

## ORIGINAL ARTICLE



# Determination of trace Cadmium in water and fish species from estuaries in Tien Hai, Thai Binh, Vietnam By GF-AAS

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## Abstract

**Objective:** This study aims to determine the trace cadmium in water and fish species from estuaries in Tien Hai, Thai Binh province, Vietnam by graphite furnace atomic absorption spectrometry (GF-AAS). **Methodology:** The optimal conditions has been investigated by studying the effects of analysis parameters such as spectral line, current of cathode lamp, slit width, furnace temperature, acid concentration and subtracted solution on absorbance. The validation method was evaluated by linear range, accuracy, repeatability, limit of detection (LOD), limit of quantitation (LOQ), recovery (Re), and determination of trace cadmium in water and fish species. **Findings:** The results showed that the spectral line of 228.3 nm, current of cathode lamp of 4 mA, slit width of 0.5 nm, furnace temperature of 1800 °C, HNO<sub>3</sub> concentration of 1%, CH<sub>3</sub>COONH<sub>4</sub> concentration of 1% were optimal conditions for determination of cadmium. At these conditions, the analytical procedure exhibited the high accuracy and repeatability. The linear range of cadmium was 0-4 ppb. The LOD and LOQ values were 0.0058 and 0.019 ppb, respectively. **Application/Improvements:** Determination of the trace cadmium in the water and fish samples was done by the development of analytical procedure. It was applied to determine the water and fish species from Ba Lat and Lan estuaries in Tien Hai, Thai Binh, Vietnam.

**Keywords:** GF-AAS; Trace; Cadmium; Analysis; Fish

## 1 Introduction

The development of industry, agriculture, health care, tourism and trade have made the environment seriously polluted, especially the presence of heavy metals in the soil, water, and ecosystems<sup>(1)</sup>. Waste from factories and craft villages, domestic sewage and even wastewater from agriculture can increase the concentration of heavy metals such as mercury, cadmium, lead, arsenic, etc. in the water and in the creatures at the estuaries<sup>(2)</sup>. Vietnamese government is interested in addressing sources of environmental pollution. The analysis and evaluation of environmental indexes will play an important role in addressing this problem of pollution<sup>(3)</sup>.

In nature, heavy metals exist in air, soil, and water. Heavy metals exist in water in the form of ions or complexes, and they can diffuse to be the widest and furthest

in the water when compared to air and soil in the environment<sup>(4)</sup>. Under appropriate conditions, heavy metals in aquatic environment can be dispersed into soil and air leading to contamination of crops, vegetables, and fishes<sup>(5)</sup>. Fish are often at the top and the main part of the food chain. It is an essential ingredient in the human diet because it contains a high proportion of protein in the presence of fats, omega-3 fatty acids and vitamins with many minerals. However, according to scientists, fish may be the main source of some toxic heavy metals. And, heavy metals residue in fish reflects high concentrations of toxic heavy metals in water and sediments<sup>(6)</sup>.

Cadmium accumulates mainly in the kidneys for a relatively long time from 10-35 years. Eating foods containing a high content of cadmium will lead to digestive disorders such as nausea, vomiting, abdominal pain, and diarrhea<sup>(7)</sup>. Cadmium also causes calcium metabolism disorders, leading to bone diseases such as bone weakness, bone deformation, bone tissue destruction. In addition, cadmium also causes respiratory damage<sup>(8)</sup>. Long-term occupational exposure to high levels of cadmium may cause symptoms of bronchitis, chronic pneumonia (cough, shortness of breath, chest pain, fever) that contribute to the development of lung cancer. Several studies show that cadmium can cause kidney, lung and prostate cancers<sup>(9,10)</sup>. The International Agency for Research on Cancer (IARC) classifies cadmium and cadmium compounds as Group 1 carcinogens<sup>(11)</sup>. Therefore, the determination of trace cadmium in soil, water, food and environmental samples is becoming a matter priority.

