

# Ultrasensitive determination of formaldehyde in environmental waters and food samples after derivatization and using silver nanoparticle assisted SERS

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**Abstract** A selective and ultrasensitive surface-enhanced Raman spectroscopy (SERS) method was developed for the determination of formaldehyde (HCHO) in environmental waters and food samples. It is based on derivatization of HCHO with 4-amino-5-hydrazino-3-mercapto-1,2,4-triazole (AHMT) with HCHO. One of the products of the derivative reaction, 6-mercapto-5-triazolo[4,3-b]-s-tetrazine (MTT), can be quantified by SERS at  $832\text{ cm}^{-1}$  using silver nanoparticles (AgNPs) as substrates. The incubation time for derivatization, the volume of reagents and the mixing times were optimized. The peak areas of the SERS are linearly related to the concentration of HCHO in the  $1\text{--}1,000\text{ }\mu\text{g L}^{-1}$  range, the limit of detection is  $0.15\text{ }\mu\text{g L}^{-1}$ , and the limit of quantification is  $0.45\text{ }\mu\text{g L}^{-1}$ . Recoveries obtained by analyzing two spiked samples of environmental water and two spiked food samples were in the range between 91.0 and 108.7 %. There is no

significant difference between the results obtained by the present method and the liquid chromatographic method (Chinese industrial standard method, SN/T 1547-2011).

**Keywords** Surface-enhanced Raman spectroscopy · Formaldehyde · Environmental water · Food

## Introduction

Formaldehyde (HCHO) is a colorless gas at room temperature with a pungent and irritating odor. It is a common contamination in air, water, industrial products and food samples [1]. In aqueous systems, atmospheric deposition is a significant source of HCHO. HCHO in drinking water arises mainly from the oxidation of natural organic (humic) matter during ozonation and chlorination [2]. In foodstuffs, HCHO come mainly from two ways: one is natural production during fermentation; the other is used illegally in the food processing industry, because the adulteration of HCHO in some foodstuffs not only prolong their storage lives but also change their colors and smells to attract consumers [3, 4]. The effects of HCHO on human body are well known: irritations of eye and upper respiratory tract, headache, nausea, drowsiness, and allergic skin reactions [5]. It is also a potential mutagen and carcinogen in laboratory animal tests for its serious toxicological properties [6]. The World Health Organization (WHO) determined that the concentration of HCHO in residential indoor areas must not exceed 82 ppb (parts per billion) [7]. The United States Environment Protection Agency (USEPA) has established a maximum daily reference dose (RfD) of  $0.2\text{ mg kg}^{-1}$  per day for HCHO [8]. Rapid methods are suitable for the analysis of large numbers of samples on site in order to obtain accurately and timely analysis results, especially in food safety and environmental concerns [9].

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Therefore, it is essential to develop rapid methods for the accurate determination of trace HCHO in environmental water and food samples.

Many analytical methods have been reported for the determination of HCHO in various samples, including spectrophotometry [3], fluorimetry [2, 10], chemiluminescence [11, 12], gas chromatography (GC) [13], and high-performance liquid chromatography (HPLC) [14]. Although the precision, the accuracy, and the sensitivity of fluorimetry, chemiluminescence, GC and HPLC are high enough for the determination of trace HCHO, the expensive and large apparatuses of which make the on-site rapid determination hardly. Spectrophotometry is widely used for the determination of HCHO due to its inexpensive and simple instrumentation, using various chromogenic agents, such as chromotropic acid [15], pararosaniline [16], acetylacetone [17], 4-amino-5-hydrazino-3-mercaptop-1,2,4-triazole (AHMT) [18], 3-methyl-2-benzothiazolone hydrazone (MBTH) [19]. The derivative reaction of HCHO with AHMT occurs under alkaline conditions at room temperature, one of the products, 6-mercaptop-5-triazolo[4,3-b]-s-tetrazine (MTT), could be characterized by UV-Vis spectroscopy for the calculation of the concentrations of HCHO in samples [20]. This method is also one of the Chinese national standard methods for the determination of HCHO [21, 22]. However, the limit of detection and the selectivity of this method are poor due to the limitation of UV-Vis absorption analysis, such as the low sensitivity and lack of characteristic spectrum. Thus, it is meaningful to improve the sensitivity and selectivity of the analytical methods for the determination of HCHO coupled with AHMT derivative reaction.

