparticles with a core size of 55 nm proved to be efficient for SERS under near-infrared (785 nm) excitation. To improve the sensitivity of SERS detection, the gold colloid was cleaned by centrifugation. Typically, a 1500-µL aliquot of the prepared gold colloid was centrifuged at 6000 rpm for 10 min. The supernatant was removed to keep the volume of concentrated gold colloid at 30 µL before use. The concentrated gold colloid might effectively reduce interparticle spacing, induce electromagnetic enhancement, and amplify the gained SERS signal. However, over centrifugation would lead to the precipitation of gold colloid, resulting in a low SERS signal.

Preparation of SWCNTs-oxide test strips.

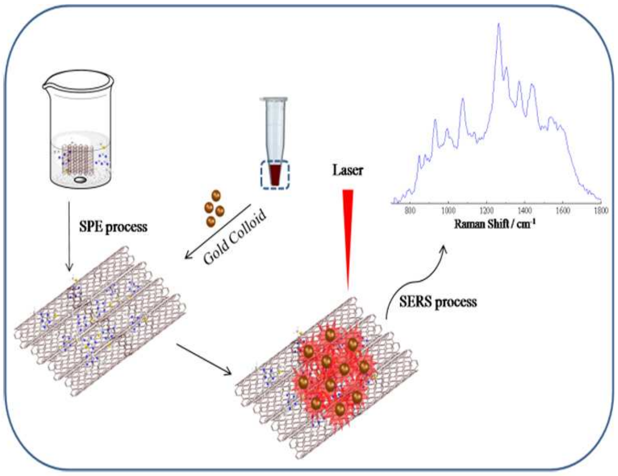
50 mg of SWCNT powder was purified by refluxing in a mixture of HCl and H_2O_2 (3:1 v/v) at 60 °C for 5 h, and dried at 80 °C in an oven overnight. 25 mg of the pretreated SWCNTs were collected to disperse in 50 mL DMF solution with 0.1 g acetyl cellulose using an ultrasonic cleaner at room temperature for 0.5 h.

A relatively dense film was prepared by filtration of the SWCNTs-oxide solution through the Nylon membrane. After being cleaned several times using ultrapure water and methanol under vacuum, the film was dried at 60 °C, and cut into small test strips (5 mm×5 mm) before use.

SPE-SERS process

As shown in Scheme 1, a 10-mL aliquot of aqueous sample was transferred to a 50-mL beaker together with a magnetic bar. Then, the SWCNTs-oxide test strip was completely dipped into the aqueous sample and kept at the immersion depth using stainless steel tweezers. After SPE for 30 min at the stirring rate of 500 rpm, the test strip was removed and placed on a slide glass with the SWCNTs-oxide coating upwards.

10-µL of the concentrated gold colloid was dropped onto the SWCNTs-oxide test strip surface and the SERS signals were then recorded. In the SERS measurement, the output power of the Inspector Raman was selected at a high grade of 60 mW, and the spectral resolution was set low for decreasing the background noise. The manual integration time was set as 1 second.



Scheme.1 Schematic of the SPE-SERS procedure with SWCNTs-oxide test strips.

Results and discussion

Mechanism of SPE-SERS

Strong background interference is the main technical problem for SERS monitoring of real samples, and SERS activities for nanostructured substrates largely depend on the activity and density of hot spots[11]. When the interaction force between nanostructured substrates and target molecules is weaker than that of contaminants, it is difficult for the target molecules to occupy the surface active sites[16]. Adsorption competition occurs between the target compounds and the contaminants. Thus, gold colloid cannot be used directly in the analysis of real water systems with a strong matrix background, and purification and enrichment of the target molecules is necessary for SERS analysis.

A homemade relatively dense SWCNTs-oxide test strip has been produced in our work, not only for the extraction of target compounds from aqueous samples, but also for direct SERS detection. When the SWCNTs-oxide test strip was completely dipped into the aqueous sample, the target molecules began to distribute between the carbon nanotubes and the water. Because of the selectivity of SWCNTs-oxide, the target molecules were cleaned up and focused on the adsorbent. By increasing the number of target molecules in the probed volume and decreasing the background of the matrix, the sensitivity of SERS improved.

