

# Determination of Zinc and Copper in Edible Plants by Nanometer Silica Coated, Slotted Quartz Tube, Flame Atomic Absorption Spectrometry

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**ABSTRACT:** Nanometer SiO<sub>2</sub> was coated onto the inner wall of a slotted quartz tube atomizer (STAT) and then was used as a new atomizer (NSC-STAT) for the determination of Zn and Cu by flame atomic absorption spectrometry (FAAS). Compared to conventional STAT-FAAS, the analytical performance of NSC-STAT-FAAS was improved as follows: (a) the linear range of calibration curves was expanded from 30.0–200.0 ng mL<sup>-1</sup> to 5.0–400.0 ng mL<sup>-1</sup> for Zn, and from 100.0–1000.0 ng mL<sup>-1</sup> to 50.0–2000.0 ng mL<sup>-1</sup> for Cu; and (b) the characteristic concentration was decreased from 6.0 ng mL<sup>-1</sup>/1% to 2.7 ng mL<sup>-1</sup>/1% for Zn and from 25.0 ng mL<sup>-1</sup>/1% to 10.1 ng mL<sup>-1</sup>/1% for Cu. NSC-STAT-FAAS was applied for the determination of Zn and Cu in edible plants, including herbal medicine, marine algae, tomato leaves (NIST 1573), and apple leaves (NIST 1515).

**KEYWORDS:** edible plants, flame atomic absorption spectrometry, atom trap, zinc, copper, nanometer SiO<sub>2</sub>-coated slotted quartz tube atomizer

## ■ INTRODUCTION

The monitoring of Cu and Zn in edible plants is of great importance for protecting the public from the hazards of possible toxic effects and also for informing the population about the nutritional value of the plants.<sup>1–4</sup> Herbal medicines are widely consumed by about 70–80% of the world's population as home remedies and food additives.<sup>5</sup> *Aconitum Carmichaeli* and *Paeonia lactiflora* have long been utilized for rheumatoid arthritis treatment.<sup>6</sup> Edible marine algae, *Laminaria japonica* and *Porphyra haitanensis*, are an important food source in many parts of the world and could reduce the risk of intestinal or mammary cancer<sup>7</sup> for their antioxidant and antitumor activities. Complexes of Cu and Zn as drugs have been used in clinical treatment.<sup>8</sup> However, Cu is also potentially toxic, e.g., the consumption of beverages containing high levels of Cu could cause abdominal pain, cramps, nausea, diarrhea, and vomiting.<sup>9</sup> Zinc overload is a key factor of neuronal death in acute brain injury.<sup>10</sup> The tolerable upper intake level (UL) was the highest level of daily nutrient intake that is likely to pose no risk of adverse health effects to almost all individuals in the general population.<sup>9</sup> Set by the U.S. Food and Nutrition Board of the Institute of Medicine, the UL values of Zn and Cu for male and female (>19 years) were 40.0 mg day<sup>-1</sup> and 10.0 mg day<sup>-1</sup>, respectively.<sup>9</sup>

The concentrations of Zn and Cu in edible plants were at the level of μg g<sup>-1</sup>, and their content ranges were wide.<sup>11–13</sup> Flame atomic absorption spectrometry (FAAS) is one of the most popular analytical methods for metal determination in the mg L<sup>-1</sup> concentration range, because FAAS is fast, is cheap, and does not require expert operators. But the sensitivity of FAAS is limited by several factors. The analyte atoms generated in the flame pass rapidly and continuously through the measurement zone during sample aspiration. A further limitation is the poor efficiency of the nebulizer/burner system. The nebulization and atomization efficiency are directly correlated with the sensitivity

of analytical methods.<sup>14</sup> Using a thermospray flame furnace, the sensitivity of FAAS can be improved by increasing the efficiency of aerosol generation and prolonging the free analyte atoms' residence time in the absorption volume.<sup>15</sup> Keeping the atomic vapor in the optical path for a long time with the so-called slotted tube atom trap (STAT) system, STAT-FAAS method has been found to be more popular recently.<sup>16–18</sup> The atomizers, including heated quartz tube, W-coil, and metal furnace, have been used.<sup>19</sup> Because quartz has a sufficiently high melting point and a low thermal expansion coefficient, it has been chosen as the material for the atom trap. The sensitivity improvement is attributed to the increased residence time of the analyte atoms in the light path due to slower flame speed in STAT. Furthermore, the more stable chemical environment due to homogeneous temperature in the quartz tube enhances the numbers of neutral atoms, thereby increasing the sensitivity.

