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Cadmium and lead in seafood samples determined by solid phase extraction and graphite furnace atomic absorption spectrometry

Pipat Chooto[a], **Chalermpol Innuphat**[a], **Puchong Wararattananurak**[a,*], **Chaipat Lapinee**[b]

[a] Department of Chemistry, Analytical Chemistry Division, Faculty of Science,
Prince of Songkla University, Hatyai, Songkhla 90112 Thailand
[b] Department of Chemistry, School of Science, University of Phayao, Muang Phayao,
Phayao 56000 Thailand

*Corresponding author, e-mail: puchong.w@psu.ac.th

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ABSTRACT: A sample preparation method has been developed to detect cadmium and lead in commercial frozen seafood samples. After being digested with concentrated HNO_3 in a closed polypropylene vessel, the clear sample solution was separated and preconcentrated by solid phase extraction using octadecyl silica membrane discs modified with 8-hydroxyquinoline prior to determination by graphite furnace atomic absorption spectrometry (GFAAS). The preconcentration conditions including pH, ligand quantity, eluent concentration, and volume were found to be effective with 10.0 mg of 8-hydroxyquinoline in 2.0 ml ethanol and pH 6.0. The retained cadmium and lead were efficiently eluted with 5.0 ml of 1.0 M HNO_3 and determined by GFAAS. The detection limits for cadmium and lead were 0.073 µg/l and 0.332 µg/l, respectively. The proposed method was tested with the certified reference material, DORM-2 (Dogfish muscle), with good agreement. The recoveries were found to be 100–103% ($n = 4$) for Cd and 92–108% ($n = 5$) for Pb with relative standard deviation ($n = 5$) of 3% for Cd and 4% for Pb. The extraction was found to be unaffected by coexisting ions. The method was applied satisfactorily to the seafood samples and trace levels of cadmium and lead were found.

KEYWORDS: preconcentration, 8-hydroxyquinoline, GFAAS

INTRODUCTION

Cadmium and lead are well recognized to be highly toxic elements to human being[1,2]. They are widely dispersed in the environment[3–5], and the exposure to either element can produce adverse health effects due to their toxicity after accumulation in multiple organs in human body[6]. Most contaminations to human by cadmium and lead arise from food consumption[7,8] hence the importance of their determinations in food samples[9–11].

Graphite furnace atomic absorption spectrometry (GFAAS) is one of the most common techniques used for trace analysis of heavy metals as it is highly sensitivity, has low detection limits, and requires low sample volumes[12]. Direct determination of trace amounts of cadmium and lead in complicate matrices as food samples by GFAAS is usually difficult owing to interferences and insufficient detection power[13–15]. These difficulties however have been recently overcome by research on digestion[16–18], preconcentration, and separation methods including solvent extraction, coprecipitation, ion exchange, and solid phase extraction procedures[19]. Solvent extraction of different metal ions has been widely employed in chemistry and industry for many years. However, classical extraction methods are usually time consuming, labour-intensive and require relatively large volumes of high purity solvents. Additional concern is the disposal of used solvent which can create severe environmental problems. Much interest has been recently focused on replacing conventional solvent extraction methods in isolating environmental pollutants with solid phase extraction (SPE) techniques which are capable of selectively removing trace metal ions from complex matrices with minimal usage of organic solvent[20]. The application of SPE to metal ions is generally based on chelating matrices with current interest in designing macromolecular chelators with high sorption capacity, selectivity, and suitability[21].

8-hydroxyquinoline[22] (oxine) is a well-characterized and versatile chelating organic ligand which can form covalent compounds with a number of metal ions under controlled pH. It has been immobilized on a variety of supports such as glass beads[23], silica gel[24], polystyrene divinylbenzene[25], silicon tube[26], and ionic imprinted polymer[27]; thus becoming suitable to be used with sorbents in metal analysis.

Effective sorbents for solid phase extraction should possess unique characteristic including negligible swelling capacity to resist swelling and shrinking with changes in pH or solvent conditions, strong mechanical stability to withstand high flow rate and high chemical resistibility to endure harsh conditions. Octadecyl silica membrane discs are comprised of polytetrafluoroethylene (PTFE) polymer and chemically modified silica particles tightly bound in a web of micro-PTFE fibrils. They have a number of advantages as a solid support including chemical inertness, elevated resistibility, low friction coefficient and swelling resistance[1].

