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Quantitative determination of ametryn in river water using surface-enhanced Raman spectroscopy coupled with an advanced chemometric model

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ABSTRACT

In this contribution, surface-enhanced Raman spectroscopy (SERS) coupled with an advanced chemometric method-multiplicative effects model (MEM_{SERS}) has been applied to quantitative analysis of ametryn in water samples of the Xiangjiang River (Changsha, China). The adoption of MEM_{SERS} calibration model was to eliminate the detrimental effects caused by variations in the physical properties of enhancing substrates, the intensity and alignment/focusing of laser excitation source. Experimental results showed that the combination of SERS with MEM_{SERS} can provide quite precise concentration predictions for ametryn in water samples of the Xiangjiang River with an average relative prediction error of about 4.8%. The combination of SERS with MEM_{SERS} can compete with LC-MS/MS in terms of precision and accuracy of quantitative results. The limit of quantification was about 0.09 μM. More importantly, no laborious reference methods (e.g., HPLC) were needed to build the MEM_{SERS} calibration model, since the MEM_{SERS} calibration model built on the calibration samples prepared with ultrapure water could provide satisfactory quantification results for the test samples prepared with water collected from the Xiangjiang River. Therefore, it is reasonable to expect that SERS in combination with MEM_{SERS} model would become a competitive alternative in routine quantitative analysis of ametryn in environmental water samples.

1. Introduction

Ametryn (2-ethylamino-4-isopropylamino-6-methylthio-1, 3, 5-triazine), a member of the triazine chemical family, is a selective systemic herbicide and widely used for the pre and post emergence control of weeds in plantations of sugarcane, banana, coffee, etc. It has been reported that only 0.1% of herbicides applied to crops reach their targets, and a large proportion remains in the environment [1]. The Environmental Protection Agency (EPA) classifies ametryn as toxicity class III [2,3]. Because of its toxicity, persistence and accumulation in the environment as well as its effects on the environment and human health, it is listed as a chemical pollutant that needs to be monitored.

Over the years, various analytical techniques have been developed for the detection of ametryn. For example, microwave-assisted solvent extraction coupled with anodic stripping voltammetry was used to determine ametryn in soils by Tavares et al. [4]. Solid-phase extraction (SPE) and solid-phase microextraction (SPME) have been employed for quantitative analysis of ametryn in environmental matrices [5–8]. The application of high-performance liquid chromatography (HPLC) and liquid chromatography-tandem mass spectrometry (LC-MS-MS) to the determination of ametryn in river water and processed cereal samples was reported by Jacomini et al. [2] and Li et al. [9], respectively. The above methods are generally costly and time-consuming, and not readily adaptable for use in the field.

Since the discovery of surface-enhanced Raman spectroscopy (SERS) technique in the late 1970s [10], SERS has been successfully applied to many areas such as biological detection and environmental monitoring [11–13] due to its unique advantages, such as narrow spectroscopic bands with excellent molecular specificity, reduced photo-bleaching, simple sample pretreatment and ultra high sensitivity as well. For instance, Costa et al. [14] applied SERS to qualitative study of pesticides including ametryn. However, since the SERS signals of analyte depend on not only the analyte concentration but also the physical properties of enhancing substrates (e.g., the particle size and shape of colloids, the degree of aggregation), the intensity and alignment/focusing of laser excitation source, SERS is more frequently used as a qualitative tool rather than quantitative one. Recently, our research group [15,16] proposed a multiplicative effects model for surface-enhanced Raman spectroscopy (MEM_{SERS}), which can effectively eliminate the detrimental effects caused by variations in SERS enhancing substrates and focusing of laser excitation source. Nevertheless, the potential of MEM_{SERS} has not

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been fully exploited yet. In this contribution, surface-enhanced Raman spectroscopy was coupled with MEM_{SERS} to quantitatively determine ametryn in water samples of the Xiangjiang River (Changsha, China).

2. Experimental

2.1. Reagents and chemicals

Ametryn (98.8%) and *p*-thiocresol (98%) were purchased from Aladdin. Sodium citrate dehydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$) and chlorauric acid hydrated ($HAuCl_4 \cdot 4H_2O$) were obtained from Sigma-Aldrich Chemical Reagent Co., Ltd. (Shanghai, China). Ethanol was purchased from Titan Technology Co., Ltd. (Shanghai, China). All chemicals were of analytical grade and used as received without further purification. Ultrapure water (18.2 MΩ cm^{-1}) used in this paper was produced by a Milli-Q water purification system (Millipore, USA).

2.2. Preparation of Au Nanoparticles

Au nanoparticles with approximate diameter of 50 nm were prepared by citrate reduction of $HAuCl_4$ [17–19]. All glasswares were cleaned in aqua regia (HCl: HNO_3 = 3:1 v/v), rinsed with ultrapure water and then dried in an oven prior to use. A 50 mL aqueous solution of $HAuCl_4$ (0.01% m/v) was brought to reflux temperature while stirring. Then 1 mL 1% (m/v) trisodium citrate solution was quickly added, resulting in a change in the color of the solution from pale yellow to purple. Subsequently, the mixture was refluxed for an additional 30 min and allowed to cool to room temperature. The solution was finally concentrated 10 times prior to use.

