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# Direct determination of Cd in seawater by graphite furnace-atomic absorbance spectrometry with Zeeman-effect background correction

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**Abstract** This article describes an accurate method for direct determination of cadmium in seawater using an end-heated atomizer graphite furnace atomic absorbance spectrometry. To avoid interferences caused by matrix elements, ammonium nitrate and di-ammonium hydrogen phosphate were added as matrix modifiers to the sample before analysis. Experiments showed that best Cd signal was obtained for a sample volume of 15  $\mu\text{l}$  with the addition of 13  $\mu\text{l}$  of  $\text{NH}_4\text{NO}_3$  (16%) and 3  $\mu\text{l}$  of  $(\text{NH}_4)_2\text{HPO}_4$  (4%), an ashing temperature of 400–550°C and an atomization temperature fixed at 1200°C. Detection limit ( $3\sigma$  from ten blank replicas) was 0.013 ppb and determination limit ( $10\sigma$  from ten blank replicas) was 0.044 ppb.

**Key Words:** GF-AAS, seawater, cadmium, matrix modifier, Zeeman background correction.

## Introduction

The direct measurement of cadmium in seawater by graphite furnace atomic absorption spectrometry represents a great interest for environmental studies allowing a fast and simple way to measure trace elements and to avoid contamination or loss risk during concentration process. However, seawater is a complex solution containing high levels of salts. These matrix elements strongly disturb trace element analysis. Ahsan *et al.* (1999), Barrera *et al.* (1998) and Cabon & Bihan (1995) reported procedures to minimize these matrix interference problems for Cr, Mn, Ni or Cu, in which matrix modifiers were added to the samples. Ahsan *et al.* (1999) published a protocol to measure Cd using a thiourea solution added to calcium matrix. Chang & Huang (2000) investigated with a side-heated atomizer (transversely heated graphite atomizer-type) and found that the direct determination of Cd in seawater is possible using matrix modifier ammonium nitrate and di-ammonium hydrogen phosphate, which allows to evaporate chlorides and halogens and to improve signal intensity and reproducibility. In this paper, I present a procedure for conventional end-heated atomizer using ammonium nitrate and di-ammonium hydrogen phosphate matrix modifier for direct Cd determination in seawater.

## Material and method

### Reagent and instrumentation

Cadmium spiked seawater solutions were prepared at 1 ppb from Kanto Chemical Co Ltd./Cicca standard solutions of 1000 mg/l and natural seawater blank. Two matrix modifier solutions were prepared by dissolving 3.33g and 0.8g of  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{HPO}_4$  respectively in 20 ml of MilliQ water. Wako chemical Co. Ltd. 99.9% acetic acid and Merck Suprapur ammonia solution 25% were used. Cadmium concentration was measured by an atomic absorption spectrometry (Hitachi model Z-8270) with pyrocoated graphite furnace (Platform type). Zeeman-effect background correction was made for all Cd data to remove potential background absorbance caused by salt particles arisen from the sample.

### Seawater blank and matrix modifier preparation

A blank of seawater (salinity = 28‰) and a cadmium free matrix modifier solution were prepared by removing Cd from the solutions using the Toyopearl AF-Chelate 650M iminodiacetate resin. Both 1 ml of seawater filtered using 0.45  $\mu\text{m}$  membrane-filter and matrix modifier solutions were added with 50  $\mu\text{l}$  of resin in 1.5 ml centrifugation tube. Prepared solutions were buffered at pH = 5.6 $\pm$ 0.2 with 23  $\mu\text{l}$  of acetic acid and 37  $\mu\text{l}$  of ammonia solution and were mixed for 30 minutes to allow complete Cd absorbance.

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**Table 1** Initial GF-AAS setup conditions.

Lamp current	7.5 mA
Wavelength of analytical line	228.8 nm
Slit width	1.3 nm
Cuvette type	Platform
Carrier gas flow rate during atomization	30 ml/min
Injected sample volume	15 $\mu$ l
Drying stage	60°C to 110°C for 70 sec
Ashing stage	110°C to 500°C for 60 sec
Atomization stage	1300°C for 10 sec
Cleaning stage	2800°C for 8 sec
Zeeman correction	Activated