After extraction, the concentrated gold colloids were added to the test strip and dispersed on the surface of carbon nanotubes or among the network of carbon nanotubes. Based on the mechanism of electromagnetic resonance, nanoscale-featured noble metals are capable of supporting localized surface plasmons, but the enhanced electromagnetic fields quickly decay away from the metal nanoparticle surface. The surface of the test strip was rough enough to hold more gold nanoparticles (shown in Fig. S2,), which might provide a higher density of "hot spots" for SERS effect. In consideration of the special electrical properties of carbon nanotubes, the synergy-type enhancement effect might also occur among gold nanoparticles, target molecules and carbon nanotubes. Therefore, the SWCNTs-oxide test strip not only acted as an adsorbent for the target molecules, but also as a good support for the concentrated gold colloids. As shown in Fig. 1, two lake water samples spiked with 100 μg L^{-1} simetryn were prepared, one was pretreated using SWCNTs-oxide test strips while another directly injected into glass tubes. After addition of the same volumes of gold colloid, Raman signals using SPE-SERS greatly increased rather than those using in-tube-SERS. This proved that the combination technique of SPE and SERS was a facile and effective approach for environmental analysis.

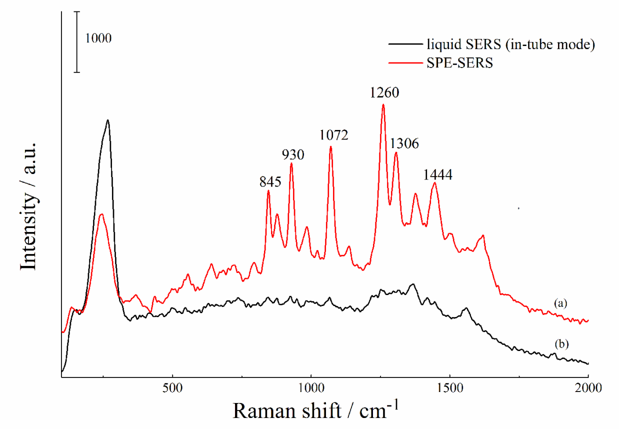


Fig. 1 SERS spectra of (a) lake water spiked with 100 μg/L simetryn using SPE-SERS and (b) In-Tube-SERS.

Properties of SWCNTs-oxide test strip

In this work, non-oxidative treatment (HCl treatment) and oxidative treatment (a mixture of HCl-H_2O_2, and HNO_3) were applied to eliminate the metal impurity and amorphous graphitic platelets of the as prepared SWCNTs. Since Raman spectroscopy is one of the most powerful techniques for the characterization of functionalized SWCNTs, different types of functionalized SWCNTs were evaluated using RAMAN-11 with a 532 nm laser source. Generally, two characteristic bands, the D-band (defect-related band) at ~1341 cm^{-1} and the G-band (graphite-like band) at ~1590 cm^{-1} are found in Raman spectroscopy[17, 18]. The D-band is aroused by the presence of amorphous or disordered carbon in pristine samples, which should be avoided in Raman spectra of SWCNTs[19]. The carbon structural disorder is due to the finite or nanosized graphitic planes and other forms of carbon. The G-band originates from in-plane tangential stretching of the carbon-carbon bonds in graphene sheets. The intensity ratio of the D-band and G-band usually represents the degree of defect in the graphite structure. By integrating the areas of the D and G peaks in Fig. 2(a), the corresponding ratio I_G/I_D increased sharply from 1.49 to 3.35 after the SWCNTs were refluxed with HCl. This indicated an appreciable elimination of graphitic nanoparticles so that the non-oxidative treatment might efficiently purify the pristine SWCNTs. Obviously, after the treatment of HCl-H_2O_2 and HNO_3, the ratio of I_G/I_D decreased to 2.34 and 2.19, respectively. The produced carboxyl (1625 cm^{-1}) and hydroxyl groups (3427 cm^{-1}) in the IR spectra shown in Fig. 2(b) supported the destruction of the graphitic integrity after the oxidation process. Fig. 2(c) indicates a schematic of SWCNTs-oxide. The oxidation using HCl-H_2O_2 and HNO_3 increased the defect formation in the SWCNTs. However, the covalent functionalities on the SWCNT surface, such as carboxylates, impart a negative charge and, therefore, could create electrostatic stability[20]. Both oxidation treatments by HCl-H_2O_2 and HNO_3 were found to improve the dispersion stability of SWCNTs in DMF with the aid of acetyl cellulose (as shown in Fig. S3). After sonication in DMF for 10 min, the SWCNTs treated with HCl precipitated while the SWCNTs treated with oxidative reagents maintained colloidal stability for 24 h.

