8th National and International Academic Conference
Huachiew Chalermprakiet University

เรียนรู้เพื่อรับใช้สังคม

Determination of Cadmium in Water Samples by Dispersive Solid Phase Extraction with UV–visible Spectrometric Detection

Apinya Navakhun[1*] and Patiphan Piaokhot[2]

[1] Department of Chemistry, and Center of Excellence on Environmental Health and Toxicology (ETH), Faculty of Science, Burapha University, Chonburi, Thailand

[2] Department of Chemistry, Faculty of Science, Burapha University, Thailand

*e-mail: apinyan@go.buu.ac.th

Rationale

Cadmium is known as a toxic heavy metal. Cadmium has been classified by The International Agency for Research on Cancer in Group 1 as human carcinogen. Cadmium is released into the environment through natural processes such as volcanic eruptions, sea spray and forest fires, but the greatest contamination arises from human activities. Due to cadmium occurs and contaminates in the environment at low levels, it is essential to develop sensitive analytical strategies for the determination of cadmium at trace levels. Different techniques have been investigated for the extraction and pre-concentration of cadmium in various environmental. Techniques as liquid-liquid extraction (LLE) and solid phase extraction (SPE) have been reported. However, the LLE extraction techniques require the uses of large amounts of solvent, which is flammable, volatile, toxic, and harmful to the environment. To overcome the disadvantages mentioned above, miniaturized, and green extraction methods have been developed.

Research Objectives

The development of cadmium extraction and preconcentration method using dispersive solid phase extraction technique for trace level cadmium determination in water samples is the main objective of this research. Factors affecting the extraction and determination of cadmium by UV-visible spectrophotometry technique were optimized to reach the high measurement sensitivity. The validation of the method has been evaluated to verify that it was an acceptable method according to international standards. In addition, to confirm the practicality of the proposed method, this method was applied to determine the cadmium contamination in the surface water sample.

Methodology

Complex formation and dispersive solid phase extraction (DSPE)

Diphenylthio-carbazone or dithizone (H_2Dz) was used as complexing agent to form Cd-dithizone complex ($Cd(HDz)_2$). The dithizone adsorbed on silica was prepared by stirring the silica gel in the dithizone solution for 40 minutes, then the silica was filtered and dried with nitrogen gas. The DSPE extraction procedure was performed by adding a certain amount of dithizone absorbed silica into the cadmium solution. The buffer solution was added to control the pH of the solution. Stir the solution in a dark place for 30 minutes, strain the silica and dry it. The $Cd(HDz)_2$ is eluted from the silica with 5 mL acetone. Finally, the UV-visible absorbance was monitored at 491 nm for absorption of the $Cd(HDz)_2$ complex. The extraction parameters which affected the extraction efficiency including pH of solution, extraction time, and type of elution solvent were studied and compared. All the experiments were three replicate analyses.

Method validation and sample determination

Method validation parameters including limit of detection, limit of quantification, calibration curve, precision and accuracy were evaluated in this study. Moreover, the proposed method was applied for determination of Cadmium in water samples collected from Saensuk Subdistrict, Bang Phra Subdistrict, Mueang District and Laem Chabang Port, Sriracha District, Chonburi Province, Thailand. Water samples were collected in December 2019. The water samples were acidified, filtered the large particles, and stored at -20 °C prior to analysis.

Discussion

In this research, dispersive solid phase extraction (DSPE) techniques were used to extract and preconcentrate low level cadmium concentration in water samples. Dithizone adsorbed on silica was synthesized. Then cadmium was extracted from the aqueous solution by complex formation and adsorbed on solid silica. After that, the complex was eluted with a small volume of organic solvent. The absorption of colored complexes was measured for the cadmium determination. In this research, dithizone was used as a ligand for the complex formation. This is because dithizone can form complexes with many heavy metals. Thus, this extraction method can be applied to extract other heavy metals such as Lead. In addition, the DSPE technique is an environmentally friendly extraction technique due to the use of small amounts of organic solvent. Which can increase the analyte concentration more than 10 times. Moreover, easy procedure and less extraction time are the advantages of this technique when comparing with conventional liquid-liquid extraction. For assessing the reliability of the proposed method, analytical characteristics such as precision and accuracy were studied within the AOAC peer-verified standard method. The results of the study demonstrated that this method was acceptable to the international standard method.

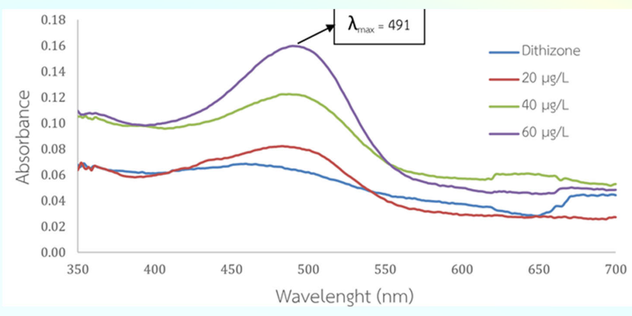
However, the proposed method used the UV-visible spectrophotometry for determination of cadmium. The sensitivity of the UV-visible spectrophotometry was lower than that of other atomic spectrometry techniques such as AAS or ICP-OES. This causes the method LOD and LOQ value higher than that of other previous research reports. For example, Yang and co-workers (2020) used DSPE extraction techniques coupled with AAS determination. They reported the LOD of 0.04 μg/L that lower than this research. However, the LOD obtained in this method (3.87 μg/L) was lower than the surface water quality standard (50 μg/L). This indicates that this proposed method can be apply for the analysis of the cadmium content in water samples from the environment.