This study develops a simple and rapid method for Cd and Pb determination in seafood samples by GFAAS by using 8-hydroxyquinoline modified octadecyl silica membrane disc as solid adsorbent for solid phase extraction to preconcentrate the metals. The developed method was optimized in terms of pH, 8-hydroxyquinoline quantity, elution type and volume to obtain its analytical performance. The optimized method was then applied to seafood samples.

MATERIALS AND METHODS

Apparatus

A Perkin-Elmer Model A Analyst 800 atomic absorption spectrometer with Zeeman background correction equipped with transverse heated graphite atomizer and a Perkin-Elmer AS-800 autosampler was used to determine Cd and Pb. Suction pump (BuCHI Laboratoriums-Technik AG, CH-9230 FLAWIL/SCHWEIZ, 300 W, 220 V AC, 50–60 Hz, Switzerland), Standard Millipore apparatus (47 mm diameter; Pyrex, USA) and 3 M Empore disc octadecyl silica membrane disc (47 mm diameter, thickness 0.50 ± 0.05 mm; St. Paul, MN) were used for solid phase extraction. Polypropylene vessels and water bath (S.V. Medico, Co. Ltd.) were used for sample digestion.

Reagents and standard solutions

Analytical reagent grade chemicals were employed for the preparation of all solutions. De-ionized water prepared from a Milli Q water purification system (Millipore, Bedford, MA, USA) was used throughout this work. Stock standard solutions (1000 mg/l) of Cd(II) and Pb(II) were obtained from the National Institute of standard and Technology (NIST) and diluted for obtaining reference and working solutions. Certified reference material (DORM-2) was obtained from the National Research Council Canada (NRC) for method verification. $Mg(NO_3)_2$ and $NH_4H_2PO_4$ were used in the preparation of chemical modifiers.

Sample collection and preparation

Seafood samples were collected from frozen seafood companies in Trang, Pattani, and Songkhla provinces. The seafood samples were stored in polyethylene bags and were frozen at −5 °C until further processing. The frozen seafood samples were defrosted and homogenized. The homogenized tissue samples were dried to a constant weight at 80 °C for 24 h. The dried homogenized samples were collected in polyethylene bags until analysis.

Sample digestion

Three types of sample digestion including dry ashing, hot plate digestion and water bath digestion were experimented with the certified material. It was found that all three methods are equally efficient in terms of accuracy and precision (data not shown). The water bath digestion is preferable and recommended only because of its less time consuming and less contamination. A portion (0.2 g dry weight) of sample was accurately weighed into polypropylene tube and 5.0 ml of HNO_3 were added. The polypropylene tube was covered with the spiral plastic cap and heated in water bath at 65 °C for 3 h. The solution was diluted to 25.0 ml with de-ionized water.

Solid phase extraction

For solid phase extraction of samples under study, first octadecyl silica membrane disc (C18-Disk) was placed in the standard Millipore filtration apparatus and then washed with 10.0 ml ethanol to remove all contaminants. After all the solvent has passed through the disc, it was dried by passing air for 5 min. The disc conditioning was achieved by passing 10.0 ml deionized water and 10.0 ml ethanol onto the disc. A solution of 10.0 mg of 8-hydroxyquinoline in 2.0 ml ethanol was then introduced and was drawn slowly through the disc by vacuum. Finally, the disc was washed with 25.0 ml deionized water and dried by passing air to obtain the modified disc ready for extraction. The sample solution was passed through the modified membrane disc and then the disc was dried by passing air through it for 5 min. The analytes retained on the disc were eluted with 5.0 ml of 1.0 M HNO_3.

RESULTS AND DISCUSSION

Optimization of solid phase extraction

Both Cd(II) and Pb(II) ions are Lewis acid that exhibits a high tendency to form complexes with ligands containing N donor atoms with basic properties. The existence of N and O donating atoms in 8-hydroxyquinoline was expected to increase both the stability and selectivity of its complex over other metal ions, especially alkali and alkali earth cations. The experiment to investigate the quantitative retention of Cd(II) and Pb(II) ions by the octadecyl silica membrane disc modified by 8-hydroxyquinoline revealed that the discs were capable to retain both ions.

The optimized conditions for the extraction procedure were established by using 1.0 µg/l Cd and 20.0 µg/l Pb as the sample solutions. Parameters including pH of sample solutions, amount of 8-hydroxyquinoline, eluent solution types, and concentrations and eluent solution volumes were investigated as follows.

