MINISTRY OF EDUCATION AND TRAINING

VIETNAM ACADEMY OF SCIENCE AND TECHNOLOGY

GRADUATE UNIVERSITY OF SCIENCE AND TECHNOLOGY

Nguyen Thi Xuyen

DEVELOPMENT OF ANALYTICAL PROCEDURE FOR DETERMINATION OF DIOXINS/FURANS AND INITIAL ASSESSMENT OF THE EMISSION LEVELS AND HEALTH RISKS AT SOME CRAFT VILLAGES IN BAC NINH

SUMMARY OF DISSERTATION ON SCIENCES OF MATTER

Major: Analytical Chemistry
Code: 9 44 01 18

Hanoi - 2025

The dissertation is completed at: Graduate University of Science and Technology, Vietnam Academy Science and Technology

Supervisors:
Supervisor 1: Assoc. Prof. Dr. Tu Binh Minh - VNU University of Science, Vietnam National University, Hanoi
Supervisor 2: Dr. Vu Duc Nam - Center for High technology research and Development, Vietnam Academy of Science and Technology

Referee 1: Assoc. Prof. Dr. Ta Thi Thao
Referee 2: Dr. Nguyen Hung Minh
Referee 3: Assoc. Prof. Dr. Trinh Thi Tham

The dissertation is examined by Examination Board of Graduate University of Science and Technology, Vietnam Academy of Science and Technology at 9:00 am, May 15, 2025

The dissertation can be found at:

1. Graduate University of Science and Technology Library
2. National Library of Vietnam

LIST OF THE PUBLICATIONS RELATED TO THE DISSERTATION

1. **Xuyen Nguyen Thi,** Hung Nguyen Xuan, Dinh Binh Chu, Quang Minh Bui, Tien Dat Nguyen, Tuan Anh Le Hoang, Thuy Minh Le, Binh Minh Tu, Tri Manh Tran and Duc Nam Vu (2023), *Analysis of PCDD/Fs in environmental samples by using gas chromatography in combination with high resolution mass spectrometry: optimization of sample preparation*, International Journal of Environmental Analytical Chemistry, Vol. 105, No. 2, pp.355–371; SCIE; IF-2.3.
2. Mai Thi Hong Hang, **Nguyen Thi Xuyen**, Nguyen Xuan Hung, Le Minh Thuy, Nguyen Phuc Anh, Tu Binh Minh, Vu Duc Nam (2025), *Method development for the simultaneous determination of 2378-substituted PCDD/Fs and non-2378-substituted TCDD in Ash sample*, Vietnam Journal of Chemistry, Vol. 60, pp. 276-284, Scopus.
3. **Nguyen Thi Xuyen**, Nguyen Phuc Anh, Nguyen Thi Thu Tra, Nguyen Thi Phuong, Kieu Thuy Linh, Dinh Thi Minh Chang, Tu Binh Minh, Vu Duc Nam, *Preliminary determination of PCDD/Fs in ambient air samples in several typical craft villages by gas chromatography coupled with high resolution mass spectrometry (GC-HRMS)*, Vietnam Journal of Science and Technology, accepted for publication 14/10/2024, Scopus.
4. **Nguyen Thi Xuyen**, Nguyen Xuan Hung, Mai Thi Hong Hang, Nguyen Thi Thu Tra, Nguyen Tien Dat, Bui Quang Minh, Tu Binh Minh, Vu Duc Nam (2023), *Validation of sample preparation for analysis of Dioxins/Furans: Application for flue gas and fly ash samples collected from waste-to-energy plants,* Conference proceedings: The 8th analytica Vietnam Conference, Vietnam National University Press, Hanoi, ISBN: 978-604-336-529-0.
5. **Xuyen Nguyen Thi**, Dinh Binh Chu, Hang Thi Hong Mai, Phuc Anh Nguyen, Tra Thi Thu Nguyen, Tien Dat Nguyen, Quang Minh Bui, Tuan Anh Le Hoang, Binh Minh Tu, Duc Nam Vu (2025), *Dioxins and related compounds in sediment and soil from craft villages and industrial areas in northern Vietnam*, Bulletin of Environmental Contamination and Toxicology, 114, 30. SCIE; IF-2.7.

INTRODUCTION

Dioxins/Furans (PCDD/Fs) are the most toxic group of 21 persistent organic pollutants (POPs) groups banned or restricted under the Stockholm Convention due to their harmful effects on the environment, food, and humans. In recent years, the control of small-scale, handicraft, and backward production facilities has received little attention in Vietnam due to the complexity of the production activities of these models, typically the production facilities in Vietnamese craft villages. Environmental pollution in craft villages has been mentioned in many previous research reports. However, no systematic study has been conducted on dioxin pollution caused by emissions from production activities in traditional craft villages. Therefore, the thesis focuses on the analysis of PCDD/Fs in the craft village environment, which is both novel and feasible in international publication and has high practical significance, initially showing the relationship between dioxin contamination and the community's health in the polluted area.

