



## Original article

## Determination of carbendazim in tea using surface enhanced Raman spectroscopy

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## ARTICLE INFO

## Article history:

Received 6 September 2015

Received in revised form 20 October 2015

Accepted 22 October 2015

Available online 28 October 2015

## Keywords:

Carbendazim

Tea

Surface enhanced Raman spectroscopy

Half-life

*In-situ* detection

## ABSTRACT

Surface-enhanced Raman scattering (SERS) is applied to detect the concentration of carbendazim (CBZ) in tea leaves. Au colloid is selected and used for active surfaces, and the extraction conditions are optimized in the experiment. The linearity range for the SERS intensity and the concentration of CBZ is found to be 0.5 to 8 mg kg<sup>-1</sup>. The detection limit for CBZ is 0.1 mg kg<sup>-1</sup> and its recovery in tea samples is 72.3%. The detection results for CBZ using this method are compared with those of HPLC, and no obvious difference can be found. In addition, by dripping the condensed Au colloid on the tea leaves, the proposed SERS approach could be used to the *in-situ* determination of the half life period of CBZ on tea leaves.

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## 1. Introduction

Tea is one of the important cash crops in some area of China. During the tea cultivation, insecticides are inevitably used for the pest and plant disease control. Carbendazim (CBZ) is a kind of benzimidazole fungicide (its chemical structure was shown as Fig. 1), which is often used as foliage spraying, seed dressing and soil treatment [1]. CBZ is of lower toxicity to mammals [2], but its higher dose damages their reproduction and growth. Animal experiments reveal that CBZ increases the sexual hormone activity of male [3]. The National Food Regulatory Agencies sets its maximum residue limits in tea and other foods. In China food safety standards, the tolerance for CBZ residue in tea is 5 mg kg<sup>-1</sup> [4].

There have been reports focusing on the study of CBZ in tea. Wang [5] reported the transfer rates of pesticide residues from dried tea to brewed tea leaves and found that CBZ was one of the three most frequently found pesticide among 12 pesticide residues. Several analytical methods have been applied in the detection of CBZ including high performance liquid chromatography (HPLC) [6,7], electrochemical [8,9] and fluorescence approaches [10]. Generally, these techniques require complex

sample preparations and the time-consuming detection process, resulting in the inconvenience for the *in-situ* detection. It is becoming important to develop rapid analytical methods for the CBZ detection. Surface enhanced Raman scattering (SERS) provides a very interesting option, which has attracted much attention for food monitoring [11,12], chemical [13] and pesticide analysis such as phosmet residues on navel orange surface [14] tricyclazole and paraquat in food [15], carbaryl in apple juice and vegetables [16], as well as pesticide on fruit peel [17,18]. Although there have been some reports on the determination of CBZ for fruit or vegetable sample using SERS [19,20], there is still few report on the SERS analysis of CBZ for tea samples.

In this work, we developed a fast method to detect CBZ in tea and on tea leaves without complex sample preparations. The all analytical process could be finished within 30 min. It can be applied in the quantitative analysis of CBZ in tea samples with a low LOD, and will be helpful to control the tea quality.

## 2. Experimental

CBZ was purchased from Sigma-Aldrich. Methanol was obtained from TEDLA Co. Ltd. Ultrapure water (18.2 MΩ cm) was produced from a Simplicity Water Purification System (Millipore, USA) and used in the all experiments throughout. ENVI-Carb solid phase extraction columns (Supleco) were obtained

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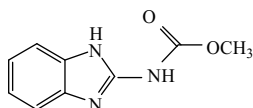


Fig. 1. Chemical structure of carbendazim.

from Sigma-Aldrich, which were activated according to the instruction before use.

The synthesis of Au colloid was performed using chemical reduction of chloroauric acid with a sodium citrate method introduced by Frens [21]. 1.5 mL aliquot of the prepared gold colloid was centrifuged at 6000 rpm for 10 min, and then, the supernatant was removed to keep the volume of concentrated gold colloid at 10  $\mu\text{L}$  before use.

All surface enhanced Raman spectra were collected using an Inspector Raman (Deltanu Inc.) equipped with 785 nm laser excitation source. The laser power was approximately 60 mW. The accumulation time for each spectrum was set as 1 s.

A high performance liquid chromatography (HPLC, Shimadzu, LC-20AT) equipped with a SPD-20A detector and a Synchris C18 column (4.6 mm  $\times$  250 mm, 5.0  $\mu\text{m}$ ) was used for the experimental verification. In the HPLC experiments, methanol and water (50:50, v/v) was used as the mobile phase, and the flow rate was set as 0.6 mL  $\text{min}^{-1}$ . The injection volume of samples was 5  $\mu\text{L}$ .

The tea samples from local supermarkets were dried and then ground through 40 mesh. 0.3 g ground tea sample was put into a centrifuge tube. After the addition of 100  $\mu\text{L}$  0.25 mol  $\text{L}^{-1}$  HCl and 3 mL water, the suspension was ultrasonically extracted for 20 min at room temperature (25  $^{\circ}\text{C}$ ), and then centrifuged for 3 min at the speed of 5000 rpm. The suspension was filtered through an ENVI-Carb extraction column. The filtered solution was used for SERS measurements.