Most chelating ligands are conjugate bases of weak acids with a very strong affinity for hydrogen ions making the pH an important factor in the separation of metal ions by chelation, as it determines the value of the conditional stability constants of metal complexes on the surface of sorbent. The presence of OH and NH groups on the 8-hydroxyquinoline structures suggests that the extent of complexation is sensitive to pH. The influence of the pH of aqueous samples on the recovery of 1.0 µg/l Cd and 20.0 µg/l Pb from 25.0 ml sample solutions was studied in the range of pH 1.0–8.0 (adjusted by 0.1 M HNO_3 or 0.1 M ammonium hydroxide solutions). Values of pH higher than 8.0 were not investigated due to the possibility of hydrolysis of octadecyl silica which consequently decreases the active lifetime of the discs[19]. As shown in Fig. 1, the recoveries increase gradually for both metals up to pH 6 and then decrease. This is because at low pH the NH group in 8-hydroxyquinoline is protonated whereas at high pH the deprotonation of the OH group occurs along with hydrolysis and precipitation reaction of both metals, resulting in less complexation of 8-hydroxyquinoline with Cd(II) and Pb(II). The best recovery of Cd(II) and Pb(II) ions was obtained at pH 6.0 which was then adopted for further studies.

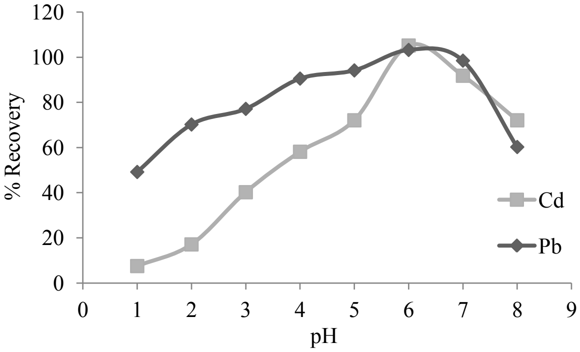

Fig. 1 Effect of pH on the recovery of 1.0 µg/l Cd and 20.0 µg/l Pb from 25.0 ml sample solutions extracted by membrane disc modified with 10.0 mg of 8-hydroxyquinoline.

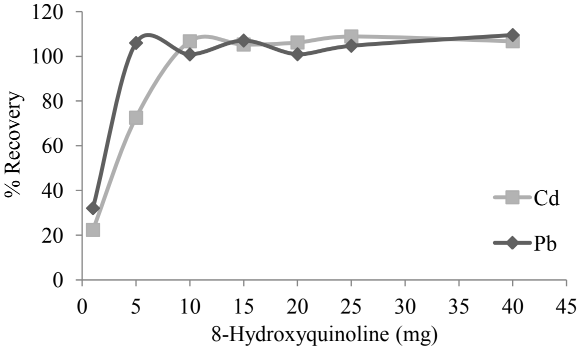

Fig. 2 Effect of 8-hydroxyquinoline quantity (in 2.0 ml ethanol) on the extraction of 1.0 µg/l Cd(II) and 20.0 µg/l Pb(II) by octadecyl silica membrane discs from 25.0 ml sample solution at pH 6.0.

For the effect of 8-hydroxyquinoline amount on the quantitative extraction of Cd(II) and Pb(II) by the membrane disc, the investigation was conducted by varying the amount of 8-hydroxyquinoline from 1.0–40.0 mg in 2.0 ml ethanol for the extraction of 1.0 µg/l Cd(II) and 20.0 µg/l Pb(II) ions from 25.0 ml sample solutions. Fig. 2 shows that the amounts of metals increased sharply to reach 100% recovery plateau at 8-hydroxyquinoline quantity of 10.0 mg, indicating quantitative extraction of both metals at this value and above. Hence 10 mg was chosen.