As a vibrational spectroscopy, Raman spectroscopy could provide detailed information of concentrations and molecular structures of analytes [23]. However, Raman scattering is very weak and is difficult to be applied to the analysis of trace level of analytes in high matrix samples. Surface-enhanced Raman spectroscopy (SERS) is an ultrasensitive vibrational spectroscopic technique to detect molecules on or near the surface of plasmonic nanostructures [24, 25]. The advantages of SERS include limits of detection at the ppb level or lower, real-time response, qualitative and quantitative capabilities, high degrees of specificity, simultaneous multiplex detection and trace amount of analysis [26]. Moreover, due to its simple operation, rapid detection and the recent developments of miniature Raman spectrometers, SERS has been considered a potentially excellent on-site analytical technique [27]. However, HCHO has not been detected directly by SERS owing to the weak signals.

In this work, the determination of trace amounts of HCHO was carried out by SERS coupled with derivative reaction. The product of the derivative reaction of HCHO with AHMT, MTT, which demonstrates a high SERS-activity, was employed as the probe for the determination of HCHO. The

colloidal silver nanoparticles (AgNPs) were used as SERS substrates. By using the present method combined with a portable Raman spectrometer, on-site determination of HCHO could be performed easily and efficiently. The present method was applied for the rapid quantification of trace HCHO in environmental water and food samples.

## Experimental

### Reagents

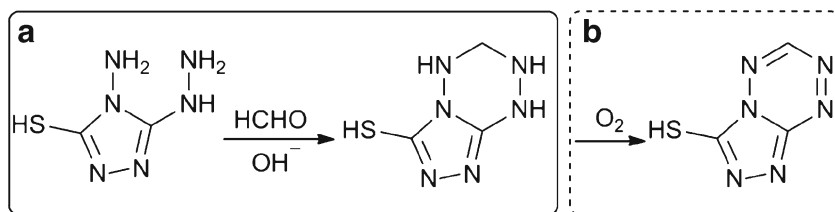
Silver nitrate ( $\text{AgNO}_3$ , 99.85 % w/w), sodium citrate (anhydrous, 99 % w/w), sodium hydroxide (NaOH), HCHO (solution, 36–38 % w/v), 4-amino-5-hydrazino-3-mercaptop-1,2,4-triazole (AHMT) (98 % w/w) and hydrochloric acid (HCl, 36–37 % w/v) were purchased from Sinopharm Chemical Reagent Co., Ltd. (<http://www.sinoreagent.com>). All aqueous solution was prepared with deionized water from a Milli-Q water purification system (18.2  $\text{M}\Omega\cdot\text{cm}$ ) (<http://www.emdmillipore.com/US/en>). All glassware was cleaned with freshly prepared aqua regia (HCl/ $\text{HNO}_3$ , 3/1, v/v) and rinsed thoroughly with deionized water prior to use. Other reagents used here were of analytical reagent grade and used without further purification or treatment.

A stock solution of HCHO was prepared by diluting 3.5 mL of 36–38 % HCHO solution to 1 L with deionized water, which was quantified by iodometry to be  $1.286 \text{ g L}^{-1}$ . HCHO solutions with various concentrations used in experiments were prepared by diluting the stock solution with deionized water.  $5 \text{ g L}^{-1}$  AHMT was prepared by dissolving 0.5 g AHMT and 1.7 mL of 36–37 % HCl in 100 mL deionized water.

### Instruments

Raman spectra were obtained using a portable Raman spectrometer (Changchun Jilin University Little Swan Instruments Co., Ltd., Changchun, China, <http://www.ccjx.com>) with 1 cm quartz cells, a 785 nm laser, a fiber optic Raman probe, and a miniature fiber optic spectrometer. The laser power was chosen as 200 mW. The transmission electron microscope (TEM) image was scanned with a Hitachi H 800 transmission electron microscope operated at an accelerating voltage of 200 kV (<http://www.hitachi-hitec.com/global/em/>). Absorption spectra were recorded on a Beijing Purkinje General Instrument Co., Ltd. TU-1810C (UV-Vis) spectrometer (<http://www.pgeneral.com>). Reference concentrations of HCHO in environmental water and food samples was obtained according to the Chinese industrial standard method [SN/T 1547–2011] by a Shimadzu LC-20ADXR UFLC-UV system, which was equipped with two LC-20 AD pumps, a SIL-20A automatic sample injector, a CTO-20A column oven, a SPD-20A UV-Vis detector and a