**Table 2** Cd atomic absorbance from 0.1N nitric acid solution, matrix modifiers and seawater blank.

	Atomic absorbance
HNO <sub>3</sub> 0.1N solution	0.0036 $\pm$ 0.0010
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> solution	0.0049 $\pm$ 0.0008
NH <sub>4</sub> NO <sub>3</sub> solution	0.0036 $\pm$ 0.0014
Seawater blank	0.0051 $\pm$ 0.0004

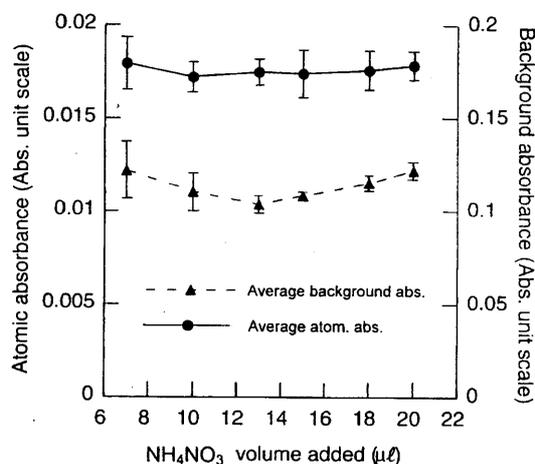
## Results and discussion

For determination of best conditions, spectrometer was programmed at first according to Table 1. Platform-type cuvette was chosen as graphite furnace rather than standard type to reduce interferences (matrix effect) induced by coexisting elements. Interferences result largely as a consequence of temperature gap between cuvette wall and carrier gas during atomization stage. In the case of sample like seawater, coexisting elements present in atomic vapor are cooled by argon gas and return to molecular state, which can disturb atomic absorbance. Platform cuvette heats sample by radiation rather than conduction. Carrier gas and sample are heated at the same time, reducing the matrix effect.

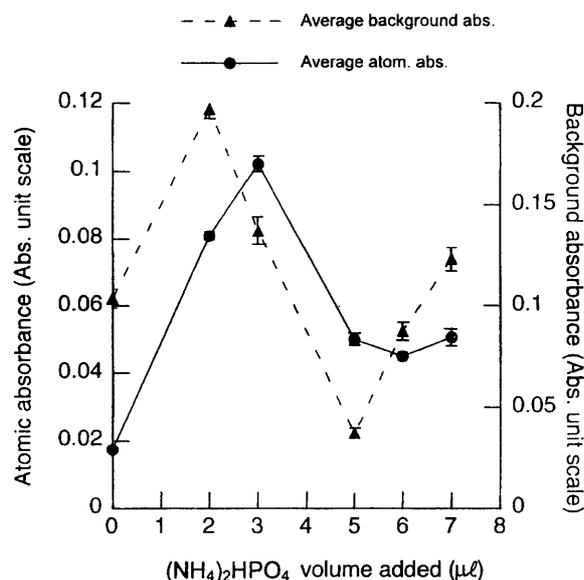
Drying stage has been set up at 70 seconds to prevent sudden boiling ebullition of NH<sub>4</sub>NO<sub>3</sub> solution; likewise ashing time has been set to 60 seconds to allow soft matrix evaporation without loss of cadmium. Cleaning stage has been set up at 2800°C to avoid accumulation of elements like calcium in the cuvette.

### Cd contamination

Following the initial spectrometer setup presented in Table 1, 0.1N nitric acid solution, matrix modifier solutions and seawater blank added with 13  $\mu$ l of NH<sub>4</sub>NO<sub>3</sub> (16%) and 6  $\mu$ l of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> (4%), were analyzed. Results are presented in Table 2. Nitric acid solution (0.1N) contained 0.008 ppb maximum (Merck analysis certificate). Results of matrix modifier and nitric acid solution analysis were not significantly different. Seawater blank analysis showed a slightly higher absorbance.



**Fig. 1** Effect of ammonium nitrate on Cd absorption signal and background signal. Plotted values are the average of three replicates and error bars are standard deviation.



**Fig. 2** Effect of di-ammonium hydrogen phosphate on Cd absorption and background signal. Plotted values are the average of three replicates and error bars are standard deviation.

### Determination of the best amount of ammonium nitrate

Ammonium nitrate was added first to sample as matrix modifier with variable volume. Result on background absorbance (before Zeeman correction) and atomic absorbance (after Zeeman correction) are plotted in Fig. 1, raw data are reported in Table 3-A. The effect of ammonium nitrate solution has been tested between 7  $\mu$ l to 20  $\mu$ l. The atomic absorbance range between 0.0172–0.0180 and background absorbance were in the range 0.1–0.12 (absorbance units), which is very low compared to atomic absorbance and background absorbance measured without matrix modifier, respectively of 0.2021 and 3.3608.

