

Determination of Trace Cd and Pb in Edible Salt and Soy Sauce by ETAAS Using Fluorescent Carbon Nanoparticles (FCNs) as Matrix Modifier

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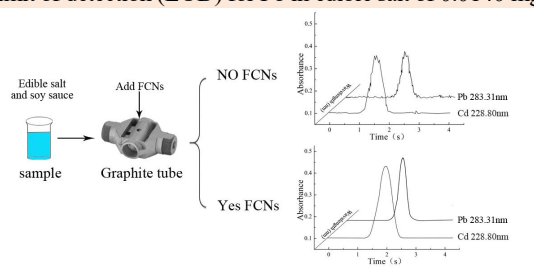
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ABSTRACT: Lead (Pb) and cadmium (Cd) are non-essential but extremely noxious metallic elements, and the study of their impact on environmental pollution is of utmost importance. In this report, an economical and environmentally friendly matrix modifier, fluorescent carbon nanoparticles (FCNs), is utilized for the electrothermal atomic absorption spectrometry (ETAAS) determination of trace Pb and Cd in edible salt and soy sauce. FCNs have been characterized for use with UV-Vis spectroscopy, fluorescence (FL), Fourier transform infrared spectrum (FT-IR) and transmission electronic microscopy (TEM). In comparison to traditional matrix modifiers, FCNs can effectively eliminate matrix interference. Using the proposed FCNs, the ETAAS method achieved a linearity of 10–50.0 $\mu\text{g L}^{-1}$ for Pb and 0.4–4.0 $\mu\text{g L}^{-1}$ for Cd; a limit of detection (LOD) for Pb in edible salt of 0.0140 mg kg^{-1} and in soy sauce of 0.0470 mg kg^{-1} , and for Cd in edible salt of 0.0015 mg kg^{-1} and in soy sauce of 0.0005 mg kg^{-1} . The method of additions chemical matrix modifier was used for Pb and Cd detection in this study. Excellent accuracy (93.0–101.0% recovery) and precision (0.19–0.85 %) of this procedure were obtained for soy sauce and edible salt. This work provides a new and economical strategy for the determination of trace Pb and Cd and is expected to facilitate future studies in the use of FCNs as a matrix modifier.



INTRODUCTION

Salt and high-salt foods with a relatively complicated production process, such as soy sauce and edible salt, may contain high levels of Pb and Cd when produced near Pb and Cd sources¹. Therefore, the accurate and rapid detection of trace Pb and Cd in high-salt foods is considered to be an important area for contamination studies.^{2,3} Establishing whether edible salt and high-salt foods are contaminated with Pd or Cd is important to properly assess their risk to humans.^{4,5} In China, the guideline values for Pb is set at 1.0 mg kg^{-1} in condiments, in addition, the limit value of Pb are 2.0 mg kg^{-1} and 3.0 mg kg^{-1} in edible salt and fish sauce, and for Cd are set at 0.5 mg kg^{-1} and 0.1 mg kg^{-1} in salt and fish seasonings (GB 2762-2017), respectively. These levels of Pb or Cd are difficult to determine accurately by available analytical methods due to their low content and the NaCl interference effects in mass

and/or spectral superposition.⁶⁻⁹

A new, sensitive and reliable method for determining trace Pb and Cd levels in high-salt food samples is an important tool to identify and treat poisoning cases. At present, electrothermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma mass spectrometry (ICP-MS) are the two main methods for trace elements determination in food testing and risk assessment laboratories.¹⁰⁻¹⁷ Although ICP-MS has high sensitivity for multi-elemental analysis, it has many disadvantages, such as high cost, risk of sample contamination, requires sophisticated operation and results in mass interferences.¹⁸⁻²⁰ Therefore, ETAAS may be more attractive for real sample analysis.

In general, the use of a matrix modifier allows high pyrolysis temperatures, thereby reducing or eliminating evaporation and vapor phase interferences and minimizing background signals. As

early as 1975, Ediger *et al.*²¹ reported Ni(NO₃)₂ as a matrix modifier. At present, there are more than 60 conventional matrix modifiers reported for ETAAS analysis which can roughly be divided into organic reagents, inorganic reagents and reactive gases.²¹⁻³¹ Traditional matrix modifiers, a matrix technique eliminating interference, are used for routine analysis of trace Pb and Cd because of their simplicity and adaptability. However, some shortcomings, such as the use of Pd, make matrix modifiers expensive, non-environmentally friendly and not good for use with high-salt samples. With the development of matrix modifiers, some carbon-based matrix modifiers have emerged, including activated carbon,³² palladium-bearing activated carbon³³ and multiwalled carbon nanotubes³⁴. FCNs are generally small oxygenous carbon-supported with good water solubility, low toxicity, high chemical stability and of low environmental hazard.^{35,36} In addition, FCNs are easy to prepare without heating, *i.e.*, simply mix acetic acid, water with di-phosphorus pentoxide, and dissolve the mixture to obtain FCNs in minutes.³⁷ Their use has been widely studied, but less as matrix modifiers.