Table 1 Vibrational assignment of the observed SERS band of ~~triazines~~ simetryn

Experimental shift (cm^{-1})	Reported shift (cm^{-1})	Proposed assignment	References
845	847	δ(triazine ring), ν(C-Cl), τ(CH_2)+τ(CH_3)	23,24,25,27
930	930	ω(CH_3)	24,25,26,27
1072	1072	ν(C-C)+δ(NH) +ω(CH_3)	23,24,26,27
1260	1250	ω(triazine ring)+τ(CH_2)	24,26,27
1306	1301	ν(triazine ring)	24,25,27
1444	1443	δ(CH_3)	24,25,27

□τ = twisting; ν = stretching; ω = wagging; δ = bending

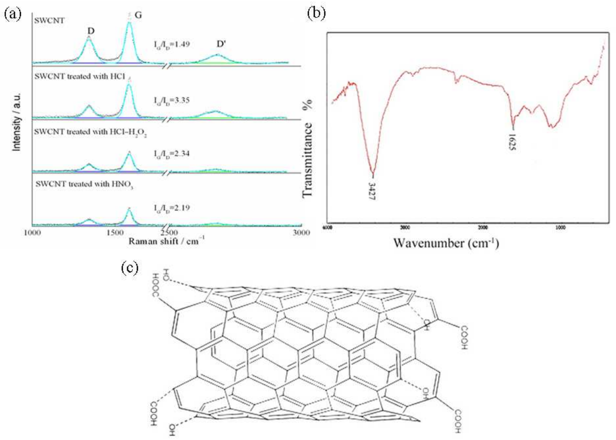


Fig. 2 (a) Raman spectra of SWCNT samples after treatment wih different agents (Excitation wavelength: 532.00 nm; laser current: 100%; excitation power: 0.10 mW; exposure time (/line): 120 s; CCD temperature: -69.5 °C; objective lens: L Plan ×50/0.45). (b) IR spectrum of HCl-H_2O_2 treated SWCNT. (c) Schematic of SWCNTs-oxide.

Acetyl cellulose was added for further improving the dispersion of SWCNTs-oxide in DMF organic solvent, which may thread themselves onto or wrap themselves around the surface of carbon nanotubes and disrupt the van der Waals interactions among the carbon nanotubes[21, 22]. This kind of noncovalent functionalization of carbon nanotubes with carbohydrates not just increases the solubility of SWCNTs-oxide but also provides good affinity between the carbon nanotubes and their scaffold. Since SWCNTs-oxide was dissolved in organic solvent, an organic phase filter, nylon membrane, was selected as scaffold to immobilize carbon nanotubes here. Because of the softness of nylon membrane, it was easily cut into small test strips before use. No carbon nanotubes were observed to be lost from the test strips during the extraction, indicating the superior durability of SWCNTs-oxide test strip. A tunable thickness of SWCNTs-oxide was obtained by filtering different volumes of the SWCNTs-oxide solution.