Varied methods have been carried out to determine the trace cadmium. The kinetic method could determine cadmium in water samples with the LOD of 0.1  $\mu\text{g/mL}$ <sup>(12)</sup>. The UV-VIS spectrophotometric method was developed by using the solid phase extraction to analyze cadmium (II), the LOD was 0.07  $\mu\text{g/mL}$ <sup>(13)</sup>. The ICP-OES and F-AAS methods determined cadmium by addition of pre-concentration step with 2,2'-Bipyridyl and erythrosine, the LOD values were 4.0 and 7.75 ng/mL for ICP-OES and F-AAS, respectively, and the recoveries were more than 93%<sup>(14)</sup>. ICP-AES with the online adsorption and pre-concentration step via using micro-columns of DPTH-gel and TS-gel could analyze cadmium in water, the linear ranges were 5 to 100 ng/mL and 10-100 ng/mL and the RSD for ten independent analyses were 1 and 2.5% for DPTH gel and TS-gel, respectively<sup>(15)</sup>. The AAS method with the sample preparation by HNO<sub>3</sub> and H<sub>2</sub>O could determine the cadmium in cockles along the estuary of Sungai Tampok and Sungai Sanglang, showing the cadmium concentration in ranges of 0-4.25 and 03.85  $\mu\text{g/g}$ , respectively<sup>(16)</sup>. The graphite furnace atomic absorption spectroscopy (GF-AAS) displayed high sensitivity, selectivity and accuracy for the determination of cadmium in practical samples<sup>(15,17,18)</sup>.

In the current study, analytical procedure by GF-AAS was developed to determine cadmium in water and fish species from estuaries in Tien Hai, Thai Binh, Vietnam. Sample preparation was done using a microwave oven. The effects of acid concentration, substrate solution and releasing reagent on spectral line intensity determined the optimal analysis conditions. The effect of foreign ions on analytical method in addition to statistical methods used in the evaluation of the reliability and accuracy of the analytical method, were carried out.

## 2 Experiment

### 2.1. Apparatus and chemicals

The standard solutions were diluted from a stock solution of 1000 ppm (Merck) to make standard curve. The concentrated solutions HNO<sub>3</sub> (Merck, 65%), HCl (Merck, 37%) and H<sub>2</sub>O<sub>2</sub> (Merck, 30%) were used without further purification. NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (99%), CH<sub>3</sub>COONH<sub>4</sub> (99%), CH<sub>3</sub>COONa (99%) and LaCl<sub>3</sub> (99%) were used to study the effect of substrate solution to absorbance. Double distilled water, volumetric flask, filter paper, glass beaker, analytical balance (accuracy  $\pm 0.0001\text{g}$ ), technical weighing (accuracy  $\pm 0.01\text{ g}$ ), and heating plate were used for sample preparation. The absorbance of the sample measured using an Agilent 200 series AA. The samples were prepared by a microwave reaction system (Anton Paar, Austria).

### 2.2. Sample preparation

#### 2.2.1. Sample collection and preservation

The water samples were collected by clean plastic cans from two estuaries, Ba Lat and Lan in Tien Hai, Thai Binh, Vietnam, the map of these estuaries is shown in Figure 1. The samples were collected at two times a day, at ebb tide (around 8:00 am) and at high tide (around 16:30 pm). The samples were collected at the different depths from the surface: 0.5m (surface layer), 2m (middle layer), and 8m (bottom layer). And, the samples were collected during the rainy season (July 2019) and dry season (October 2019). The water after sampled from the estuaries were stored at 4°C to avoid changing the volume.

The fish samples were collected from boat that has just docked, the fresh fishes were taken into the sampling equipment then labeled the location and time. Three species of fishes such as mullet, croaker, and goby were selected. From the collected fishes, removal of head, viscera, fins and backbone were done and the meat of fishes was crushed by a mill, then thinly spread on a plate and 50 g of crushed fish was taken from five positions by the diagonal rule.