Because of the large specific surface area and high adsorption capacity, nanometer SiO<sub>2</sub> has been used for solid-phase extraction and preconcentration of trace metals in natural waters,<sup>20</sup> but its application on the atom trap for metal determination by FAAS has not been reported until now. Most of the atoms of nanometer SiO<sub>2</sub> were on the surface. The surface atoms were unsaturated and might easily bind with the analyte atoms, and then the residence time of the analyte atoms in the light path could be increased. For this purpose, a new design of atom trapping technique, nanometer SiO<sub>2</sub> coated, slotted quartz tube, was used for the first time for FAAS.

## ■ MATERIALS AND METHODS

**Apparatus.** A GBC 932AA model atomic absorption spectrometer (GBC Co., Australia) equipped with hollow cathode lamps of zinc and

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**Table 1.** Operating Conditions of the Determination of Zn and Cu by Nanometer Silica Coated, Slotted Quartz Tube, Flame Atomic Absorption Spectrometry

metal	lamp current, mA	wavelength, nm	read time, s	slit width, mm	atomizer height, mm	acetylene flow, L min <sup>-1</sup>	air flow, L min <sup>-1</sup>
Zn	5	213.9	1	0.5	57	1.8	8
Cu	3	324.7	1	0.5	57	1.8	8

copper was used for all of the metal determinations. All signals were processed in the peak area mode. The specifications of slotted quartz tube (Beijing kinglass quartz Co., Ltd. China) were as follows: tube length 150 mm, wall thickness 2 mm, outer diameter 10 mm, upper slot length 25 mm, upper slot width 0.5 mm, under slot length 110 mm, and under slot width 1 mm. The pH values were measured using a Mettler Toledo 320-S pH meter (Mettler Toledo Co., China) with a combined electrode. A KQ-250B model ultrasonic cleaner (Kunshan ultrasonic instrument Co., Ltd. China), a KSW-40-11 model resistance furnace temperature controller (Shanghai botian medical instrument Co., Ltd. China), a DHG-9036A model electrothermal thermostatic drying oven (Shanghai jinghong laboratory instrument Co., Ltd. China), a HJ-6A model magnetic stirrer (Jintan science analysis instrument Co., Ltd. Jiangsu, China), a BS110S model electronic analytical balance (Beijing sartorius balance Co., Ltd. China), an MK-III model microwave digestion system (Shanghai Sineo Microwave Chemistry Technology Ltd. Co., China), and a Milli-Q water system (Millipore Co., Bedford, MA) were used for the test.

**Chemicals.** Concentrated nitric acid, 69–70% (Merck KGaA, Germany), and hydrogen peroxide, 30% (Merck KGaA, Germany), were used for digestion of seaweed samples. The vegetal standard reference materials (tomato leaves, NIST 1573; apple leaves, NIST 1515) were supplied from the National Institute of Standards and Technology. All other chemicals were of analytical reagent grade from Shanghai Experiment Reagent Co., China. Ultrapure water of 18 MΩ cm<sup>-1</sup> specific resistivity, obtained in a Milli-Q plus Millipore system, was used to prepare all the solutions and to rinse the previously cleaned laboratory material. The working standard solutions of Zn and Cu were prepared daily by diluting the stock solutions (1000 mg L<sup>-1</sup>, GBC Co.) with 1% (v/v) HCl and 2% (v/v) HCl, respectively. All stock solutions were stored in the dark at 4 °C. To avoid metal contamination, all glassware and plastic ware was washed and kept for 48 h in 10% (v/v) nitric acid and then rinsed several times with ultrapure water before use.