Selecting a suitable eluent is vital for the analytical performance of solid phase extraction. Here, two eluents, 0.1–2.0 M HNO_3 and 0.1–1.0 M EDTA, were tested by investigating the recoveries of 1.0 µg/l Cd(II) and 20.0 µg/l Pb(II) in 25.0 ml

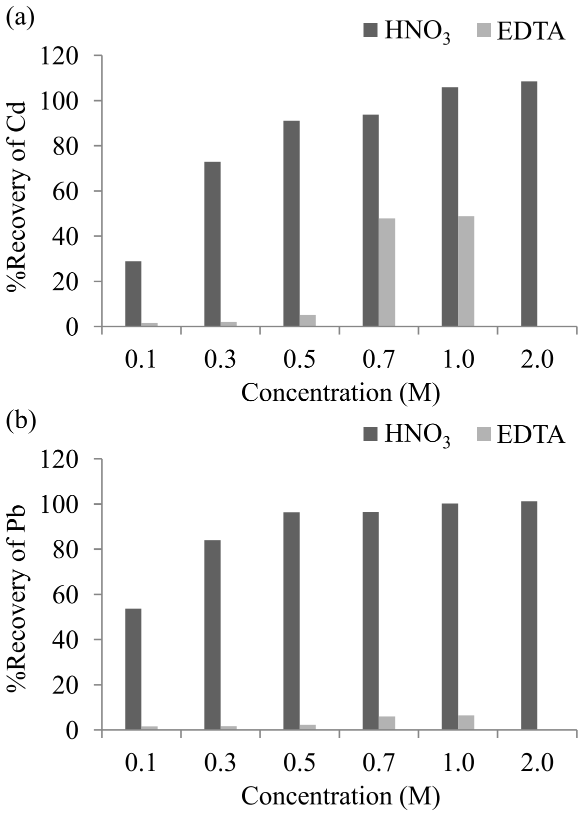

Fig. 3 Effect of the concentration of nitric acid and EDTA as eluents on the extraction of (a) 1.0 µg/l Cd(II) and (b) 20.0 µg/l Pb(II) in 25.0 ml of sample solution at pH 6.0 using 10.0 mg of 8-hydroxyquinoline in 2.0 ml ethanol modified octadecyl silica membrane discs.

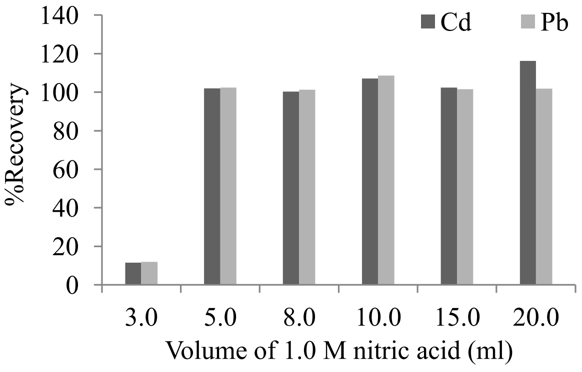

Fig. 4 Effect of volume of 1.0 M HNO_3 on the elution of adsorbed 1.0 µg/l Cd(II) and 20.0 µg/l Pb(II) on the modified membrane discs.

Table 1 The optimum conditions for solid phase extraction using 8-hydroxyquinoline modified octadecyl silica membrane disc.

Parameters	Optimum conditions
pH	6.0
8-hydroxyquinoline	10.0 mg
Eluent type	HNO_3
Eluent concentration	1.0 M
Eluent volume	5.0 ml

sample solution at pH 6.0 with the extraction by 10.0 mg of 8-hydroxyquinoline in 2.0 ml ethanol modified octadecyl silica membrane discs. It is evident from Fig. 3 that the recovery percentages for both metals are higher in the case of HNO_3, reflecting its greater efficiency in quantitative elution of the adsorbed Cd(II) and Pb(II). Despite of the fact that EDTA is the chelating agent that can be complexed with various metal ions and was selected as an eluent to decomplex the adsorbed Cd and Pb complexed with 8-hydroxyquinoline on the extraction disc, the stability constants of EDTA complexes with Cd and Pb are less than those of 8-hydroxyquinoline. For 8-hydroxyquinoline (OX), its acid dissociation constants are $pK_{a1} = 4.94$ and $pK_{a2} = 9.66$; and its cumulative stability constants (β) for Pb and Cd are $\log\beta(\text{CdOX}^+) = 8.22$, $\log\beta(\text{CdOX}^+) = 15.22$, $\log\beta(\text{PbOX}^+) = 10.03$ and $\log\beta(\text{PbOX}_2) = 17.34$ whereas for EDTA $pK_{a1} = 2.00$, $pK_{a2} = 2.69$, $pK_{a3} = 6.18$, and $pK_{a4} = 10.15$; $\log\beta(\text{CdH(EDTA)}^-) = 9.07$, $\log\beta(\text{PbH(EDTA)}^-) = 9.68$, and $\log\beta(\text{PbH}_2\text{(EDTA)}) = 6.22$ [26]; hence it is not strong enough to decomplex the adsorbed metals. The optimum eluent for Cd and Pb extraction was therefore 1.0 M HNO_3.

