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Indirect glyphosate detection based on ninhydrin reaction and surface-enhanced Raman scattering spectroscopy

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ABSTRACT

Glyphosate is one of the most commonly-used and non-selective herbicides in agriculture, which may directly pollute the environment and threaten human health. A simple and effective approach to assessment of its damage to the natural environment is thus quite necessary. However, traditional chromatography-based detection methods usually suffer from complex pretreatment procedures. Herein, we propose a simple and sensitive method for the determination of glyphosate by combining ninhydrin reaction and surface-enhanced Raman scattering (SERS) spectroscopy. The product (purple color dye, PD) of the ninhydrin reaction is found to SERS-active and directly correlate with the glyphosate concentration. The limit of detection of the proposed method for glyphosate is as low as $1.43 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$ with a relatively wider linear concentration range (1.0×10^{-7} – $1.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$), which demonstrates its great potential in rapid, highly sensitive concentration determination of glyphosate in practical applications for safety assessment of food and environment.

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1. Introduction

Glyphosate is one of the world's most popular and non-selective herbicides. It is used for killing a wide variety of harmful plants in agriculture primarily, and can also be used on some genetically modified crops, such as wheat, alfalfa, canola, corn, cotton, and soybean [1]. Thus, it directly pollutes the environment and contaminate foods. Although its safety for human health is a subject of wide debate, several reports have demonstrated that the toxicity of glyphosate cannot be neglected *in vivo* and *in vitro* [2]. Therefore, detection of pesticide residues is an essential step in regulating and monitoring the levels of pesticides [3]. Since the 1980s, glyphosate residue determination has been conducted by chromatographic methods, including gas or liquid chromatography (GC/LC) combined with mass spectroscopy (MS) [4]. However, glyphosate itself is of highly polar, difficult to volatilize and soluble in water, thus it is usually derived with 2,2,3,3,4,4,4-heptafluoro-1-butanol and trifluoroacetic anhydride and then is detected with GC–MS [5,6]. Moreover, it has no fluorescence group that can be detected by fluorescence detector, thus it is needed to be derived with 9-fluorenylmethylchloroformate (Fmoc–Cl) over night and then detected by LC–MS [7]. These chromatographic methods are widely used but still suffering from complex cleanup process and multiple derivative

operation steps [8]. Thus a simple and effective approach to assessment of glyphosate's damage to the natural environment is thus quite necessary [9].

Surface-enhanced Raman scattering (SERS) spectroscopy is an advanced analytical technique that enhances Raman spectrum of molecules adsorbed on or in the vicinity of SERS-active surfaces [10]. Raman technique is suitable for pesticide detection in aqueous solution, and SERS was first used for glyphosate detection by Costa et al. [11,12]. They reported the analytical application of SERS in the trace analysis of glyphosate on silver nanocubes aqueous suspensions, and assigned the experimental Raman and SERS bands of glyphosate. Moreover, they indicated that SERS was a useful tool which could be used in glyphosate. In more recent studies, Sharma et al. developed an method for fabrication of SERS substrate with regular dendritic silver nano-structures on carbon coated Ag–Cu-grids, which can be used for glyphosate detection [13]. The preparation process of such SERS-active substrate is however complicated. On the other hand, De Góes et al. developed $^{100}\text{s}\text{CO}$ -Au NPs as highly-sensitive SERS substrates to detect glyphosate with a limit of detection as $0.1 \times 10^{-6} \text{ g} \cdot \text{L}^{-1}$, but osmium is relatively expensive with potential toxicity to humans [14]. Therefore, an economically viable, simple, fast SERS method is needed for glyphosate detection.

Pesticides with certain groups, such as thiol and amine can bind to Au or Ag substrates strongly, which could be direct detected by SERS. Alternatively, those pesticide molecules without these special groups could be coupled by some probe molecules and thus bind to the

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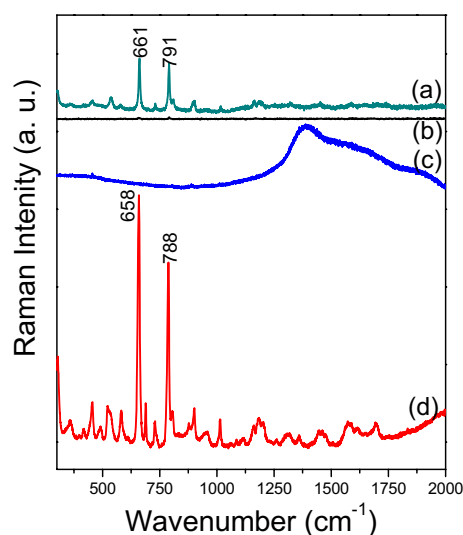


Fig. 1. Laser wavelength-dependent Raman spectra of the PD product (a, 633 nm; b, 532 nm; c, 785 nm); SERS spectra absorbed onto Ag NPs (d) with 633 nm laser line at a concentration of $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$.

substrates indirectly [15,16]. On the basis of the similarity between the structure of glyphosate and amino acids, it is likely that glyphosate can also react with ninhydrin from its amino group and the product could be detected by SERS. Ekstrom et al. firstly reported this reaction [17], and Bhaskara et al. detected the purple's product by Ultraviolet-visible spectroscopy (UV-Vis) with a limit of detection as $4 \times 10^{-5} \text{ g} \cdot \text{L}^{-1}$ [18].

In the present study, we establish a simple and indirect method for glyphosate quantification by combing ninhydrin reaction and SERS. The glyphosate is initially changed to a ninhydrin derivative with a purple color, which is SERS-active with Ag nanoparticles (NPs). In this way, glyphosate can be indirectly determined by typical SERS bands of the reaction product.