**Coating Nanometer SiO<sub>2</sub> on the Internal Wall of the Slotted Quartz Tube.** Before the coating of nanometer SiO<sub>2</sub>, the slotted quartz tube was activated as follows: (a) it was vibrated ultrasonically in 0.1 mol L<sup>-1</sup> NaOH solution for 20 min; (b) after washing with ultrapure water, it was vibrated ultrasonically again in 1 mol L<sup>-1</sup> HCl solution for 20 min and then was washed ultrasonically with ultrapure water for 10 min; and (c) it was weighed after drying at 105 °C for 24 h.

According to the literature,<sup>21,22</sup> the procedures of coating the slotted quartz tube with nanometer SiO<sub>2</sub> were as follows:

- Preparation of nanometer SiO<sub>2</sub> sol: 40 mL of ethyl silicate and 64 mL of absolute alcohol were mixed adequately; this mixture was added drop by drop to 12 mL of ultrapure water and 3 mL hydrochloric acid (as a catalyst, pH = 2.0–3.0) with strong stirring with a magnetic stirrer for 30 min; the mixture was transformed into a clarified transparent solution, i.e., a nanometer SiO<sub>2</sub> sol.
- Coating the slotted quartz tube: The activated slotted quartz tube was immediately immersed into nanometer SiO<sub>2</sub> sol for 48 h, air-dried at room temperature for 24 h, placed in a furnace at 105 °C for 8 h to remove completely the residual water, heated up to 400 °C at a rate of 2 °C min<sup>-1</sup> for 2 h, and then weighed after its temperature was decreased naturally to room temperature. The weight of the coating of nanometer SiO<sub>2</sub> on the internal wall of slotted quartz tube could be calculated by the weight differences.

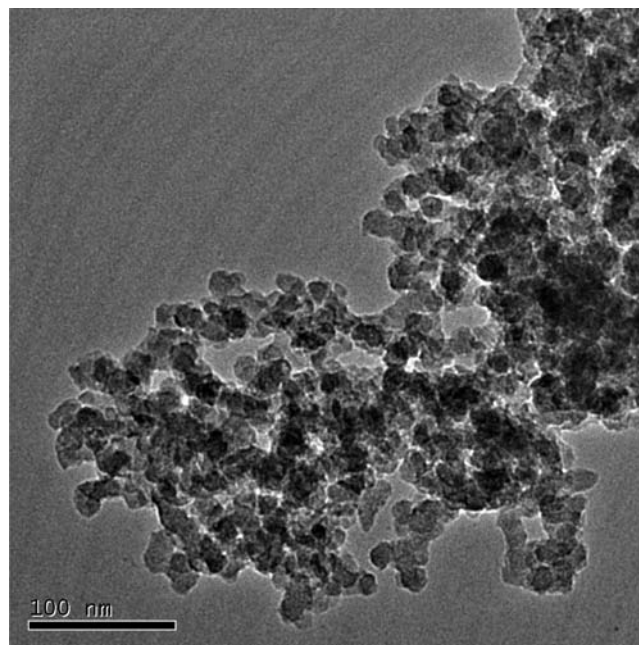
**Microwave Digestion of Edible Plants and Tomato Leaves.** Herbal medicines (*Aconitum carmichaeli* and *Paeonia lactiflora*) were