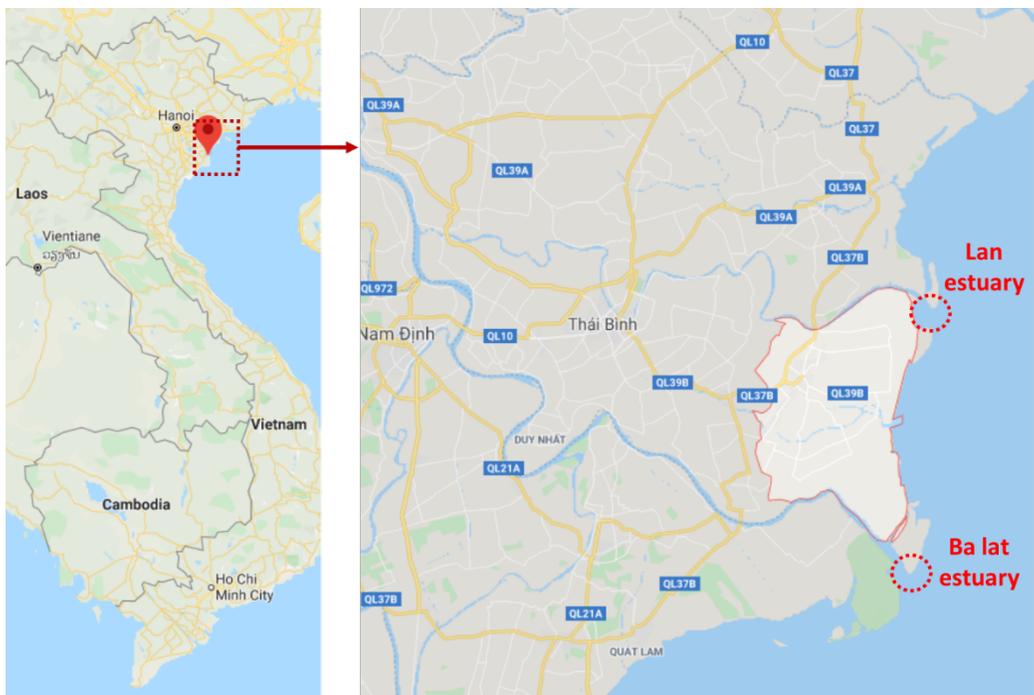


Fig 1. Map of sampling points

### 2.2.2. Treatment of samples

The water samples were filtered and acidified by HNO<sub>3</sub> until pH<2.0, then the samples were directly analyzed. Whereas, the treatment of fish samples was relatively complicated, 0.5 g of milled fish was put into a Teflon chamber, 7 mL of HNO<sub>3</sub> (65%) and 1 mL of H<sub>2</sub>O<sub>2</sub> (30%) were added, the mixture was heated at ~80°C for complete removal of NO<sub>2</sub>. Then the Teflon chamber was placed in a microwave for complete decomposition. After cooling to room temperature, the sample was transferred to a 25 mL volumetric flask and added with HNO<sub>3</sub> 1% up to the mark. Finally, the fish sample was analyzed by a GF-AAS.

The relative error ( $\bar{Er}$ ) standard deviation (SD), and relative standard deviation (RSD) were calculated to evaluate the error and repeatability of the measurement by the following equations:

$$\bar{Er} = \frac{((x_i - x_t))}{x_t} \times 100 \quad (1)$$

$$SD = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{(n-1)}} \quad (2)$$

$$RSD = 100 \times \frac{SD}{\bar{x}} \quad (3)$$

Where  $\bar{x}$  is mean value and  $x_t$  is the true or acceptable value.

Limit of detection (LOD) is the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value) with a stated confidence level (generally 99%) and limit of quantitation (LOQ) were determined by the following equations:

$$LOD = \bar{x}_{blank} + 3SD \quad (4)$$

$$LOQ = \frac{10 \cdot LOD}{3} \quad (5)$$

The content of Cd in water and fish was determined by the equations (6) and (7):

$$C = \frac{Cx \times 25}{24.2}$$

$$X = \frac{Cx \times V}{m}$$

Where C ( $\mu\text{g/L}$ ) is the concentration of Cd in the water sample, X (mg/kg) is the content of Cd in fish sample, Cx ( $\mu\text{g/L}$ ) is the concentration of Cd from standard curves, V (L) is the volume of sample (25 mL) and m (kg) is mass of the fresh fish.