2.3. Sample preparation and SERS measurement

Stock solutions of ametryn (12 mM) and *p*-thiocresol (98 mM) were prepared in ethanol and stored at 4 °C. Twenty-seven samples (Table 1) with different concentrations of ametryn were prepared by mixing appropriate amount of stock solution of ametryn with ultrapure water. Another 27 samples with the same experimental design as shown in Table 1 were prepared by mixing ametryn with water collected from Xiangjiang River in Changsha (China), which was tested ametryn free by tandem mass spectrometry coupled to liquid chromatography (LC-MS/MS). The working solution of *p*-thiocresol (1.70 μM) was prepared by diluting the stock solution of *p*-thiocresol with ultrapure water. Thirty microliters of each sample was mixed with 10 μL of concentrated gold nanoparticles (AuNPs), 10 μL of different concentrations of ametryn and 10 μL of working solution of *p*-thiocresol for SERS spectral acquisition. All the mixtures prepared were allowed to set for 2 min before spectral acquisition. SERS spectrum of each sample was measured on a Renishaw Invia confocal Raman spectrometer (Renishaw, Wotton-under-Edge, UK) equipped with a Peltier CCD detector, a Leica microscope and a 633 nm He-Ne laser (17 mW of power) for excitation. All spectra were collected in static mode in the centre of 1100 cm^{-1} with an accumulation of 3 scans and an exposure time of 10 s using a × 50 objective.

Some previous studies [20,21] have shown that the nitrogen-rich melamine have excellent binding capability to AuNPs. There is a strong interaction between AuNPs and melamine with three exocyclic amino groups and three-nitrogen hybrid ring, which can decrease the stability of citrate-stabilized AuNPs against the aggregation. Ametryn has the same three-nitrogen hybrid ring as melamine. Moreover, ametryn has other binding sites, i.e., two exocyclic secondary amines and one sulfur atom. Therefore, ametryn can coordinate with unmodified AuNPs and induce the aggregation of AuNPs [22]. The quantification of ametryn was carried out using internal standard tagging detection mode as shown in Fig. 1. *p*-Thiocresol can bind to AuNPs through Au-S bonds [23–26] and was used as an internal standard.

Table 1
The experiment design of ametryn samples.

No.	c (μM)	No.	c (μM)	No.	c (μM)
1–3	0.20	10–12	1.20	19–21	2.40
4–6	0.40	13–15	1.60	22–24	2.80
7–9	0.80	16–18	2.00	25–27	3.20

2.4. LC-MS/MS experiments

For the purpose of comparison, the 27 samples prepared with water collected from the Xiangjiang River was analyzed by a 1290 HPLC system (Agilent Technologies) equipped with a C18 reversed-phase column (2.1 mm i.d. × 150 mm length, a bead size of 3.5 μm). The column was maintained at 30 °C. The mobile phase consisted of water (eluent A) and methanol containing 0.1% formic acid (eluent B). The volume ratio between eluent A and eluent B was 15%:85%. The flow rate was set to 0.3 ml/min. For each sample, a volume of 10 μL was loaded onto the column via an autosampler from a 54-well sample tray. Each sample was analyzed three times. LC-MS/MS data of samples were collected by an Agilent G6460 Triple Quadrupole mass spectrometer (Agilent Technologies) with electrospray interface (ESI) operated in the positive mode using the following settings: nebulizer pressure = 15 psi, fragmentor voltage = 135 V, capillary voltage = 4000 V, drying gas flow rate = 11 L/min, and drying gas temperature = 300 °C. The MS detector was operated in multiple reaction monitoring (MRM) mode. The precursor to production ion transition selected for quantification of ametryn was *m/z*: 228 → 186.

2.5. Data analysis

The 27 ametryn samples prepared with ultrapure water were divided into calibration set 1 (No. 1–6, 10–12, 16–18, 22–27) and test set 1 (No. 7–9, 13–15, 19–21). Another 27 samples prepared with water from the Xiangjiang River were partitioned into calibration set 2 (No. 1–6, 10–12, 16–18, 22–27) and test set 2 (No. 7–9, 13–15, 19–21). SERS signals in the range from 497 to 1645 cm^{-1} were selected for the subsequent quantitative analysis. The SERS peaks of both the analyte of interest (832, 879, 918, 964, 1260 and 1305 cm^{-1}), and the internal standard (1075 and 1592 cm^{-1}) can be readily observed in the selected region (Fig. 2).

The following multiplicative effects model for surface-enhanced Raman spectroscopy (MEM_{SERS}) [15,16] was adopted for subsequent quantitative SERS assays (a detailed description of MEM_{SERS} is also provided in Supporting Information):

$$\mathbf{x}_k = b_k \cdot \left(c_{\text{p-thiocresol},k} \cdot \mathbf{r}_{\text{p-thiocresol}} + c_{\text{ametryn},k} \cdot \mathbf{r}_{\text{ametryn}}\right) + \mathbf{d}_k;\ \ (k = 1, 2, \cdots, K) \quad (1)$$

where $\mathbf{x}_k$ is the SERS spectrum of the *k*th sample; $c_{p\ -\ \text{thiocresol},k}$ and $c_{\text{ametryn},k}$ are the concentrations of *p*-thiocresol and ametryn in the *k*th calibration sample, respectively; and $\mathbf{r}_{p\ -\ \text{thiocresol}}$ and $\mathbf{r}_{\text{ametryn}}$ represent the molecular scattering properties of *p*-thiocresol and ametryn, respectively. The multiplicative parameter b_k explicitly accounts for the multiplicative confounding effects on SERS intensities caused by changes in variables other than analytes' concentrations in the *k*th calibration samples, such as physical properties of the enhancing substrates, the intensity and alignment/focusing of laser excitation source; $\mathbf{d}_k$ is a composite term that represents background interference(s) and the non-multiplicative effects caused by variations in physical properties of the enhancing substrates on the *k*th sample. Since the concentration of the internal standard *p*-thiocresol $c_{p\ -\ \text{thiocresol},k}$ was constant across samples, the multiplicative parameters b_k ($k = 1, 2, \ldots, K$) for *K* calibration samples in the above MEM_{SERS} model can be estimated from their SERS spectra by the modified optical length estimation and correction