In this study, FCNs are used as a new matrix modifier to improve the accuracy and precision of ETAAS determination of Pb and Cd in high-salt samples. The proposed FCNs assisted ETAAS method was evaluated for the analysis of soy sauce and edible salt samples.

EXPERIMENTAL

Instrumentation. The UV-Vis absorption spectra were studied using a Cary 5000 spectrophotometer (Varian, USA). The fluorescence (FL) spectra were measured with a Cary Eclipse fluorescence spectrophotometer (Agilent, Australia). A FT-IR spectrum was obtained using the Varian 660-IR spectrometer in the range of 500–4000 cm⁻¹ (Varian, USA). Transmission Electron Microscopy (TEM) of the FCNs was obtained on a JEM-2100 microscope (Japan Electron Optics, Japan). The PinAAcle 900Z atomic absorption spectrometer (AAS) (PerkinElmer, USA), equipped with graphite furnace and coated graphite tube with integrated platform, including an AS-900 autosampler furnace autosampler, were used for the determination of Cd and Pb in high-salt food products (purchased at local supermarket). The system consists of an eight-lamp mount with a Pb hollow cathode lamp operated at 10.0 mA and a spectral bandwidth of 0.7 nm. The analytical wavelength of Pb was set at 283.31 nm and the analytical wavelength of Cd was set at 228.80 nm. Syngistix software was used for data integration and processing. Absorbance was calculated by the area of the atomic absorption peak and the pyrolysis and atomization temperatures were adjusted to obtain maximum absorbance signal and excellent peak. The samples were digested using the Titan MPS microwave sample preparation system (PerkinElmer, USA).

Reagents and sample procedures. Deionized water used for the

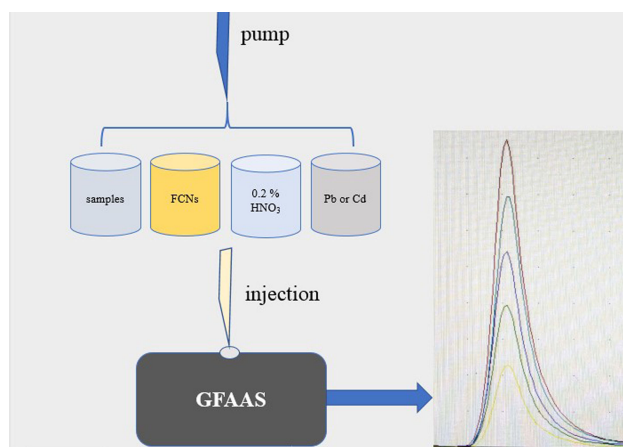


Fig. 1 Schematic diagram of the ETAAS system.

preparation of all blank, standard and sample solutions were obtained from a Milli-Q system (Millipore, USA). Standard solutions containing 4.0 µg L⁻¹ Cd and 50.0 µg L⁻¹ Pb were freshly prepared by appropriate dilution of the stock solutions containing 1000 mg L⁻¹ of each element (National Center for Analysis and Testing of Organic Metals and Electronic Materials, P.R. China) in 0.2% (v v⁻¹) nitric acid (Suzhou Crystal Clear Chemical Co., China). The reagents (CH₃COOH and P₂O₅) were purchased from Tianjin Kermel Chemical Reagent Co. Ltd. (China). All solutions were prepared with deionized water. All glassware and plastic containers were washed with tap water, soaked in 20% nitric acid overnight, then filled to volume with tap water and deionized water, the containers emptied and dried at room temperature. Salt was used in the studies of optimization, and validation and application of the methodology was carried out. After optimization, the validated methods were applied to the analysis of both the edible salt and soy sauce samples.