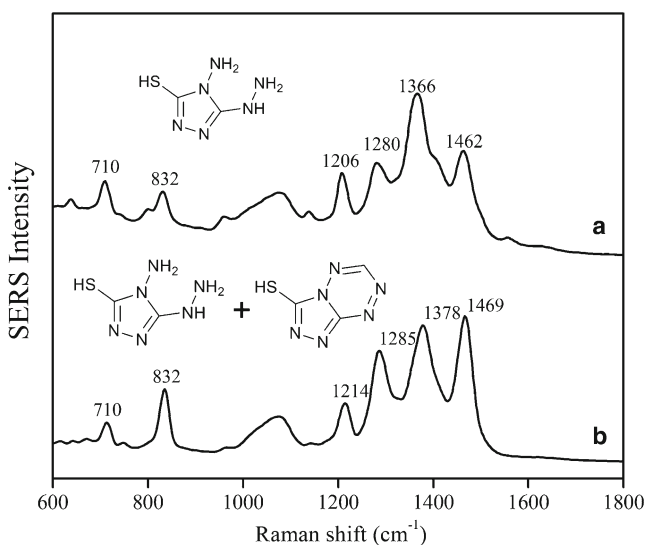
**Fig. 1** Derivative reaction of HCHO and AHMT under alkaline conditions



Shimadzu XR-ODS column (75 mm×2 mm, 2.2 μm particle size) (<http://www.shimadzu.com/>)

### Synthesis of AgNPs

The AgNPs were prepared by using a chemical reduction method according to Lee and Meisel [28]. 18 mg of AgNO<sub>3</sub> was dissolved in 100 mL of deionized water and heated to boiling. 2 mL of 1 % sodium citrate solution was added into the boiling AgNO<sub>3</sub> solution with vigorous stirring. The mixed solution was kept at boiling for 1 h. After the flask was cooled, green-gray and transparent colloid solution was obtained. Finally, the colloidal silver was stored in refrigerator for further experiments. The average diameter of the silver nanoparticles is about 50 nm. UV–Vis spectrum shows a maximum absorption at 420 nm. The TEM image and the UV–Vis spectrum of the colloidal AgNPs are shown in Fig. 1S (Electronic Supplementary Material, ESM). The colloidal AgNPs could be stored in brown glass bottle at 4 °C for 3 months with little loss in activity.



**Fig. 2** SERS spectra of AHMT (a) and AHMT-MTT mixture (b) 500 μL of deionized water (a) or HCHO solution (b), 200 μL of 1.0 mol L<sup>-1</sup> NaOH solution and 200 μL of 5 g L<sup>-1</sup> AHMT solution were added into the 1 cm quartz cell; 785 nm laser wavelength, 10 s integration time, 200 mW laser power

### Preparation of sample

Food samples, including beers and Chinese cabbages, were purchased from local markets and left to stand at room temperature for 1 day after adulterating with trace amounts of HCHO. 5.0 g of food sample was added into 25 mL centrifuge tube, followed by addition of deionized water to 20 mL. The mixture was ultrasonically shaken for 10 min and then centrifuged for 5 min at 13,000 rpm. The supernatant was analyzed.

Environmental water samples were collected from local water sources (Nanhu Lake and Jingyuetan Reservoir, Changchun, China). All the samples were filtered with 0.45 μm microporous membranes and stored in brown glass bottles at 4 °C.