The next parameter is the eluent volume. Generally, the higher the eluent volume, the greater the extracted amount of metals. However, the volume of eluent should be just enough to quantitatively extract the metals. In our case, the percentages of recoveries were increased but not beyond the eluent volume of 5.0 ml (Fig. 4). Hence 5.0 ml of 1.0 M HNO_3 was selected for further studies.

The optimum conditions for Cd and Pb preconcentrations using 8-hydroxyquinoline modified octadecyl silica membrane discs are summarized in Table 1.

Analytical performance of the proposed method

The efficiency of the solid phase extraction by using octadecyl silica membrane discs modified by 8-hydroxyquinoline under the optimum conditions was investigated in terms of maximum capacity of the modified membrane disc to retain the analytes, effect of coexist ions interference, detection limit, as well as accuracy and precision. The maximum capacity of the modified membrane disc is defined as the maximum amount of Cd and Pb which can be absorbed on the modified membrane disc with 10.0 mg 8-hydroxyquinoline in 2.0 ml ethanol. The investigation was carried out by passing 25.0 ml of 1000 μg/l Cd and Pb at pH 6.0 and the retained metal ions in the elution solution were determined by GFAAS. The maximum capacity of the disc obtained from three measurements was 28.7 ± 1.4 μg/l and 109.1 ± 2.1 μg/l of Cd and Pb on the modified membrane discs, respectively.

In order to investigate the interference of coexisting ions in the determination of Cd(II) and Pb(II) ions, 25.0 ml aqueous solution containing 1.0 μg/l Cd(II) and 20.0 μg/l Pb(II) and interfering ions were experimented by solid phase extraction and GFAAS. The absorbance of the Cd and Pb in the presence of other ions were compared with that in the solution without interference. It was found that the absorbances with and without coexisting ions including Na^+, K^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, and Cl^- were 0.1202 and 0.1219 for Cd; 0.0972 and 0.1062 for Pb. Interference was therefore insignificant according to t-test at 95% confidence level with relative standard deviation (RSD) $\leqslant 5$ ($n = 3$), $t_{\mathrm{cal}(n=6)} = 0.50$ for Cd, $t_{\mathrm{cal}(n=6)} = 1.81$ for Pb, and $t_{\mathrm{crit(at\,95\%)}} = 2.78$ for both Cd and Pb.

The detection limits of the proposed method for Cd and Pb determination were studied by measuring ten replicates of the blank solution. The detection limits of Cd and Pb from $3\sigma/\mathrm{m}$, where σ is the standard deviation of blank signal and m is the slope of the calibration graph, were 0.073 and 0.332 μg/l, respectively.

The accuracy of the developed method was evaluated by analysis of certified reference material (DORM-2). With the certified concentrations of 0.043 ± 0.008 μg/g for Cd and 0.065 ± 0.007 μg/g for Pb, the determined concentrations were 0.045 ± 0.001 μg/g for Cd (RSD = 2.45) and 0.071 ± 0.003 μg/g for Pb (RSD = 4.49) which are in good agreement according to t-test (RSD $\leqslant 5$ ($n = 3$), $t_{\mathrm{cal}(n=3)} = 2.75$ for Cd, $t_{\mathrm{cal}(n=3)} = 2.66$ for Pb, and $t_{\mathrm{crit(at\,95\%)}} = 4.30$ for both Cd and Pb). The precision of the proposed method was investigated by measuring of five replicates of 1.0 μg/l Cd(II) and 20.0 μg/l Pb(II) sample solution in terms of RSD of the absorbance ($n = 5$) which was found to be 3% for Cd and 4% for Pb. The recovery for Cd was found to be 100–103% ($n = 4$) and for Pb 92–108% ($n = 5$). The analytical performance of the investigated method is summarized in Table 2.

Table 2 Analytical performance of the proposed method with solid phase extraction using 10.0 mg 8-hydroxyquinoline modified octadecyl silica membrane discs.