The determination of Pb and Cd by ETAAS was carried out using an injection solution of 0.2% nitric acid, FCNs, salt sample (1%) and standard solution (Fig. 1). In order to determine the concentration of Cd and Pb in the salt sample, 0.500 g salt was dissolved in 50.00 mL solution with HNO₃ 0.2% (v/v). In the optimization of the graphite furnace heating procedure, 50.0 µg L⁻¹ Pb solution and 4.0 µg L⁻¹ Cd solution were added to the salt sample. 16.0 µL of the salt solution and 5.0 µL FCNs were injected into the graphite tube for the analysis of Pb and Cd.

Synthesis of FCNs. The FCNs were synthesized according to the literature³⁷ with some modifications. A homogeneous mixture consisting of 1 mL glacial acetic acid and 80 µL water was quickly added to 2.5 g P₂O₅ in a 50 mL beaker without stirring. In this system, the upper temperature was mainly controlled by vaporizing the glacial acetic acid at its boiling point (117 °C). The nanobubbles of glacial acetic acid vapor then served as the templates for the nano-sized structures. Finally, the dark brown FCNs were collected by dispersing them in deionized water (18.2

MΩ cm), followed by adjustment of the pH to 7.0 with NaOH, and dilution to 100 mL by deionized water in a brown volumetric flask. The obtained FCNs solution is stable for at least one month in the refrigerator. The concentration of the FCNs was 4.2 g L⁻¹ as calculated by the C element in the glacial acetic acid.

RESULTS AND DISCUSSION

Spectral characteristics of FCNs. Fig. 2A shows the typical TEM images of as-prepared FCNs at low magnification. It can be

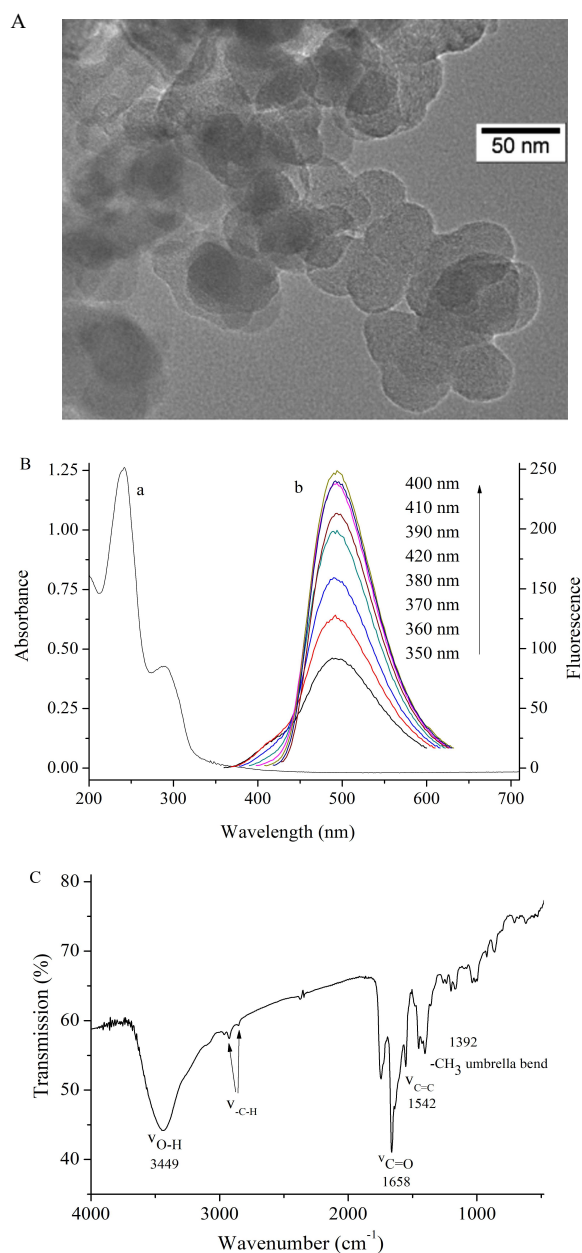


Fig. 2 (A) TEM of FCNs; (B) UV-Vis (a) and FL spectra (b) of FCNs; (C) FT-IR spectra of FCNs.

seen that most of the FCN particles are spherical in shape and uniformly distributed. The sizes of the FCNs are less than 25 nm, which clearly shows that a nano-sized morphology is achieved. The particle sizes and shapes are similar to those reported in the literature.³⁷ Fig. 2B shows the UV-Vis and FL spectra of the FCNs. A broad absorption around 297 nm and a sharp absorption at 247 nm were observed. The peak at 247 nm was ascribed to a π - π^* transition of the aromatic C=C bonds,²⁹ while the shoulder at 297 nm is attributed to a n - π^* transition of the C=O bonds.³⁷ When the excitation wavelength was between 350 and 420 nm, the FL emission peak was located at 500 nm. Thus, there was essentially no change in the emission wavelength and agrees with information from the literature.³⁷ The FL spectra show that the FCNs have fluorescence properties.