Results

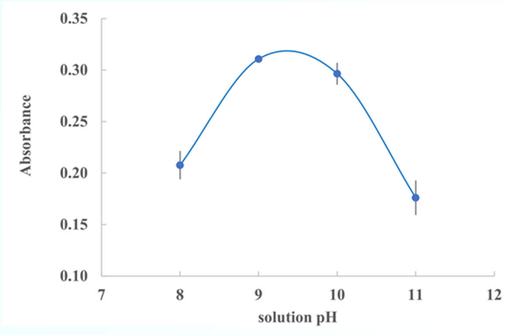
Complex Formation and Extraction Parameters

$Cd(HDz)_2$ absorption monitoring

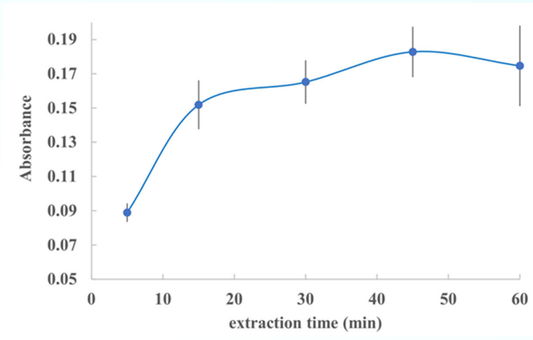
- λ_{max} of $Cd(HDz)_2$: 491 nm



pH of solution
Optimum pH : 9



Extraction time
Optimum time : 30 min



Type of elution solvent Optimum solvent: acetone

Elution solvent	λ_{max} (nm)	Absorbance (±SD)
Dichloromethane	500	0.1736 ± 0.1123
Acetone	491	0.9923 ±0.1967
Methanol	491	0.1488 ±0.0267

Method validation

characteristics	value
LOD	3.87 μg/L
LOQ	12.90 μg/L
Calibration curve	
Concentration range	20-200 μg/L
Linear equation	y = 0.0021x-0.0126
R^2	0.9939
Precision (%RSD, n=9)	
Repeatability	4.28
Intermediate precision	12.32
% Recovery	92.54 -98.89

Determination of Cadmium in environmental sample

Station	Location	Cd found (μg/L)
A	Laem Chabang Port	44.57
B	Laem Chabang Port	ND*
C	Bang Phra Subdistrict	ND*
D	Saensuk Subdistrict	6.48

References

Ali F., Mand Yadeghari, A. (2018). Extraction and preconcentration of nickel, cadmium, cobalt, and lead cations using dispersive solid phase extraction performed in narrow-bore tube. *J. Ind. Eng. Chem.*, 59, 377-387.

AOAC international. (2012). Guidelines for standard method performance requirements. United State of America.

Behbahani, M., Ghareh Hassanlou, P. M., Amini, M., Omidi, F., Esafili, A., Farzadkia, M., & Bagheri, A.(2015). Application of solvent-assisted dispersive solid phase extraction as a new, fast, simple and reliable preconcentration and trace detection of lead and cadmium ions in fruit and water samples. *Food Chem.*, 187, 82-88.

Burguera, L.,& Burguera, M. (1983). Determination of cadmium in human urine by extraction with dithizone in a flow injection system. *Anal. Chim. Acta*, 153, 207-212.

Environmental Protection Agency, Drinking water action plan, Washington, 2016. https://www.epa.gov/dwstandardsregulations

Islas, G. S., Ibarra, I., Hernandez, P. M., Miranda, J., & Cepeda, A. (2017). Dispersive solid phase extraction for the analysis of veterinary drugs applied to food sample. *Int. J. Anal. Chem.,* 2017, 16.

Mayakao, K., Santaladchaiyakit, Y., Srijaranai, S., & Vichapong, J. (2018). Preconcentration of trace neonicotinoil insecticide residues using vortex-assisted dispersive micro solid-phase extraction with montmorillinite as an efficient sorbent. *Molecules*, *23*(4), 883.

Sadeghi, M., Rostami, E., Kardestai, D., Veisi, H & Shamsipur, M. (2017). Simultaneous determination of ultra-low traces of lead and cadmium in food and environmental samples using dispersive solid-phase extraction (DSPE) combined with ultrasound-assisted emulsification microextraction based on the solidification of floatinf organic drop (UAEME-SFO) followed by GFAAS. *Royal Society of Chemistry*, 7, 27656-27667.