purchased from Zhongmin Supermarket in Zhangzhou, Fujian, China, and they were identified by Professor Chen Yu-Lin (Zhangzhou Institute for Drug Control, State Food and Drug Administration, China), following the methods described in Chinese Pharmacopoeia 2010.<sup>23</sup> Marine algae (*Laminaria japonica* and *Porphyra haitanensis*) were obtained from the State Key Laboratory for Marine Environmental Science, Xiamen University, China. The edible plants, including herbal medicines and marine algae, were rinsed rapidly with Milli-Q purified water 3 times, heated at 80 ± 5 °C to constant weight, and then powdered carefully in an agate mortar. To each of *Aconitum carmichaeli*, *Paeonia lactiflora*, *Laminaria japonica*, *Porphyra haitanensis*, and tomato leaves of 0.10 g were added 2.0 mL of concentrated HNO<sub>3</sub> and 1.0 mL of 30% (w/w) H<sub>2</sub>O<sub>2</sub>; the contents were heated for decomposition in microwave digestion system under a pressure of 15 atm, at a temperature of 250 °C for 10 min; this procedure was repeated three times. After being cooled naturally to room temperature, the decomposed solution of *Aconitum carmichaeli*, *Paeonia lactiflora*, *Laminaria japonica*, *Porphyra haitanensis*, or tomato leaves was diluted to 10 and 50 mL for the determination of copper and zinc concentration in the sample, respectively. Blank digests were carried out using the same procedures.

**Operating Conditions of the Determination of Zn and Cu by NSC-STAT-FAAS.** The optimal conditions of nanometer silica coated, slotted quartz tube, flame atomic absorption spectrometry (NSC-STAT-FAAS) and slotted quartz tube, flame atomic absorption spectrometry (STAT-FAAS) for the determination of Zn and Cu were studied and are shown in Table 1.

## RESULTS AND DISCUSSION

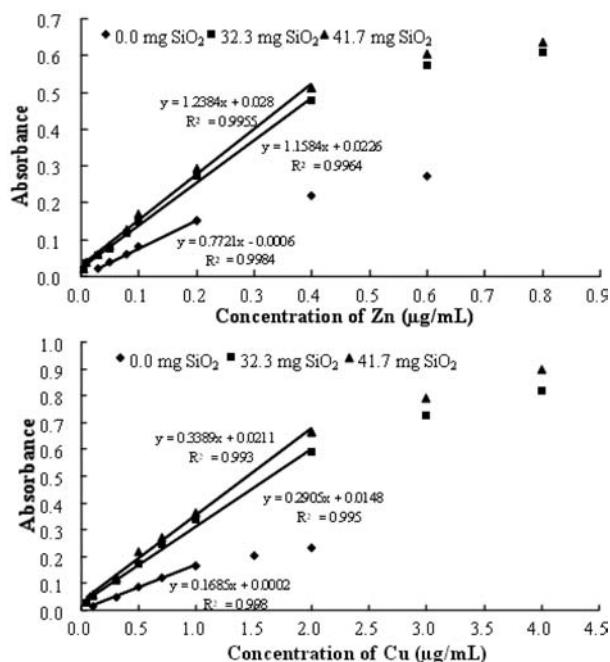
**Analytical Performance.** The linear range of a calibration curve is determined by a lower limit and an upper limit. For the requirement of practical application, the calibration curves were obtained by practical analyses. In Figure 1, the transmission



**Figure 1.** Transmission electron microscope image of nano-SiO<sub>2</sub>.

electron microscope image shows that nano-SiO<sub>2</sub> could be coated on the internal wall of a slotted quartz tube with a three-dimensional network, and the size of SiO<sub>2</sub> was 15.49 nm. Using a sol-gel dip-coating procedure on a slotted quartz tube, coating weights of 32.3 mg and 41.7 mg were achieved.

Using different coating weights of nanometer SiO<sub>2</sub>, the obtained calibration graphs were tested and are given in Figure 2, including the calibration curve and the equations of the