In the detection of CBZ in a tea infusion, 0.5 g tea sample spiked CBZ 8.0 mg  $\text{kg}^{-1}$  was put into a cup and then brewed with 11 mL boiling water. In the tea infusion preparation, the first immersing time for the tea brewing was set as 1 min, 2 min for the second brewing, and 5 min for the third (simulating to the tea organoleptic examination procedure). The tea infusion was filtered through the ENVI-Carb extraction column. 200  $\mu\text{L}$  filtrate was added into a sample tube. After the addition of 10  $\mu\text{L}$  condensed Au colloid uniformly, the collected Raman signal could be obtained.

A tea plantation in Wuyi University was selected for the study of CBZ residue on tea leaves. Before spraying, 50% CBZ was diluted to 1000 times. The sprayed tea leaf samples were collected in different time interval, which was selected as 1 to 7 day with per day interval. In the detection of CBZ residue on tea leaves, 10  $\mu\text{L}$  of condensed gold colloid was dipped onto the leaf surface. In order to mix the analyte well, the Au colloid solution was repeatedly sucked several times using a pipette, and the dipping area should be controlled around 1  $\text{cm}^2$ . The SERS signals from the picked tea leaves were finally measured and collected.

In the HPLC control experiments, the sample preparation was similar with that of SERS method. In the experiments, the supernate of the tea sample was filtered through an extraction column and a 0.45  $\mu\text{m}$  membrane before the sample injection. All the analysis for both brewed tea and tea leaves were performed in triplicate.

### 3. Results and discussion

The prepared gold nanoparticles (GNPs) is shown in Fig. 2, the GNPs are spherical in shape and about 55 nm in diameter.

CBZ molecule consists of benzimidazolyl, amino and methyl formate, including C–H, N–H, C=C, C=O and  $-\text{CH}_3$  group, which

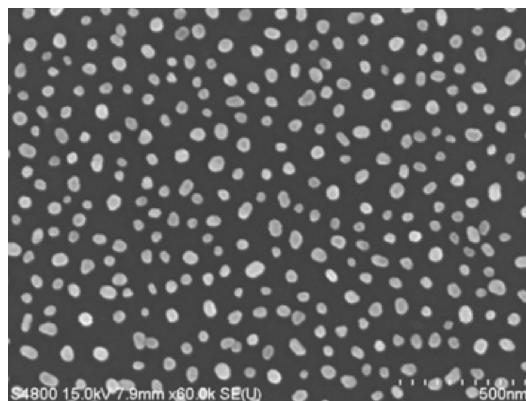


Fig. 2. The scanning electron microscopy (SEM) of gold nanoparticles.

functional group has its characteristic vibrational frequency and mode [22]. The spectrum of carbendazim in water was shown in Fig. 3, and the assignments of Raman bands of CBZ are presented in Table 1. The Raman shifts between the wavenumber from 400 to 1000  $\text{cm}^{-1}$  are mainly attributed to the inner bending vibration of C–C–C, and the shifts with higher intensity from 1000 to 1400  $\text{cm}^{-1}$  are attributed to C–H outer bending, imidazole inner ring vibration and C–N stretching vibration [3,23]. The shifts in the range of 1400 to 2000  $\text{cm}^{-1}$  mainly relate to C=C stretching vibration. A typical SERS spectrum of CBZ aqueous solution is shown in Fig. 3. The obvious shift peaks at 1021, 1283 and 1392  $\text{cm}^{-1}$  can be used as the characteristic peak of CBZ. In the experiments, the peak at 1021  $\text{cm}^{-1}$  was used to the analysis of CBZ.

Under the consideration of sensitivity and the simplicity of the proposed approach, several parameters such as pH value, extraction time and temperature, which affect the extraction efficiency, were studied and optimized using 0.3 g tea sample spiked CBZ (final amount 6.0 mg  $\text{kg}^{-1}$ ). CBZ is soluble and stable in acidic conditions, but changes to its salt in an alkaline condition. The pH effect on the SERS signal of CBZ was investigated. As shown in Fig. 4a, no obvious SERS signal of CBZ could be found at pH 2, while the signal obviously increased with the increase of pH, and a maximum response at pH could be obtained. pH affects Raman intensity hugely since gold colloid aggregates at very low pH conditions, however, in an appropriate pH condition, gold

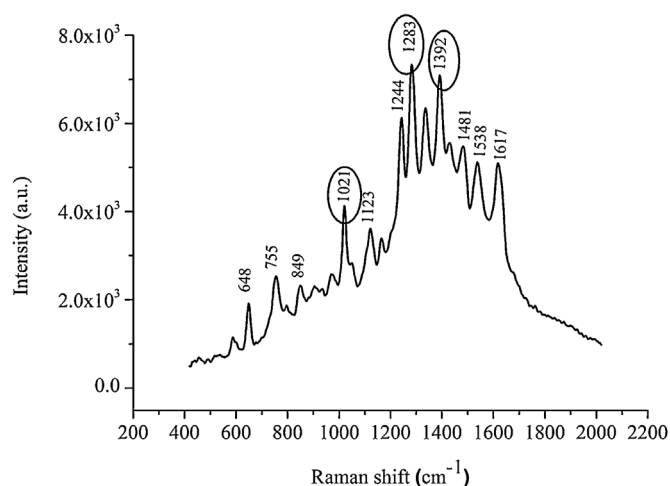


Fig. 3. SERS spectrum of carbendazim.

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