### 3 Results and Discussion

#### 3.1. Study the effects of analysis parameters

The cadmium standard solution of 0.6 ppm was used to investigate the effect of spectral lines on absorbance, other conditions were fixed ( $\text{HNO}_3$  1%, hollow cathode lamp current of 4 mA, slit width of 0.5 nm, atomization temperature of  $1800^\circ\text{C}$ , and substrate solution of  $\text{CH}_3\text{COONH}_4$  1%), the results are presented in Table 1. The absorbance at 228.3 nm was higher but the RSD was lower than those of 326.1 nm. The absorbance and RSD at 228.3 nm were 0.227 and 0.441% and these were 0.136 and 0.960%, respectively, for 326.1 nm. Therefore, the spectral line of 228.3 nm was selected for further analysis.

**Table 1.** The absorbance of sample at different spectral lines

Experiment No.	Absorbance	
	228.3 nm	326.1 nm
1	0.227	0.137
2	0.226	0.136
3	0.225	0.134
4	0.228	0.137
5	0.227	0.135
$\bar{X}$	0.227	0.136
RSD (%)	0.441	0.960

In order to investigate the effect of the current of hollow cathode lamp on the absorbance, cadmium standard solution of 0.6 ppm was measured at the fixed conditions ( $\text{HNO}_3$  1%, spectral line of 228.3 nm, slit width of 0.5 nm, atomization temperature of  $1800^\circ\text{C}$ , and substrate solution of  $\text{CH}_3\text{COONH}_4$  1%), the current was varied from 2-10 mA. The analytical results are presented in Table 2. The absorbance was the highest and the RSD was the lowest among selected currents, showing the absorbance of 0.227 and RSD of 0.441 at 4 mA. Therefore, the current of hollow cathode lamp of 4 mA was suitable for further study.

**Table 2.** The absorbance of sample at different currents of cathode lamp

Experiment No.	Absorbance			
	2 mA	4 mA	8 mA	10 mA
1	0.096	0.227	0.112	0.137
2	0.098	0.226	0.114	0.136
3	0.097	0.225	0.112	0.131
4	0.096	0.228	0.113	0.133
5	0.098	0.227	0.110	0.135
$\bar{X}$	0.097	0.227	0.112	0.134
RSD (%)	1.031	0.441	0.893	1.493

The slit width was varied from 0.2 to 1.0 nm, other conditions were retained at  $\text{HNO}_3$  1%, spectral line of 228.3 nm, current of hollow cathode lamp of 4 mA, atomization temperature of  $1800^\circ\text{C}$ , and substrate solution  $\text{CH}_3\text{COONH}_4$  1% to investigate the effect of slit width on the absorbance. The results are recorded in Table 3. It was obviously seen that the absorbance at slit width of 0.5 nm was higher and RSD was lower than those of other slit widths. Therefore, the slit width of 0.5 nm was chosen for further investigation.

The standard sample Cd (II) 1.1 ppm was measured at the fixed conditions (spectral line of 228.3 nm, hollow cathode lamp current of 4 mA, slit width of 0.5 nm, and substrate solution of  $\text{CH}_3\text{COONH}_4$  1%), but the atomization temperature was varied from 1800 to  $2300^\circ\text{C}$ . The obtained results are presented in Table 4. The absorbance at  $1800^\circ\text{C}$  was higher than those of other temperatures. Therefore, the atomization temperature of  $1800^\circ\text{C}$  was selected for further investigation.

The effect of acid concentration on the absorbance was carried out by adding the HCl and  $\text{HNO}_3$  acids with the concentration range of 1-5%. The results are presented in Table 5. The absorbance values of samples with the addition of HCl and  $\text{HNO}_3$  acids at

**Table 3.** The absorbance of sample at the different slit widths.

Experiment No.	Absorbance			
	0.2 nm	0.5 nm	0.8 nm	1.0 nm
1	0.137	0.227	0.140	0.138
2	0.136	0.226	0.137	0.140
3	0.134	0.225	0.145	0.137
4	0.137	0.228	0.139	0.139
5	0.135	0.227	0.140	0.138
$\bar{X}$	0.136	0.227	0.140	0.138
RSD (%)	0.735	0.441	2.143	0.725

**Table 4.** The absorbance of sample in different atomization temperatures.

Atomization temperature °C	1800	2000	2100	2200	2300
Absorbance	0.2090	0.2087	0.2085	0.2089	0.2089

the concentration below 5% were similar, but the RSD with the addition of HNO<sub>3</sub> at 1% was the smallest among concentrations from 1 to 5%. Thus, the HNO<sub>3</sub> 1% was chosen for analysis of cadmium sample.