Table 3 Raw data of atomic and background absorbances.

## A: Determination of the best amount of ammonium nitrate

Added volume ( $\mu\ell$ )	Average atomic absorbance	Standard deviation	Average background absorbance	Standard deviation
7	0.0180	0.0014	0.1224	0.0155
10	0.0172	0.0008	0.1104	0.0105
13	0.0175	0.0007	0.1038	0.0046
15	0.0174	0.0013	0.1086	0.0018
18	0.0176	0.0011	0.1155	0.0042
20	0.0179	0.0008	0.1221	0.0047

## B: Determination of the best amount of di-ammonium hydrogen phosphate

Added volume ( $\mu\ell$ )	Average atomic absorbance	Standard deviation	Average background absorbance	Standard deviation
0	0.0175	0.0007	0.1038	0.0046
2	0.0810	0.0012	0.1970	0.0047
3	0.1022	0.0022	0.1373	0.0067
5	0.0502	0.0018	0.0374	0.0023
6	0.0452	0.0014	0.0875	0.0046
7	0.0507	0.0026	0.1232	0.0059

## C: Determination of the best ashing temperature

Temperature ( $^{\circ}\text{C}$ )	Average atomic absorbance	Standard deviation	Average background absorbance	Standard deviation
400	0.0783	0.0020	0.1962	0.0212
500	0.0803	0.0014	0.2291	0.0225
550	0.0808	0.0031	0.2298	0.0060
600	0.0800	0.0025	0.2217	0.0218
700	0.0680	0.0028	0.1871	0.0038

## D: Determination of the best atomization temperature

Temperature ( $^{\circ}\text{C}$ )	Average atomic absorbance	Standard deviation	Average background absorbance	Standard deviation
1200	0.0805	0.0013	0.1953	0.0078
1300	0.0808	0.0031	0.2298	0.0060
1400	0.0824	0.0005	0.2805	0.0195
1500	0.0797	0.0023	0.5032	0.0070

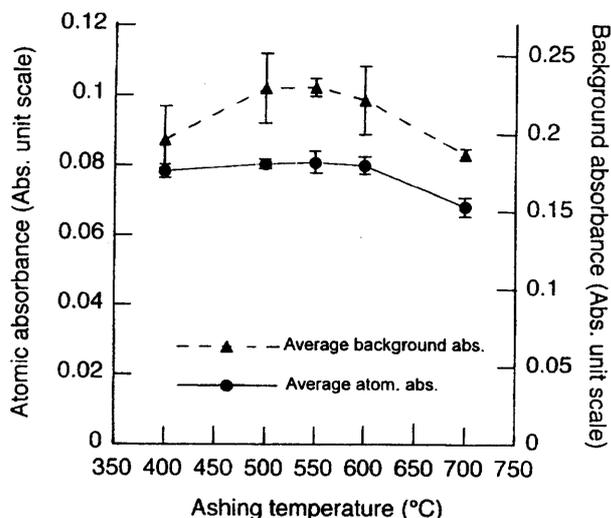


Fig. 3 Effect of ashing temperature on Cd absorption signal and background signal. Plotted values are the average of three replicates and error bars are standard deviation.

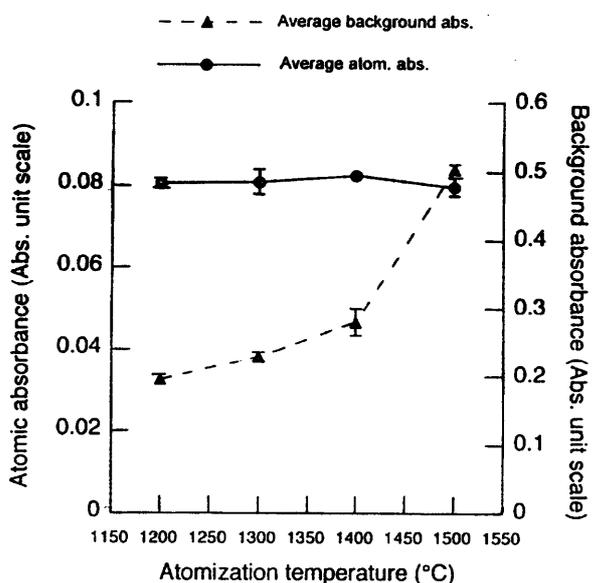


Fig. 4 Effect of atomization temperature on Cd absorption signal and background signal. Plotted values are the average of three replicates and error bars are standard deviation.