### Procedure of determination of HCHO

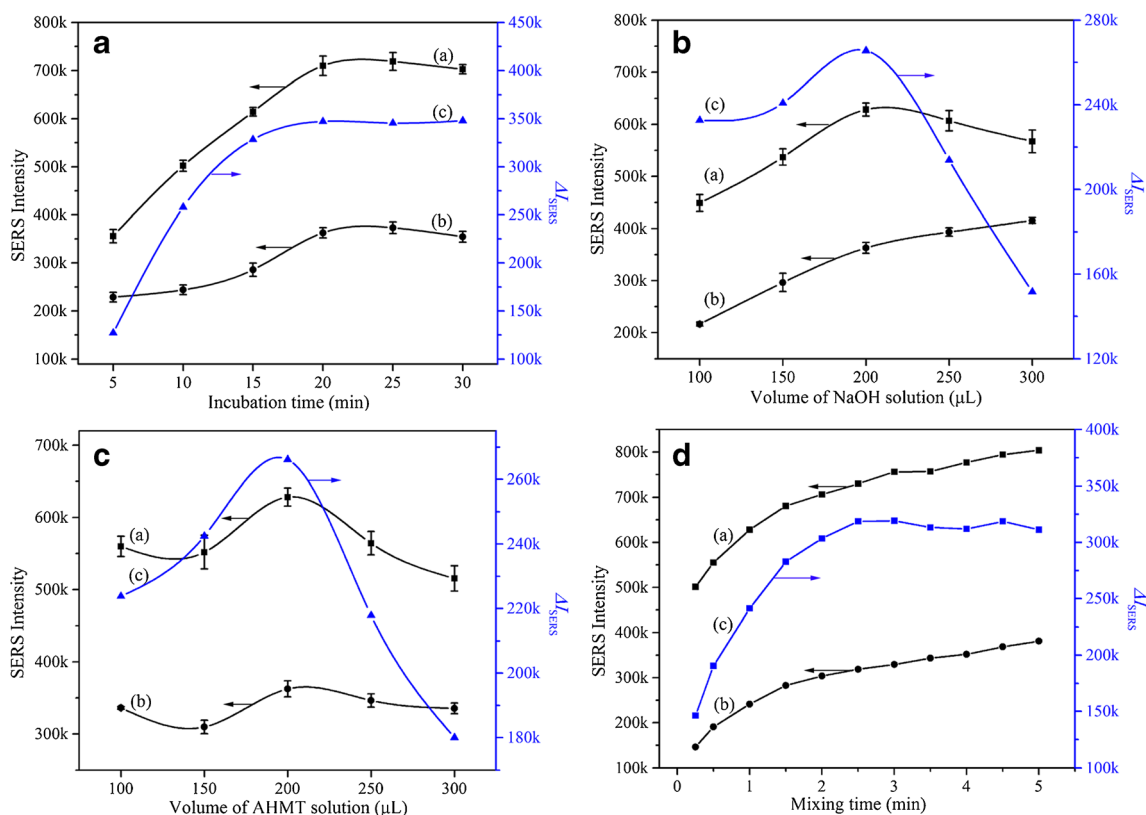
In a 4 mL centrifuge tube, 500 μL of HCHO solution or samples solution, 200 μL of 1.0 mol L<sup>-1</sup> NaOH solution and 200 μL of 5 g L<sup>-1</sup> AHMT solution were added. Then the mixture was incubated for 20 min at room temperature. 10 μL mixed solution was added into a 1 cm quartz cell, followed by the addition of 500 μL colloidal AgNPs. The resulting solution was kept at room temperature for 2.5 min. Quantitative analysis was performed using the area of SERS peak at 832 cm<sup>-1</sup>. All the experiments were performed in quintuplicate.

In order to confirm the applicability of the SERS method, all the samples were also analyzed by liquid chromatography (Chinese industrial standard method, SN/T 1547–2011) [29].

## Results and discussion

### Principle for determining HCHO

The present method is based on the derivative reaction of excess AHMT with HCHO (Fig. 1). Under alkaline conditions, the condensation reaction of HCHO with AHMT was occurred and tetrahydro-MTT was produced (Fig. 1a). After the incubation for 20 min at room temperature, tetrahydro-MTT was oxidized by O<sub>2</sub> and MTT was produced (Fig. 1b). Figure 2 shows the SERS spectra of AHMT (a) and AHMT-MTT