Parameters	Cd	Pb
Maximum capacity (μg/l)	30.7 ± 3.8	169 ± 11
Coexisting ion interference	None	None
Detection limits (μg/l)	0.073	0.332
Precision (% RSD)[a]	3.09	3.80
Recovery (%)	100–103[b]	92–108[a]

[a] ($n = 5$)
[b] ($n = 4$)

Table 3 The contamination of Cd and Pb in frozen tuna fish from the seafood companies in the South of Thailand.

Company	Lot No.	Contamination level (μg/g)	
		Cd	Pb
1	1	0.015 ± 0.001	0.129 ± 0.022
	2	0.016 ± 0.002	0.105 ± 0.026
	3	0.015 ± 0.005	0.115 ± 0.009
	4	0.009 ± 0.002	0.032 ± 0.003
2	1	0.006 ± 0.001	0.033 ± 0.004
	2	0.001 ± 0.000	0.020 ± 0.013
	3	0.007 ± 0.001	0.108 ± 0.019
	4	0.008 ± 0.002	0.041 ± 0.022
	5	0.008 ± 0.001	0.009 ± 0.001
3	1	0.003 ± 0.001	0.046 ± 0.016
	2	0.006 ± 0.001	0.032 ± 0.010
	3	0.005 ± 0.000	0.044 ± 0.007
	4	0.002 ± 0.001	0.041 ± 0.008
	5	0.005 ± 0.001	0.061 ± 0.007
4	1	0.012 ± 0.000	0.022 ± 0.008
	2	0.006 ± 0.002	0.015 ± 0.001
	3	0.008 ± 0.001	0.057 ± 0.018
	4	0.003 ± 0.001	0.035 ± 0.016
	5	0.007 ± 0.000	0.079 ± 0.006

Determination of Cd and Pb in seafood samples

The proposed method was found to be satisfactorily applicable for Cd and Pb determination in a variety of seafood samples from the frozen seafood companies in Trang, Pattani, and Songkhla provinces of Thailand with the results as shown in Tables 3 and 4, for example, 0.001–0.016 μg/g Cd(II) and 0.009–0.129 μg/g Pb(II) in the case of tuna fish, reflecting that the concentrations of cadmium and lead in those seafood samples were at trace level.

CONCLUSIONS

The proposed method demonstrated a maximum capacity of 30.7 ± 3.8 μg/l for cadmium and

Table 4 The contamination of Cd and Pb in frozen squid, cuttlefish, octopus, and prawns from seafood companies in Southern Thailand.

Sample	Lot No.	Contamination level (μg/g)	
		Cd	Pb
Squid	1	0.004 ± 0.000	0.165 ± 0.010
	2	0.003 ± 0.000	0.035 ± 0.005
	3	0.006 ± 0.000	0.089 ± 0.009
	4	0.007 ± 0.000	0.018 ± 0.002
	5	0.001 ± 0.001	0.037 ± 0.018
	6	0.009 ± 0.000	0.006 ± 0.001
	7	0.002 ± 0.000	0.005 ± 0.000
Cuttlefish	1	0.003 ± 0.000	0.003 ± 0.000
	2	0.004 ± 0.000	0.005 ± 0.000
	3	0.003 ± 0.000	0.003 ± 0.000
Octopus	1	0.019 ± 0.001	0.002 ± 0.001
	2	0.028 ± 0.000	0.005 ± 0.001
	3	0.049 ± 0.002	0.018 ± 0.003
	4	0.036 ± 0.000	0.012 ± 0.002
Prawn	1	0.002 ± 0.000	0.013 ± 0.004
	2	0.004 ± 0.000	0.005 ± 0.001
	3	0.002 ± 0.000	0.013 ± 0.000
	4	0.002 ± 0.000	0.007 ± 0.001
	5	0.002 ± 0.000	0.022 ± 0.001
	6	0.003 ± 0.000	0.025 ± 0.004

169 ± 11 μg/l for lead and detection limits of 0.073 μg/l for cadmium and 0.332 μg/l for lead with percentage of recoveries of 100–103% for Cd and 92–108% for Pb and RSD ($n = 5$) of 3% for Cd and 4% for Pb. When applied to seafood samples in Thailand, the method revealed trace level of both metals. The developed method is recommended as another potential candidate for routine industrial seafood analysis.

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