**Table 5.** The absorbance of sample in HCl and HNO<sub>3</sub> at the different concentrations.

Acid	Concentration (%)	Absorbance	RSD (%)
HCl	0	0.227	1.550
	1	0.228	1.418
	3	0.225	1.471
	5	0.228	2.19
	0	0.227	1.550
HNO <sub>3</sub>	1	0.228	0.855
	3	0.223	1.709
	5	0.225	1.754

In some cases, the sample may contain heat resistant substances, it can inhibit the atomization process, leading the reduction of the sensitivity of analytical method. Therefore, the substrates additional vaporizers were added into sample for elimination of the effect of heat resistant substances. In order to investigate the effect of substrate solution on absorbance, the solutions CH<sub>3</sub>COONa, CH<sub>3</sub>COONH<sub>4</sub>, and LaCl<sub>3</sub> were added into the sample. The results are presented in Table 6. In all cases for addition of CH<sub>3</sub>COONa, CH<sub>3</sub>COONH<sub>4</sub> and LaCl<sub>3</sub>, the absorbance at 1% was higher than that of other concentrations. The RSD and absorbance with CH<sub>3</sub>COONH<sub>4</sub> 1% were larger than those with CH<sub>3</sub>COONa 1% and LaCl<sub>3</sub> 1%.

**Table 6.** The absorbance in the different substrates at different concentrations.

CH <sub>3</sub> COONH <sub>4</sub>			CH <sub>3</sub> COONa			LaCl <sub>3</sub>		
Conc. (%)	Abs.	RSD (%)	Conc. (%)	Abs.	RSD (%)	Conc. (%)	Abs.	RSD (%)
0	0.222	1.471	0	0.222	1.471	0	0.222	1.471
1	0.228	1.493	1	0.227	1.136	0.5	0.223	2.276
2	0.225	1.527	2	0.221	1.127	1.0	0.228	1.089
3	0.223	0.752	3	0.224	1.323	1.5	0.225	1.323

Conc.; Concentration, Abs.: Absorbance

Alkaline Earth metals and some trans-metal foreign ions may affect analytical results, the solutions of Cd(II) at 0.6 ppm in addition of the cations Ca(II), Mg(II), Zn(II) and Fe(III) at the concentrations of 0-200 ppm were analyzed, the results are presented in Table 7. It could be seen that the absorbance values were relatively similar to each other. In addition, the concentration of these foreign ions in the real samples is relatively lower than 200 ppm. Therefore, it could be concluded that these ions did not affect the measurement of cadmium samples.

**Table 7. Effect of interference ions on absorbance**

Cation added	Concentration (ppm)				
	0	50	100	150	200
Ca <sup>2+</sup>	0	50	100	150	200
Mg <sup>2+</sup>	0	50	100	150	200
Zn <sup>2+</sup>	0	20	30	40	50
Fe <sup>3+</sup>	0	20	60	80	100
<b>Absorbance</b>	0.222	0.227	0.221	0.228	0.223

### 3.2. Validation method

#### 3.2.1. Determination of the linear range

Since the practical concentration of Cd(II) in water and fish species was relatively low, the linear range were studied in the concentration range of 0-4 ppb. The obtained absorbance values are presented in Table 8 and the calibration curve is presented in Figure 2. It showed a good linear relationship between the absorbance and concentration of Cd(II) at the concentration range of 0-4 ppb with the linear regression coefficient of 0.999. These results revealed that absorbance was directly proportional to the concentration, it meant that Lambert-Beer law was valid.