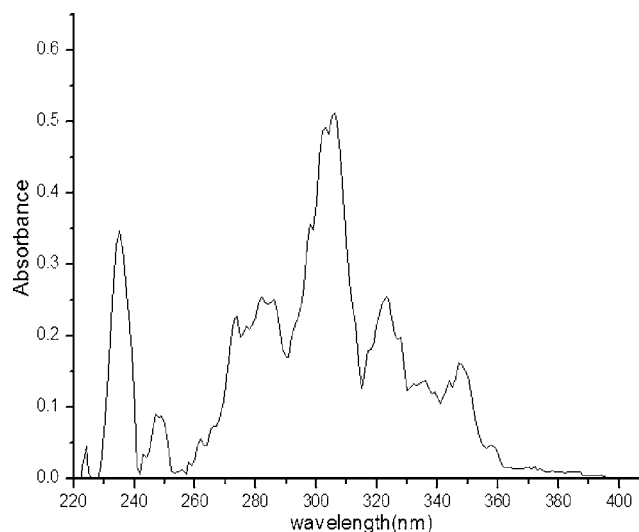


**Figure 2.** Effect of nano-SiO<sub>2</sub> coating on the linear range of calibration curves of Zn and Cu.

calibration curves for Zn and Cu. After coating 32.3 mg or 41.7 mg SiO<sub>2</sub> on the slotted quartz tube, the linear range of the calibration curve of both Zn and Cu was improved. When 41.7 mg of SiO<sub>2</sub> was coated on the internal wall of the slotted quartz tube, the linear range of the calibration curve was lengthened from 30.0–200.0 ng mL<sup>-1</sup> to 5.0–400.0 ng mL<sup>-1</sup> for Zn and from 100.0–1000.0 ng mL<sup>-1</sup> to 50.0–2000.0 ng mL<sup>-1</sup> for Cu, respectively.

Compared with STAT-FAAS, the advantage of NSC-STAT-FAAS on the applicable concentration scope was obvious, because (a) the interference of stray light on the calibration curves might be eliminated obviously by the coating of nanometer SiO<sub>2</sub> and (b) the residence time of the analyte atoms in the light path could be increased. The curvature of calibration curves could be affected by stray light.<sup>24</sup> In Figure 3, the UV-vis absorption spectrum of nano-SiO<sub>2</sub> illustrated that SiO<sub>2</sub> could absorb light of wavelengths  $\lambda \leq 360$  nm. So, the interference of stray light could be eliminated by nano-SiO<sub>2</sub> for its light absorption properties. Metal cations, including Cu and Zn, could be adsorbed and enriched on nano-SiO<sub>2</sub> by forming inner-sphere complexes.<sup>25</sup> The nebulization and atomization efficiency could be enhanced by such adsorption affinity for metals. SiO<sub>2</sub> nanoparticles have high surface adsorption capacities for free atoms of Zn and Cu, and then the residence time of free analyte atoms could be prolonged.

As shown in Figure 2, the slope of the calibration curve of both Zn and Cu was increased with the increase of the coating weight of SiO<sub>2</sub> on the slotted quartz tube, so the sensitivity of



**Figure 3.** UV-vis absorption spectrum of nano-SiO<sub>2</sub>.

NSC-STAT-FAAS was better than that of STAT-FAAS. The effect of the SiO<sub>2</sub> coating on characteristic concentration and detection limit of Zn and Cu is shown in Table 2. When the

**Table 2.** Effect of Nanometer Size SiO<sub>2</sub> Coating on the Character Concentration and Detection Limit of Zn and Cu

coating wt of SiO <sub>2</sub> (mg)	character concn (ng mL <sup>-1</sup> /1%)		detection limit (ng mL <sup>-1</sup> )	
	Zn	Cu	Zn	Cu
0.0	6.0	25.0	5.0	32.6
32.3	3.1	12.9	3.9	24.3
41.7	2.7	10.1	3.8	20.9

analytical method of STAT-FAAS was replaced by NSC-STAT-FAAS, the detection limits were improved from 5.0 ng mL<sup>-1</sup> to 3.8 ng mL<sup>-1</sup> for Zn and from 32.6 ng mL<sup>-1</sup> to 20.9 ng mL<sup>-1</sup> for Cu, respectively; the characteristic concentration was decreased from 6.0 ng mL<sup>-1</sup>/1% to 2.7 ng mL<sup>-1</sup>/1% for Zn and from 25.0 ng mL<sup>-1</sup>/1% to 10.1 ng mL<sup>-1</sup>/1% for Cu. Furthermore, the analytical performance of NSC-STAT-FAAS (i.e., the efficiency of nanometer SiO<sub>2</sub>-coated slotted quartz tube atomizer) was stable for at least 100 determination cycles.