Optimization of SPE-SERS

SERS activity and vibrational assignment for triazines. The main observed SERS bands for simetryn triazines and their its vibrational assignment are shown in Table 1. Compared to previous research, most of the observed SERS bands in the experiments showed high level of consistency. Since the 1260 cm-1 band is characteristics wagging vibration mode for triazine ring and is the most obvious in the SERS spectra, it was chosen for quantification. Several experimental conditions, such as extraction time, stirring rate, pH and matrix ionic strength, were optimized in order to achieve good sensitivity.

Effect of extraction time. Mass transfer of SPE is an equilibrium-based extraction procedure and therefore a time dependent process. However, SERS is a surface detection technique so that its sensitivity depends only on the amount of ~~triazine~~ simetryn on the probed surface of the adsorbent. Keeping the other experimental conditions constant, the effect of extraction time on the SERS signal was studied. As shown in Fig. 3a, the extraction efficiency linearly increased as extraction continued for 30 mins and later reached its maximum value. It seemed that the adsorptive points on the surface area of the SWCNTs-oxide test strip could not be saturated by the ~~triazine~~ simetryn in such a short time. The rough and large surface of the SWCNTs-oxide test strip was speculated to be primary reason for the ~~triazine~~ simetryn to take 30 minutes to completely occupy the superficially adsorptive points. After saturation, the SERS signal remained constant, and no obvious discrepancies were found between 30-min and 40-min extraction. The linear increase before 30 mins also indicated that non-equilibrium quantitative detection by SPE-SERS was effective. Linear correlation between the SERS signal and the concentration of simetryn was found before saturation of the superficially adsorptive points when fixing the extraction conditions such as time, stirring rate, temperature, pH and ionic strength.

Effect of stirring rate. The velocity of the mass transfer of simetryn was mostly limited by absorption of the aqueous phase to the SWCNTs-oxide test strip because diffusion of the target compound was limited on the surface of the SWCNTs-oxide test strip. An effective way to improve the rate of diffusion was thus stirring. As shown in Fig. 3b, SERS signals were linearly increased by increasing of the stirring rate up to 500 rpm. At a stirring rate of 750 rpm, the generation of bubbles and an unstable vortex hindered the mass transfer, resulting in a decrease of the SERS

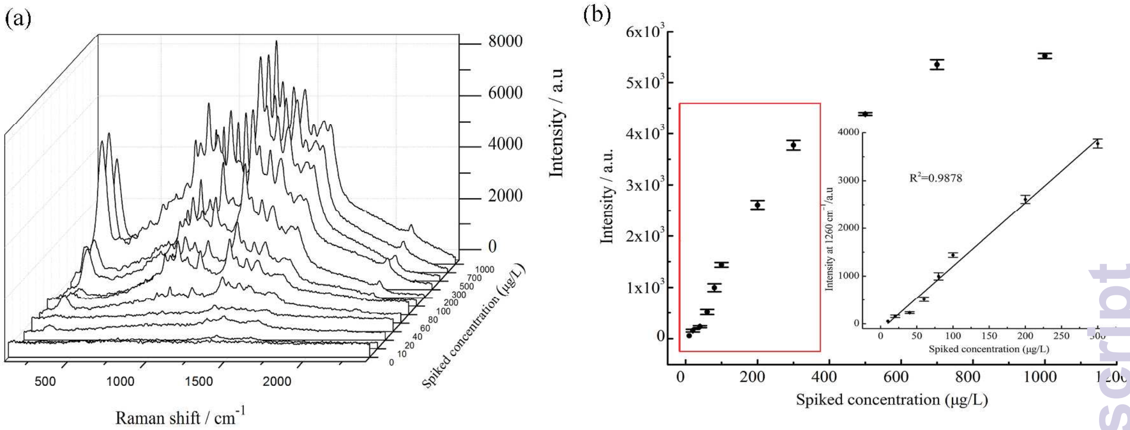


Fig. 4 (a) SERS spectra obtained in the presence of 0, 10, 20, 40, 60, 80, 100, 200, 300, 500, 700 and 1000 μg/L simetryn. (b) The calibration curve of analyte from 10 to 1000 μg/L, plotted at a peak intensity of 1260 cm^{-1}, the inset figure showed the calibration linearity ranged from 10 to 300 μg/L.

signal. Therefore, the stirring rate of 500 rpm was selected as an optimized condition.