Currently, the cost of analyzing PCDD/Fs in environmental samples in Vietnam is relatively high compared to other POP substances due to the complicated analysis procedure, time-consuming, and high costs for chemicals, standards, pure solvents, and analytical instruments. Automatic and semi-automatic cleaning columns applied in some previous studies had the advantage of saving time and labor, but a problem is the high cost and limited initiative because these types of columns are often not available and take time to import. Therefore, the objectives of the thesis focus on:

- Optimizing the analytical process, focusing on the sample extraction procedure and developing an in-house clean-up column system for environmental sample matrices, and validating the method for analyzing PCDD/Fs compounds in flue gas, ambient air, and sediment samples using high-resolution gas chromatography coupled high-resolution mass spectrometry (HRGC-HRMS),

- Apply the method for determining PCDD/Fs in flue gas, ambient air, and sediment samples collected in some craft villages in Bac Ninh province, Vietnam.
- From the analyzed data, initially assess the emission level and estimate the health risks caused by PCDD/Fs to residents in related areas.

1. Subjects and contents of thesis

Subjects and contents of thesis: 17 toxic PCDD/Fs congeners in some environmental samples (flue gas, ambient air, sediment) collected in some craft villages in Bac Ninh.

The main contents of the thesis:

1.1. Research on optimizing the procedure of analyzing PCDD/Fs in environmental samples

1.2. Validation of the method of analyzing PCDD/Fs in flue gas, ambient air, and sediment

1.3. Application of the validated procedure to analyze PCDD/Fs in environmental samples collected in some craft villages in Bac Ninh;

1.4. Initial assessment of emission levels and estimation of dioxin exposure levels for residents living in related areas.

2. New contribution of the dissertation

2.1. This is the first study to investigate and optimize an in-house packed clean-up column system to analyze PCDD/Fs compounds in environmental sample matrices with high efficiency, reduced costs, and increased initiative compared to previous methods.

2.2. Validation of PCDD/Fs analysis method using the optimized clean-up system, thereby initially assessing the concentration of PCDD/Fs compounds in some environmental sample matrices (flue gas, ambient air, sediment) collected in some craft villages in Bac Ninh, Vietnam.

2.3. The study initially assessed PCDD/Fs emissions from flue gas and health risks due to exposure through ambient air in craft villages, which is the basis for in-depth research and proposed solutions to protect the environment and human health.

II. CONTENTS OF THESIS

CHAPTER 1. OVERVIEW

1.1. General introduction about PCDD/Fs

1.1.1. Structure, classification, names

1.1.2. Physical and chemical properties

1.1.3. Toxicity of PCDD/Fs

1.1.4. Existence and transformation in the environment

1.1.5. Main activities that generate PCDD/Fs

1.1.6. Mechanisms of PCDD/Fs formation

1.2. General overview of analysis methods of Dioxin in environmental samples

1.2.1. Sample preparation

1.2.2. Gas chromatography analysis method

1.3. Research status of PCDD/Fs in craft villages and recycling areas in the world and Vietnam

1.3.1. Research status in the world

1.3.2. Research status in Vietnam

1.4. Overview of methods for assessing the emission level and health risks due to PCDD/Fs

1.4.1. Methods for assessing the emission level of PCDD/Fs

1.4.2. Methods for assessing the health risks due to PCDD/Fs in the environment

- **The overall research results show that:**

PCDD/Fs are toxic substances released into the environment through incomplete combustion. They exist and spread widely in many different environments, potentially causing environmental pollution as well as affecting human health. The process of analyzing PCDD/Fs compounds is very complicated and time-consuming, with relatively high analysis costs.

High-resolution gas chromatography-mass spectrometry (HRGC-HRMS) is considered the standard method for analyzing PCDD/Fs compounds with high selectivity and sensitivity, capable of analyzing ultra-trace amounts of dioxins in environmental samples.

In addition to the accumulated source from war, dioxins are also generated from industrial production activities, especially in areas with small-scale production facilities and handicraft industries such as craft villages. Currently, in the world, as well as in Vietnam, there were very few studies on PCDD/Fs concentration in the environmental samples from craft villages or small-scale production areas. In Vietnam, craft villages are mainly concentrated in the Northern provinces, of which Bac Ninh is the province with a large number of traditional craft villages. The control of pollution of persistent organic compounds in general and dioxin in this area, in particular, has not been strictly implemented; the limited database has not been updated regularly.