Optimization of experimental conditions. The effect of FCNs on the Pb and Cd analysis in edible salt and soy sauce was investigated since without a modifier, there is low thermal stability of the analyte.

(a) For the analysis of Pb, the highest pyrolysis temperature was 600 °C without addition of FCNs. After addition of the modifier, the pyrolysis temperature increased to 900 °C without loss of element due to volatilization. This demonstrates that the modifier adopted not only improved the sensitivity of the measurement since there was an increase in the value of the analytical sign, but also improved the thermal stability of Pb in the sample.²⁵ In the optimization study of the atomization temperature, it was observed that the lowest temperature (1600 °C) provided the highest analytical sign. Such result was already expected due to the volatile character of Pb.³⁸ In the pyrolysis study, it was observed that the background (BG) values are higher when a modifier is added. However, under the optimized conditions of pyrolysis (900 °C) and atomization (1700 °C), the BG value of the FCNs as modifier was lower. Thus, the pyrolysis and atomization temperatures adopted for Pb were 900 °C and 1700 °C for the FCNs, respectively (Table 1).

(b) For the analysis of Cd, the integrated absorbance without modifier was lower than with the FCNs. It should be noted that in the absence of a modifier, Cd started to volatilize at 400 °C and after adding the modifier, the volatilization temperature increased to 600 °C. This suggested that the thermal stability of the element in the sample was improved when FCNs were used as the modifier. In the atomization study, it was verified again that the chemical sensitivity was enhanced by using FCNs as the modifier. Thus, the optimum pyrolysis condition and atomization temperature of Cd was 600 °C and 1600 °C, respectively. These results are attributed to the good solubility, stability and large active surface area of the FCNs³⁷ and were, therefore, used as the modifier in subsequent measurements.

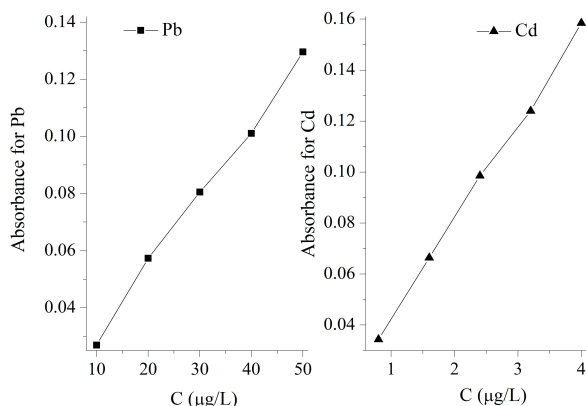
Analytical performance. Validation of the methods developed was verified by analyzing the parameters of system suitability, linearity, LOD, quantification limits (LOQ), characteristic

Table 1 Graphite Furnace Heating Program for the Determination of Cd and Pb in Salt Food Samples Employing FCNs as Chemical Modifiers

Stage	Temperature for Pb (°C)	Temperature for Cd (°C)	Ramp (°C s ⁻¹)	Hold time (s)	Ar flow rate (L min ⁻¹)
Drying 1	110	110	1	30	0.25
Drying 2	130	130	15	35	0.25
Pyrolysis	900	600	10	20	0.25
Atomization	1700	1600	0	5	0.00
Clean	2450	2450	1	3	0.25

Table 2 Recovery Values Obtained for Cd and Pb Determination in Salt Sample and Soy Sauce Sample by this method

Sample	Element	Added (mg kg ⁻¹)	Average Found (mg kg ⁻¹)	RSD (%)	Recovery (%)
Salt	Pb	0.00	0.021	0.19	/
		1.00	1.030	0.60	101.0
	Cd	0.00	0.017	0.14	/
		0.10	0.110	0.28	93.0
Soy sauce	Pb	0.00	0.013	0.85	/
		0.50	0.480	0.63	93.4
	Cd	0.00	0.012	0.17	/
		0.05	0.059	0.23	94.0