A simple flame atomic absorption spectrometry and the conventional slotted quartz tube coated with nanometer SiO<sub>2</sub> are all that are needed for NSC-STAT-FAAS. The achieved online atom trap method has much importance in comparison with the other offline enrichment techniques such as adsorption or extraction because of its simplicity, direct application, high speed, low cost, easy manufacturing, and less volume of sample required, i.e., only 1.0 mL of solution is sufficient for two metal determinations. Although the achieved improvement of the sensitivity is modest (2.2-fold for Zn and 2.5-fold for Cu), the sensitivity between the FAAS and flameless AAS for some elements such as Zn and Cu is bridged gradually via NSC-STAT-FAAS, at the same time, the concentration scope of NSC-STAT-FAAS is wider than that of STAT-FAAS.

**Application.** Due to the scarcity of standard reference materials (SRMs) for herbal medicines and marine algae certified in terms of their Zn and Cu content, the accuracy of NSC-STAT-FAAS was tested by vegetal Standard Reference Materials (tomato leaves, NIST 1573; apple leaves, NIST

Table 3. Determined and Certified Values of Zn and Cu in Certified Reference Materials ( $\mu\text{g g}^{-1}$ ,  $n = 3$ )

metals	tomato leaves (NIST 1573)			apple leaves (NIST 1515)		
	certified values	av results	RSD (%)	certified values	av results	RSD (%)
Zn	62.0 $\pm$ 6.0	62.8 $\pm$ 0.7	1.3	12.5 $\pm$ 0.3	11.9 $\pm$ 0.6	1.1
Cu	11.0 $\pm$ 1.0	10.7 $\pm$ 1.0	2.2	5.6 $\pm$ 0.2	5.7 $\pm$ 0.1	2.1

Table 4. Analytical Results for Metals in Edible Plants ( $\mu\text{g g}^{-1}$ ,  $n = 3$ )

metals	<i>A. carmichaeli</i>			<i>P. lactiflora</i>			<i>L. japonica</i>			<i>P. haitanensis</i>		
	found	added	recovery (%)	found	added	recovery (%)	found	added	recovery (%)	found	added	recovery (%)
Zn	47.8 $\pm$ 0.9	50.0	97.2	30.4 $\pm$ 0.6	30.0	95.6	14.7 $\pm$ 0.2	15.0	97.7	89.5 $\pm$ 0.2	90.0	97.6
Cu	6.7 $\pm$ 0.5	7.0	104.0	17.4 $\pm$ 0.3	18.0	96.1	1.1 $\pm$ 0.1	1.0	102.1	22.8 $\pm$ 0.1	20.0	99.5

1515), which have a similar matrix to herbal medicines and marine algae. The precision and accuracy of NSC-STAT-FAAS were tested by spiking the samples. The concentrations of Zn and Cu in *Aconitum carmichaeli*, *Paeonia lactiflora*, *Laminaria japonica*, *Porphyra haitanensis*, and tomato leaves are summarized in Tables 3 and 4.

There is good agreement for Zn and Cu in tomato leaves (NIST 1573) and apple leaves (NIST 1515) between the experimental values and certified values. The interference of the coexisting metals from tomato leaves, apple leaves, herbal medicines, and marine algae on the determination of Zn and Cu could be eliminated, because (a)  $\text{SiO}_2$  nanoparticles have different adsorption capacities for different species of metal cations and free metal atoms<sup>25</sup> and (b) owing to their extremely small size,  $\text{SiO}_2$  nanoparticles have abundant surface adsorption sites for adsorbing the analytes. The recoveries of herbal medicines and marine algae were reasonable for trace analysis, in a range of 95.6–104.0%. No systematic error could be seen in the added-found method for Zn and Cu determination in herbal medicines and marine algae. So, the precision and accuracy of the method were good.

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### Notes

The authors declare no competing financial interest.

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