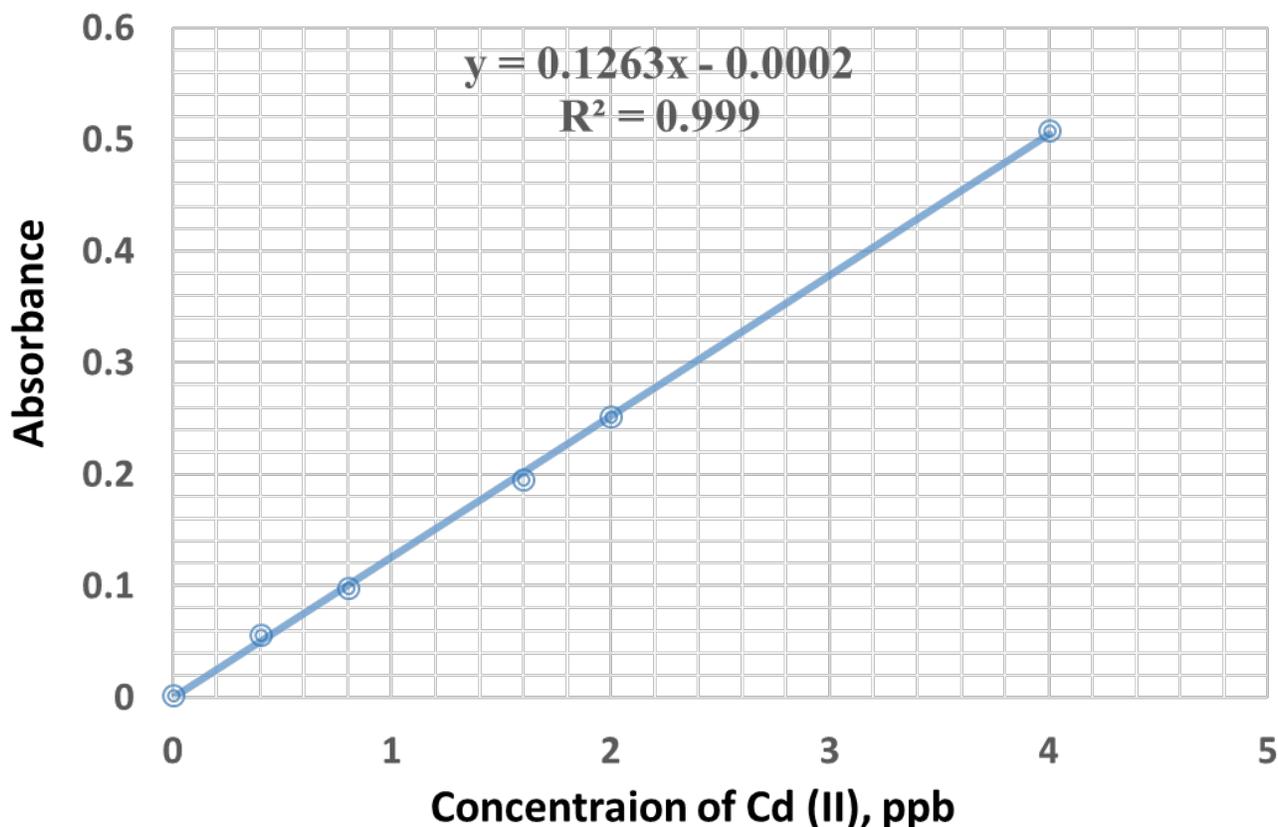


Fig 2. Calibration curve for standard solution Cd (II).

#### 3.2.2. Accuracy and repeatability of method

To evaluate the accuracy of the method, the standard samples at 0.4, 1.6 and 4 ppb were prepared. Each sample was measured and repeated in ten times. The results are presented in Table 9. It was showed that the SD values were relatively low and RSD values were in the permissible limitations of 30% according to AOAC, this meant that the GF-AAS method was highly stable,

**Table 8.** Results for the determination of linear concentration range of Cd.

Cd (II) concentration (ppb)	Absorbance				
	Abs1	Abs2	Abs3	Average value	RSD (%)
0	0.0017	0.0021	0.0019	0.0019	10.53
0.4	0.0561	0.0556	0.0558	0.0558	0.45
0.8	0.0981	0.0980	0.0980	0.0980	0.06
1.6	0.1950	0.1951	0.1955	0.1952	0.14
2	0.2510	0.2511	0.2518	0.2513	0.17
4	0.5115	0.5054	0.5085	0.5085	0.60

Abs1; Absorbance at the first measurement, Abs2; Absorbance at the second measurement, Abs3; Absorbance at the third measurement.

accurate, and fully consistent for the determination of trace Cd(II) in the water and fish species.