**Fig. 3** Verification of linearity for Pb and Cd determination by ET-AAS.

concentration, precision and accuracy, in accordance with the recommendations in the literature.^{39,40} The system suitability parameters were evaluated and found to be within the limits. The purpose of the system suitability test was to ensure that the complete testing system (including instrument, reagents and the analyst) is suitable for the expected application. These results show that ETAAS is suitable for the determination of Pb and Cd. The LOD and LOQ were calculated by $3 \times SD/b$ and $10 \times SD/b$, respectively, where b is the slope of the analytical curve and SD is the standard deviation of 10 consecutive measurements of the blank.⁴⁰ The LOD of the salt and the soy sauce samples were obtained by spiking each with 0.0140, 0.0470 mg kg⁻¹ of Pb and 0.0015, 0.0005 mg kg⁻¹ of Cd, respectively. The characteristic concentrations of the Cd and Pb obtained in the experiment were 0.05 µg L⁻¹ and 0.50 µg L⁻¹, respectively. Precision was assessed by performing a repetitive study according to the AOAC International standards.⁴¹ Repeatability was determined by calculating the RSD of five determinations of Pb (10.0 µg L⁻¹) and

Cd (0.8 µg L⁻¹) at an interval of one hour on the same day under the same experimental and laboratory conditions. The experimental data showed that the RSD for Pb (10 µg L⁻¹) and Cd (0.8 µg L⁻¹) were 0.72% and 0.21%, respectively, indicating that the method has high precision.

The analytical curves were obtained by different methods of standard addition to verify whether there was a matrix effect in the determination. For Pb and Cd analysis of the salt solution (1%), the analytical curves ranging from 10.0 to 50.0 µg L⁻¹ and 0.4 to 4.0 µg L⁻¹ were obtained, respectively. For each metal, each point of the analytical curves was analyzed in triplicate. The linearity of the analytical curves was checked at the 95% confidence level. Fig. 3 shows the regression line in the prediction interval.

Verification of the linearity of Pb and Cd was obtained by ETAAS. The salt and soy sauce samples were analyzed in the same way, and the results are listed in Table 2. The accuracy of the proposed method for the determination of Cd and Pb in these samples was evaluated by addition and recovery tests using two levels (Table 2). The recoveries of Cd and Pb in the two salt food samples ranged from 93.0% to 94.0% and from 93.4% to 101.0%, respectively. These values are in the acceptable range as recommended by GB/T27417-2017, which is 80–110% for 0.1–1.0 mg kg⁻¹.⁴⁰ In summary, the obtained results show satisfactory agreement with good precision and verify that FCNs are a suitable matrix modifier for the determination of Pb and Cd in high-salt food samples.

Possible mechanism of modification. In order to understand why the addition of FCNs can increase the pyrolysis temperature of Pb and Cd, FT-IR was used to analyze the structure of the FCNs. Fig. 2C shows the FT-IR spectrum of the FCNs. An apparent absorption peak of the –OH group at about 3449 cm⁻¹ and an absorption peak of the C=O group appeared, conjugated with aromatic carbons at 1658 cm⁻¹. These data show that the FCNs are rich in carboxylic groups. A peak at 1542 cm⁻¹ from a conjugated C=C stretching vibration was observed, indicating that unsaturated carbon bonds formed during the carbonization process. During the formation of these structures, the oxygen-containing functional groups like –OH and C=O have the ability to bind to the metal elements, which may be the reason why the Pb and Cd. Stability of the Pb and Cd by FCNs is mainly owed to the hydroxyl and carboxyl. It is broken down and produced methane, hydrogen, carbon monoxide and other deoxygenizing substances.^{31,42,43} and the complex matrix is deoxygenized by deoxygenizing substances in the pyrolysis steps. Pyrolysis temperature increased after the

FCNs were added as the modifier in the ETAAS test process, thereby reducing an amount of loss and increasing the elemental sensitivity in the pyrolysis step. In all, in the absence of a modifier, the Pb and Cd values decrease when the pyrolysis temperature is 600 °C and 400 °C, respectively, and Pb and Cd are lost proportionally with an increase in temperature. Thus, the addition of FCNs can increase the pyrolysis temperature of Pb and Cd and improve the measurement accuracy and sensitivity.

CONCLUSIONS

The FCNs were prepared without external heat treatment. The results of this study show them to be an excellent modifier that improves the detection sensitivity of Pb and Cd in ETAAS analysis. The oxygen-containing functional groups on the surface of the FCNs enable both Pb and Cd to form structures at a higher pyrolysis temperature, thereby reducing elemental loss in the heat treatment process. This work provides a new direction for the application of FCNs and a new idea for high-precision and low-cost determination of trace Pb and Cd by ETAAS.

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Notes

The authors declare no competing financial interest.

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