1.1. Experimental Section

1.1.1. Chemicals

Silver nitrate (AgNO_3 , CAS: 7761–88–8, 99%) was purchased from Sigma-Aldrich Chemical Co. Glyphosate (*N*-(Phosphonomethyl) glycine, $\text{C}_3\text{H}_8\text{NO}_5\text{P}$, CAS: 1071–83–6, 99.9%) and ninhydrin (2,2-dihydroxyindane-1,3-dione, $\text{C}_9\text{H}_6\text{O}_4$, CAS: 485–47–2, 98%) were obtained from Aladdin Industrial Corporation. Sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, CAS: 6132–04–3, 99%), sodium molybdate (Na_2MoO_4 , CAS: 7631–95–0, 99%), and all other chemicals were analytical-grade reagent and used without further purification. Ultrapure water (18.25 M Ω) was used throughout the experiments.

1.1.2. Apparatus

UV-Vis extinction spectra were measured with a UV-3600 spectrophotometer (Shimadzu). Raman spectra were collected from a Jobin Yvon/HORIBA LabRam ARAMIS Raman Spectrometer equipped with an integral BX 41 confocal microscope. The radiations from an air-cooled internal HeNe laser (633 nm) and an external cavity diode laser (785 nm) were used as the excitation sources. Moreover, a Renishaw Raman System Model 1000 spectrometer with the 532 nm excitation wavelength was used. The exposure time set at 10 s with one accumulation.

1.2. Sample Preparation

1.2.1. Preparation of Ag NPs

Ag NPs were prepared according to the Lee and Meisel method [19]. Briefly, 36 mg AgNO_3 were added into 200 mL H_2O , and 4 mL of

trisodium citrate solution (1% ω/V) was added when it started to boil. After keeping heating for 40 min at 85 °C, a grey-green colloid formed and was naturally cooled at room temperature [20].

1.2.2. Preparation of Solution

A stock solution of $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ glyphosate was prepared by dissolving 8.45 mg glyphosate in a 50-mL volumetric flask and then diluting to 50 mL with H_2O . From this stock solution, $1.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, $1.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ and $1.0 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ glyphosate solution were prepared by appropriate dilution with H_2O .

A 5% (ω/V) Na_2MoO_4 solution was prepared by dissolving 2.50 g Na_2MoO_4 in H_2O in a 50-mL volumetric flask and diluting to 50 mL with H_2O . A 5% (ω/V) ninhydrin solution was prepared by dissolving 2.50 g ninhydrin in a 50-mL volumetric flask and diluting to 50 mL with H_2O . **Ninhydrin working reagent:** A 5% ninhydrin solution + water + acetate buffer ($0.4 \text{ mol} \cdot \text{L}^{-1}$, pH 5.5) (2:1:1, V/V/V).

1.2.3. SERS-Based Ninhydrin Derivatization

Mixed working reagent: Nonhydrin working reagent + 5% Na_2MoO_4 + standard glyphosate solution (1:1:1, V/V). The mixed working solutions were heated in boiling water for 30 min; 10.00 μL of the producing solutions were mixed with 10 μL Ag colloid for SERS measurements.

1.2.4. Preparation of Natural Water Samples

Tap water, pond water, lake water and river water (50 mL) were collected from Changchun (N43°05'–45°15', E124°18'–127°05'), Yan Lake of Jilin Univerity, Youyi Park and Nanxi Wetland Park, in July 2017, respectively. All water samples were used without further clean-up process.

2. Results and Discussion

2.1. Characterization of the Ag Nanoparticles (NPs)

Ag NPs are most commonly used SERS-active substrates in fundamental and applied sciences [21]. The spheroidal Ag NPs used in this study have a maximum absorption around 430 nm with an average diameter of 60 nm, which are consistent with the results reported in the literature [22].

Table 1
Raman and SERS band assignments (cm^{-1}) of the PD product.

Experimental Raman	Experimental SERS	Assignments ^{a, b}
303	304	$\beta(\text{PO}_2)$
457	456	$\gamma(\text{CH}_2) + \beta(\text{OH})$
491	490	$\beta(\text{OH}) + \gamma(\text{CH}_2) + \rho(\text{PO}_2)$
–	523	$\beta(\text{OH}) + \beta(\text{CH})$
539	533	$3 + 18b + \beta(\text{C-C-C})$
662	659	<i>o.p.</i> $\beta(\text{C=O})$
790	788	<i>o.p.</i> $\beta(\text{C=O})$
810	805	$\gamma(\text{CH}_2) + \nu(\text{C-C})$
896	901	$1 + \text{a.v.}(\text{C-C})$
969	957	$19b + \text{a.s.}\beta(\text{C-O})$
1019	1014	$19b + \text{a.s.}\beta(\text{C-O}) + \beta(\text{O-C-C})$
1074	1086	$\nu(\text{C-N}) + \beta(\text{C-OH})$
1117	1117	$\tau(\text{CH}_2) + \beta(\text{OH})$
1162	1160	$\beta(\text{O-C-O})$
1191	1182	$19a + \beta(\text{O-H})$
1198	1206	3
1240	1261	$\beta(\text{O-H})$
1320	1312	15
1351	1359	18a
1449	1443	$\beta(\text{CH}_2)$
–	1474	18b
–	1570	9a
1584	1587	9b

^a The Wilson notation is employed.

^b s: symmetry; as: asymmetry; ν : stretching vibration; β : bending; γ : rocking; ω : wagging; *i.p.*: in-plane; *o.p.*: out-of-plane.

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