**Table 9.** Accuracy and repeatability for analysis of Cd (II).

Sample	1		2		3	
Concentration of Cd (II) (ppb)	0.4		1.6		4	
xt (A bs)	0.05032		0.20188		0.505	
Test	xi	$\bar{E}r$	xi	$\bar{E}r$	xi	$\bar{E}r$
1	0.0561	11.49	0.2033	0.70	0.5115	1.29
2	0.0556	10.49	0.2037	0.90	0.5094	0.87
3	0.0558	10.89	0.2010	0.44	0.5085	0.69
4	0.0558	10.89	0.2027	0.41	0.5085	0.69
5	0.0523	3.93	0.2031	0.60	0.5123	1.45
6	0.0517	2.74	0.2036	0.85	0.5113	1.25
7	0.0519	3.13	0.2039	1.00	0.5107	1.13
8	0.0515	2.35	0.2041	1.10	0.5102	1.03
9	0.0511	1.55	0.2043	1.20	0.5113	1.24
10	0.051	1.35	0.2038	0.95	0.5122	1.43
$\bar{x}$ (Abs)	<b>0.0533</b>	<b>5.88</b>	<b>0.2034</b>	<b>0.82</b>	<b>0.5106</b>	<b>1.11</b>
SD	<b>0.00222</b>		<b>0.00095</b>		<b>0.00140</b>	
RSD (%)	<b>4.17</b>		<b>0.47</b>		<b>0.27</b>	

### 3.2.3. Determination of LOD and LOQ

The sensitivity of the method was expressed in terms, limit of detection (LOD) and limit of quantification (LOQ). To determine the LOD and LOQ, 20 blank samples were prepared and analyzed at optimal conditions. The obtained absorbance values were used to calculate the standard deviation, b (intercept of standard curve). LOD and LOQ values determined by equations 4-5 were 0.0058 and 0.019 ppb, respectively, as seen in Table 10.

### 3.2.4. Determination of recovery method

The accuracy of method was also evaluated by recovery. The recovery study was carried out via spiking the sample at the addition standard levels of 1.6 and 4.0 ppb, each level was measured 5 times. The recoveries are presented in Table 11. The recoveries were 98.03 and 98.09% at concentrations of 1.6 and 4 ppb, respectively. These values were compatible with AOAC acceptable range of 40-120%.

## 3.3. Application in analysis of real samples

The water samples were collected from Ba Lat and Lan estuaries at the different seasons and tidal levels. The analysis results are presented in Tables 12 and 13. The concentrations of Cd(II) at Ba Lat estuary were in range of 0.258-0.918 ppb and the concentrations of Cd(II) from Lan estuary were in the range of 0.133-0.877 ppb. These results showed that Cd(II) concentration

**Table 10.** Absorbance of 20 bank samples.

Sample No.	Abs.
1	0.0017
2	0.0023
3	0.0041
4	0.0034
5	0.0027
6	0.0043
7	0.0036
8	0.0041
9	0.0038
10	0.0031
11	0.0047
12	0.0034
13	0.0027
14	0.0036
15	0.0043
16	0.0037
17	0.0044
18	0.0026
19	0.0031
20	0.0028
$\bar{x}$	0.0034
<b>SD</b>	0.00079
<b>b</b>	0.0038
<b>LOD (ppb)</b>	0.0058
<b>LOQ (ppb)</b>	0.019

**Table 11.** The recoveries of method.

Addition of standard level (ppb)	Analysis value (ppb)	Recovery (%)
	1.5550	
	1.5622	
1.6	1.5724	98.03
	1.5748	
	1.578	
	3.9501	
	3.9454	
4	3.9422	98.09
	3.8979	
	3.8820	

in two estuaries of Ba Lat and Lan at the different seasons and water layers were different, but all values were within the allowed standard of ministry of Natural Resources and Environment (QCVN 10-MT-2015/BTNMT Cd: 50 ppb) and permissible limit of the WHO (2011). The Cd (II) concentration was high in the rainy season due to the phenomenon of leaching from upper stream and it was decreased in the dry season. The Cd(II) concentration at low tide was higher than that of high tide due to the phenomenon of water flowing in to the sea at tide down.