Based on the results, the optimum volume of ammonium nitrate solution is 13  $\mu\text{l}$ , providing good reproducibility and lowest background.

#### Determination of the best amount of di-ammonium hydrogen phosphate

Measurements using di-ammonium hydrogen phosphate were performed with 13  $\mu\text{l}$  of ammonium nitrate solution. Addition of  $(\text{NH}_4)_2\text{HPO}_4$  was done after sample injection. Indeed, faster cuvette degradation has been observed previously when  $(\text{NH}_4)_2\text{HPO}_4$  was injected first. Background absorbance and atomic absorbance signal are given on Fig. 2, raw data are reported in

Table 3-B. Addition of di-ammonium hydrogen phosphate until 3  $\mu\text{l}$ , significantly increased signal intensity. Beyond 3  $\mu\text{l}$ , signal decrease to reach about half value of the best signal. According to the measurement order: 5  $\mu\text{l}$ , 6  $\mu\text{l}$ , 7  $\mu\text{l}$ , 3  $\mu\text{l}$  and 2  $\mu\text{l}$ , background absorbance increased constantly. This is interpreted as cuvette degradation by  $(\text{NH}_4)_2\text{HPO}_4$  3  $\mu\text{l}$  has been chosen as the best volume for di-ammonium hydrogen phosphate solution.

#### Ashing temperature

Matrix modifier addition allows matrix elements to be removed in the ashing stage. To prevent Cd loss during evaporation, ashing temperature must follow a soft ramp. Ashing temperature investigations were carried out with previously determined matrix modifier volumes. The temperature range of the experiments was between 400°C to 700°C and the results are shown in Fig. 3, raw data are reported in Table 3-C. Cd signal slightly increased between 400°C to 550°C, beyond the temperature 550°C, absorbance decrease, mainly after 600°C. Background signal reached a maximum at 550°C. Ashing temperature can be chosen between 400°C and 550°C, allowing good Cd detection and moderate background signal.

#### Atomization temperature

Atomization temperature has been tested between 1,200°C to 1,500°C, standard atomization temperature of Cd and results are displayed in Fig. 4, raw data are reported in Table 3-D. There is an increase of background signal while absorbance signal remains constant, showing efficiency of Zeeman effect on background correction and lack of disturbance of background until 0.5 units on signal. According to these data, best atomization temperature is 1,200°C that is providing the lowest background.

#### Spectrometer setup summary, detection and determination limits

Table 4 summarize the final spectrometer setting. The detection limit based on three times the standard deviation ( $3\sigma$ ) of seven replicate measurements of seawater blank is 0.013 ppb. Determination limit ( $10\sigma$ , ten times the standard deviation) is 0.044 ppb for cadmium. In comparison, Chan & Huang (2000) got a detection limit of 0.005 ppb using a transversely-heated GF-AAS. The best detection limit, obtained by Cabon & Bihan (1995), is 0.003 ppb using oxalic acid (as the chemical modifier) and 99  $\mu\text{l}$  of seawater sample with a THGA atomizer. This determination limit is not enough for cadmium measurement from surface seawater samples, which require preconcentration, however it can be used in case of

**Table 4** Final GF-AAS setup conditions.

Lamp current	7.5 mA
Wavelength of analytical line	228.8 nm
Slit width	1.3 nm
Cuvette type	Platform
Carrier gas flow rate during atomization	30 ml/min
Injected sample volume	15 $\mu$ l
Drying stage	60°C to 110°C for 70 sec
Ashing stage	110°C to 400–550°C for 60 sec
Atomization stage	1200°C for 10 sec
Cleaning stage	2800°C for 8 sec
Volume of $\text{NH}_4\text{NO}_3$ (16%) added	13 $\mu$ l
Volume of $(\text{NH}_4)_2\text{HPO}_4$ (4%) added	3 $\mu$ l
Zeeman correction	Activated

study on area undergoing anthropogenic cadmium input. In such case, Cd concentration can reach 1.67 ppb (Cotté-Krief *et al.* 2000).

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