Effect of pH. The effect of pH in the range 2.0 to 14.0 on the extraction of simetryn herbicide is shown in Fig. 3c. This indicated no significant effect of pH on the extraction of ~~triazine~~ simetryn by the SWCNTs-oxide test strip and, therefore, no pH modification was demanded in the experiment. Although the amino of simetryn was protonized at low pH (pK$_a$ 4.03), there was no obvious correlation between the protonized amino of simetryn and the quantitative Raman peak of 1260 cm^{-1}.

Effect of ionic strength. Ranging from 0 to 30% (w/v), the ionic strength was modified by the addition of sodium chloride to a 10-mL water sample. After extraction under optimized conditions, the SERS signal was evaluated with or without desalination by immersion of the SWCNTs-oxide test strip into ultrapure water for 10 seconds. Without desalination, the gold colloid was precipitated and then the SERS signal sharply decreased. The residue of Na$^+$ and Cl$^-$ ion on the surface of the test strip caused overreaction in the aggregation of gold colloid[16]. As shown in Fig. 3d, although the addition of salt improved the extraction efficiency, desalination of the test strip was required after extraction to avoid precipitation of the gold colloid.

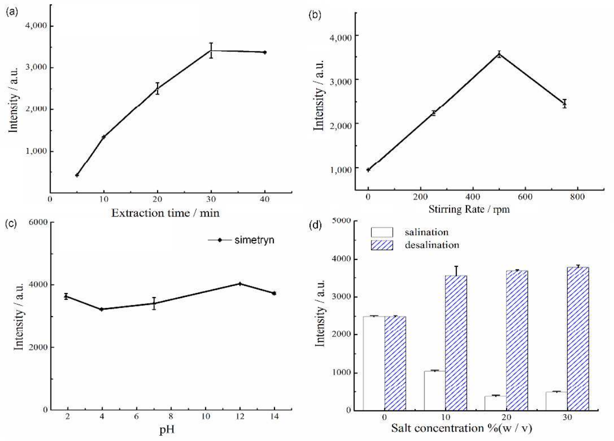


Fig. 3 (a) SPE extraction time profile for simetryn in aqueous solution. Stirring rate, 500 rpm. (b) Effect of agitation on the extraction efficiency of SPE. Extraction time, 20 min. (c) Effect of solvent pH on extraction efficiency of SPE. (d) Effect of ionic strength on extraction efficiency of SPE compared with the SERS effect. Extraction conditions: aqueous sample volume, 10 mL; concentration, 100 μg/L.

Evaluation of the analytical performance

To evaluate the performance of the SPE-SERS method developed for the determination of simetryn in water samples, the linear range and repeatability were evaluated under optimum conditions. A series of working solutions containing simetryn at twelve concentration levels (0, 10, 20, 40, 60, 80, 100, 200, 300, 500, 700 and 1000 μg L^{-1}) was prepared for the calibration curve. The SERS spectra of simetryn after SPE-SERS analysis at different concentrations were shown as Fig. 4a. We can found that the calibration curve tend to plateau at high analyte concentrations. This is the simple result of saturation of the SWCNTs-oxide test strip surface by the analyte. Linearity was found to be in the range 10 to 300 μg L^{-1} with a correlation coefficient of 0.9878 (Fig. 4b). For each level, three replicate experiments were performed. The method detection limit was 2 μg L^{-1}. To test the accuracy of this established method, a natural water sample from a lake was spiked with the standards at a concentration of 100 μg L^{-1}. The complicated matrix of the environmental water greatly influenced the recovery, so that the recovery of the method was only between 70 and 80% with the relative standard deviations varying from 2.5 to 12.9%. All the above results suggested a sensitive and reproductive SPE-SERS method for the analysis simetryn in environmental water. We also made a comparation on the performances of this method and others available technique for simetryn residue detection, the result shown as Table S1 suggests that this novel approach can reach on-site ultrafast detection simetryn residues in natural water samples.