**Table 12.** The concentration of Cd (II) in water samples of Ba Lat estuary.

Water layer	Rainy season		Dry season	
	High Tide $\bar{c} \pm SD$ (ppb)	Low Tide $\bar{c} \pm SD$ (ppb)	High Tide $\bar{c} \pm SD$ (ppb)	Low Tide $\bar{c} \pm SD$ (ppb)
Surface	0.281±0.007	0.314±0.005	0.308±0.006	0.258±0.006
Middle	0.408±0.004	0.416±0.007	0.326±0.005	0.392±0.005
Bottom	0.585±0.006	0.918±0.004	0.408±0.006	0.558±0.008

**Table 13.** The concentration of Cd (II) in water samples of Lan Estuary.

Water level	Rainy season		Dry season	
	High Tide $\bar{c} \pm SD$ (ppb)	Low Tide $\bar{c} \pm SD$ (ppb)	High Tide $\bar{c} \pm SD$ (ppb)	Low Tide $\bar{c} \pm SD$ (ppb)
Surface	0.244±0.009	0.224±0.006	0.239±0.006	0.133±0.007
Middle	0.434±0.006	0.541±0.008	0.525±0.008	0.538±0.008
Bottom	0.811±0.006	0.877±0.007	0.654±0.009	0.808±0.005

The fish samples were collected from Ba Lat and Lan estuaries at the different seasons. The analysis results are presented in Table 14. Analysis results showed that the Cd contents in croaker, mullet, and goby fishes from Ba Lat and Lan estuaries at different seasons were different, but these values were within the allowed standard of Ministry of Health (QCVN 8-2:2011/BYT Cd: 0.1 mg/kg) and permissible limit of the WHO (2011).

**Table 14.** The content of Cd in fish species from of Ba Lat and Lan Estuaries.

Fish species	Ba Lat		Lan	
	Rainy season $\bar{c} \pm SD$ ( $\mu\text{g}/\text{kg}$ )	Dry season $\bar{c} \pm SD$ ( $\mu\text{g}/\text{kg}$ )	Rainy season $\bar{c} \pm SD$ ( $\mu\text{g}/\text{kg}$ )	Dry season $\bar{c} \pm SD$ ( $\mu\text{g}/\text{kg}$ )
Croaker fish	0.023±0.001	0.062±0.003	0.028±0.001	0.036±0.001
Mullet fish	0.021±0.001	0.023±0.004	0.023±0.002	0.028±0.001
Sea goby fish	0.023±0.002	0.022±0.003	0.027±0.002	0.022±0.004

## 4 Conclusion

The optimal conditions for determination of trace cadmium in water and fish species from Ba Lat and Lan estuaries in Tien Hai, Thai Binh, Vietnam by GF-AAS were followed: spectral line of 228.3 nm, current of cathode lamp of 4 mA, slit width of 0.5 nm, furnace temperature of 1800°C, HNO<sub>3</sub> concentration of 1%, CH<sub>3</sub>COONH<sub>4</sub> concentration of 1%. At the optimal conditions, the analytical method had the high accuracy and repeatability with the RSD values of 4.17, 0.47 and 0.27% at concentrations of 0.4, 1.6, 4 ppb, respectively. The recoveries of 98.03 and 98.09% at concentrations of 1.6 and 4 ppb, respectively. The foreign ions such as Ca(II), Mg(II), Zn(II), and Fe(III) did not affect analytical method. In addition, water samples and three species of fishes were analyzed. Cadmium was detected in all the samples but the cadmium content in these samples were in the allowed standard prescribed by the Ministry of Natural Resources and Environment (QCVN 10-MT-2015/BTNMT Pb: 50 ppb), and allowed standards of Ministry of Health (QCVN 8-2:2011/BYT Pb: 0.1 mg/kg), and permissible limit of the WHO (2011).

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