**Fig. 3** Effects of the incubation time (a), the volume of 1 mol L<sup>-1</sup> NaOH solution (b), the volume of 5 g L<sup>-1</sup> AHMT solution (c), and the mixing time (d) on SERS intensity of AHMT-MTT mixture (a) and AHMT (b), and  $\Delta I_{SERS}$  value (c)

mixture (b) in the wavenumber range of 600–1800 cm<sup>-1</sup> using AgNPs substrates. The band at 710 cm<sup>-1</sup> and 832 cm<sup>-1</sup> are attributed to S-C-N stretching vibrations [30] and N-C-N stretching vibration of AHMT and MTT molecules, respectively. The hexatomic ring of MTT makes its N-C-N stretching vibration more intense than AHMT [31, 32]. The other major bands of AHMT at 1,206, 1,280, 1,366 and 1,462 cm<sup>-1</sup> are attributed to the ring breathing vibration and in-plane deformation. Compared with AHMT, several bands of MTT exhibit

blue shift due to its hexatomic ring. A quantitative analysis of MTT was performed based on the measurement of the area change ( $\Delta I_{SERS}$ ) of SERS peak at 832 cm<sup>-1</sup>.

#### Optimization of analytical parameters

In this work, the following four major influencing parameters were optimized for analysis. HCHO standard solutions at a concentration of 5  $\mu\text{g L}^{-1}$ , and Raman spectrum integration time of 10 s were employed for the experimental optimization. Each experiment was conducted five times. Once a parameter was optimized, it was set at its optimal value in subsequent experiments.

**Table 1** Effects of several commonly coexisting organic substances on the determination of HCHO

Coexisting organic substances	Coexisting concentration ( $\mu\text{g L}^{-1}$ )	Relative error (%)
Methanol	5,000	+1.3
Ethanol	5,000	+2.0
Glycol	2,000	-3.0
Acetaldehyde	1,000	+4.5
Oxalaldehyde	1,000	+5.4
Acetic acid	500	-2.6
Benzaldehyde	500	+5.3
Vanilline	500	+5.1
Salicylaldehyde	500	+4.4

**Table 2** Linear equations, correlation coefficients and linear ranges of the present method

Integration time (s)	Linear equation	Correlation coefficient (r)	Linear range ( $\mu\text{g L}^{-1}$ )
1	$\Delta I_{SERS, 1s} = 723.53 c + 79,867$	0.9993	100–1,000
5	$\Delta I_{SERS, 5s} = 6750.8 c + 34,029$	0.9993	10–100
10	$\Delta I_{SERS, 10s} = 36,259 c + 60,981$	0.9992	1–10

**Table 3** Comparison of the methods reported in literatures and the present method

Method	Reagent	LOD ( $\mu\text{g L}^{-1}$ )	Linear range ( $\mu\text{g L}^{-1}$ )	References
SERS	AHMT	0.15	1.0–1000.0	In this work
GC	o-(2,3,4,5,6-Pentafluorobenzyl) hydroxylamine hydrochloride	0.5	0.5–100.0	[15]
Chemiluminescence	Gallic acid, hydrogen peroxide	1.2	1.2–300.0	[13]
Fluorimetry	4-Amino-3-penten-2-one	3.1	3.1–1000.0	[3]
HPLC	2,4-Dinitrophenylhydrazine	5.0	0–30.0	[16]
Spectrophotometry	AHMT	50.0	50–1000.0	[23]

*Effect of incubation time*

The influence of incubation time for derivative reaction was investigated. As shown in Fig. 3a,  $\Delta I_{SERS}$  increase with the increase of the incubation time before 20 min. This suggests that the derivative reaction and oxidation reaction are complete in 20 min. The incubation time was chosen as 20 min in the following experiments.

*Effect of the volume of NaOH solution*

In this experiment, NaOH is employed as both the base media for derivative reaction and the aggregating agent for AgNPs in the SERS process. An aggregating agent is routinely added into SERS-active colloids to achieve enhancements of SERS spectrum signals [33]. The effect of the volume of  $1 \text{ mol L}^{-1}$  NaOH was evaluated in the range of 100–300  $\mu\text{L}$ . As shown in Fig. 3b, 200  $\mu\text{L}$  was the optimum volume of  $1 \text{ mol L}^{-1}$  NaOH solution.