In order to evaluate the practicability of the method to fast analysis of triazine compounds, we also measured SERS spectra of other twelve triazines on the Si/SiO$_2$ substrate (the molecular formula and structural formula are shown in Table S2). These triazines (except for metribuzin) can be divided into three types, -azine (chlorine group), -etryne (methylthio group) and -tone (methoxy group) because the ending of the common name of herbicides is indicative of the substituent on the 2-position. Fig.S4 provided the fingerprint information of these molecular structures. The SERS spectra show that the same type of triazines shared more similar Raman shifts than different types. Since the SERS spectra were inclined to bring out the characteristic peaks of the most competitive molecule in the mixture standards solution, such as the -etryne type resulting from the strong binding force between the methylthio group and the gold nanoparticle, the SPE progress provide an alternative way to avoiding the measurement deviation in this mode. However, since the same type of triazines shared more similar Raman shifts as we mentioned before, a proper chemometric resolution method still should be used to distinguish different triazines.

Conclusions

A facile method was established for the preparation of SWCNTs-oxide test strip to act as one-step SPE adsorbent and SERS substrate. After the one-step SPE process, interference from the matrix was largely eliminated. When the strip was deposited with preconcentrated gold colloid, high sensitivity Raman response of simetryn was obtained as a result of the SERS effect. The mechanism of the SPE-SERS hyphenated technique was investigated and the extraction conditions including time, stirring rate, PH and ionic strength were optimized. The linearity of the SPE-SERS method was 10 to 300 μg L^{-1} with method detection limit as low as 2 μg L^{-1}. In lake water spiked with 100 μg L^{-1} simetryn, the recovery of the SPE-SERS method was in the range 70 - 80%. This novel approach succeeded in identifying simetryn in natural water samples using a sensitive, accurate, fast and cheap SPE-SERS system. And the method provides a alternative way to fast analysis of triazine compounds in complex matrix samples.

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Notes and references

[a] Department of Chemistry and the MOE Key Laboratory of Spectrochemical Analysis & Instrumentation, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

[b] State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361005, China

* Corresponding author: E-mail: yrwang@xmu.edu.cn; Fax: +86 592 2184530; Tel: +86 13599510908.

** Corresponding author: E-mail: xichen@xmu.edu.cn; Fax: +86 592 2184530; Tel: +86 592 2184530.

† Electronic Supplementary Information (ESI) available: [Characterization of gold colloid and test strip, pictures of SWCNTs, and molecular formula and structural formula of triazine herbicides]. See DOI: 10.1039/b000000x/

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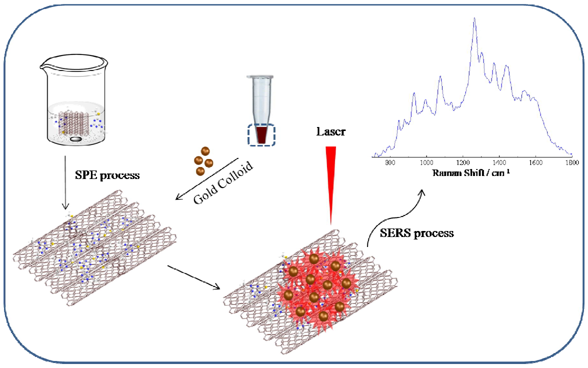
Graphical abstract



A facile method was established for the preparation of SWCNTs-oxide test strip to act as one-step SPE adsorbent and SERS substrate, which can made a fast monitor for triazine residues in lake water samples by combing solid-phase extraction and surface-enhanced Raman spectroscopy.