*Effect of the volume of AHMT solution*

The effect of the volume of  $5 \text{ g L}^{-1}$  AHMT solution on the SERS intensity was investigated and the results are shown in

Fig. 3c. When the volumes of AHMT solution vary from 100 to 300  $\mu\text{L}$ , the SERS intensities increase and then decrease. The  $\Delta I_{SERS}$  reaches its maximum value when the volume of AHMT solution is 200  $\mu\text{L}$ . Therefore, 200  $\mu\text{L}$  of the  $5 \text{ g L}^{-1}$  AHMT solution was selected for the subsequent work.

*Effect of the mixing time*

The effect of the mixing time for AgNPs and the products of the derivative reaction was also investigated. As shown in Fig. 3d, the reaction between AgNPs and AHMT-MTT molecules was rapid at room temperature, and the  $\Delta I_{SERS}$  reaches the highest value in 2.5 min.

Selectivity of the method

Under the optimum conditions, several commonly coexisting organic substances were examined for interference at the HCHO concentration of  $50 \mu\text{g L}^{-1}$ . The results were listed in Table 1 and Fig. 2S (ESM). Most of the organic substances can be allowed at very high concentrations, which indicates that the present method is selective for the determination of trace amounts of HCHO.

**Table 4** Analytical results of food and environmental water samples ( $n=3$ )

Samples	Spiked ( $\mu\text{g L}^{-1}$ or $\mu\text{g kg}^{-1}$ )	SERS method ( $832 \text{ cm}^{-1}$ )			Standard method Found ( $\mu\text{g L}^{-1}$ or $\mu\text{g kg}^{-1}$ )
		Found ( $\mu\text{g L}^{-1}$ or $\mu\text{g kg}^{-1}$ )	RSD (%)	Recovery (%)	
Chinese cabbage	0	126	2.3	-	101±2.1
	80	197	1.5	95.6	183±5.2
Beer	0	27.9	4.3	-	21.8±3.3
	100	139	2.9	108.7	124±6.0
Lake water	0	15.1	2.0	-	-
	5	18.3	3.3	91.0	-
	50	62.4	2.7	95.9	-
Reservoir water	0	24.7	2.4	-	-
	5	28.1	3.6	94.6	-
	50	69.9	3.1	93.4	-



## Determination of HCHO

### Analytical performance

The linearity of the present method for determination of HCHO was evaluated under the optimized conditions. The results are shown in Fig. 3S (ESM). The obtained equations for the calibration curves based on five parallel measurements of each point are listed in Table 2. The present method shows a good linear relationship for HCHO concentrations and  $\Delta I_{SERS}$  in the HCHO concentration range of 1–1,000  $\mu\text{g L}^{-1}$ , with the correlation coefficients ( $r$ ) greater than 0.999. The limit of detection (LOD) and the limit of quantification (LOQ) of HCHO are 0.15  $\mu\text{g L}^{-1}$  and 0.45  $\mu\text{g L}^{-1}$ , respectively. Compared with the methods reported in literatures, the sensitivity and linear range of the present method are impressive, as shown in Table 3.

### Analysis of samples

In order to validate the present method, food and environmental water samples were analyzed by the present method under the optimized conditions. The recovery test was carried out by spiking the samples at one or two levels. The results are listed in Table 3. The recoveries of HCHO were in the range of 91.0–108.7 %, with relative standard deviations (RSDs) between 1.5 and 4.3 %. Food samples were also analyzed by liquid chromatography (Chinese industrial standard method, SN/T 1547–2011) [29]. As shown in Table 4, there is no significant difference between the results obtained by the present and standard methods, which suggests that the present method is suitable for the determination of HCHO in foods and water.

## Conclusions

In this work, an organic solvent-free, easy-to-use, and low-cost SERS method for the selective and ultrasensitive determination of trace HCHO in environmental water and food samples was developed based on the derivative reaction of HCHO with AHMT, which demonstrates excellent sensitivity for the determination of trace HCHO and allows commonly coexisted interference compounds at very high concentrations. The present method can be an alternative to routine separation and detection techniques, such as HPLC and GC, for the rapid determination of trace HCHO in environmental water and food samples. Also, the idea of derivatization could be extended to detect other compounds with weak SERS signals, such as fatty amine, fatty acid, amino acid, and so on.

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