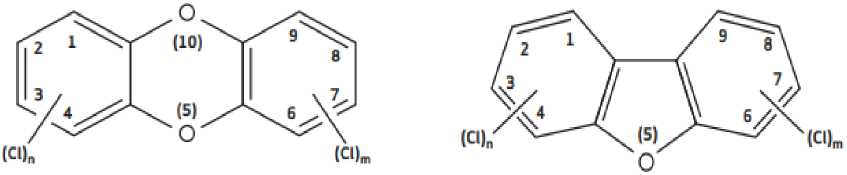
From the above practices, the main objective of the thesis is to develop and optimize the sample treatment process on the basis of standard analytical processes and apply the optimal process to analyze environmental samples in some craft villages. The thesis inherits the traditional Soxhlet extraction method and the principle of sample clean-up while improving the process by surveying the effectiveness of the accelerated solvent extraction method and building an in-house clean-up column system based on the criteria of cost savings, ensuring the efficiency of sample analysis while increasing the initiative in analysis. In addition, the thesis will also apply the optimized analytical procedure to analyze PCDD/Fs congeners in some environmental samples collected in craft villages in Bac Ninh, contributing to supplementing the database on pollution of persistent organic substances in this area, thereby providing initial assessments of emission levels and risks to human health.

CHAPTER 2: OBJECTS AND METHODS

2.1. Research object

This thesis researched the construction and optimization of the analysis procedure for 17 toxic PCDD/Fs congeners (Chlorine located at 2,3,4,8 positions in structure), including: 2,3,7,8-TCDD; 1,2,3,7,8-PeCDD; 1,2,3,4,7,8-HxCDD; 1,2,3,6,7,8-HxCDD; 1,2,3,7,8,9-HxCDD; 1,2,3,4,6,7,8-HpCDD; OCDD; 2,3,7,8-TCDF; 1,2,3,7,8-PeCDF; 2,3,4,7,8-

PeCDF; 1,2,3,4,7,8-HxCDF; 1,2,3,6,7,8-HxCDF; 2,3,4,6,7,8-HxCDF; 1,2,3,7,8,9-HxCDF; 1,2,3,4,6,7,8-HpCDF; 1,2,3,4,7,8,9-HpCDF and OCDF in environmental samples.



PCDD PCDF

Figure 2.1. General structure of PCDD/Fs compounds

2.2. Chemicals, tools, and equipment

2.3. Sample collection, preservation and information of samples

In this thesis, 15 ambient air samples and 15 sediment samples were collected at 5 craft villages in Bac Ninh province: a paper recycling village, a steel recycling village, an aluminum recycling village, and two bronze casting villages (samples at 3 different locations of one craft village). At the same time, 12 flue gas samples were collected at 4 waste incinerators (including 2 municipal waste incinerators, KT01, KT02, and 2 industrial waste incinerators, KT03 and KT04) in Bac Ninh province.

2.4. Research methods

2.4.1. Research on PCDD/Fs analysis method on HRGC-HRMS instrument

PCDD/Fs congeners were analyzed on a high-resolution gas chromatograph coupled high-resolution mass spectrometer HRGC-HRMS: model DFS from Thermo Scientific, USA. PCDD/Fs compounds were qualitatively identified based on retention time and spectral fragments of characteristic ions and quantified based on a standard curve constructed by the isotope dilution and internal standard methods. The analytical results were calculated and processed by the specialized software TargetQuan 3.0.

Table 2.1. PCDD/Fs analysis conditions on HRGC-HRMS instrument

No.	Conditions	Parameter
Sắc ký khí		
1	Column	TG-Dioxin (60 m×0,25 mm×0,25 μm)

2	Injection mode	Splitless			
3	Injection volume	2 µL			
4	Injection time	1 min			
5	Injector temperature	280ºC			
6	Carrier gas	He, purity 99.999%			
7	Carrier gas flow rate	1,3 mL/min			
8	Oven temperature program	140ºC (hold 2 min), increased to 228ºC (40ºC/min), then increased to 290ºC (1.6ºC/min) and raised 5ºC/min to 315ºC (hold 9 min). Total analysis time 56.95 min.			
Khối phổ					
9	Ion source temperature	250ºC			
10	Interface temperature	290ºC			
11	Solvent cut-off time	19 min			
12	Ionization potential	43 eV			
13	Source current	0,3 – 0,9 mA			
14	Observation mode	Selected Ion Monitoring - SIM			
15	m/z fragment				
	Compounds	*Quantitative ion*			
		m/z1	*Type*	*m/z2*	*Type*
	2,3,7,8-TCDD	319.8965	M	321.8936	M+2
	2,3,7,8-TCDF	303.9016	M	305.8987	M+2
	1,2,3,7,8-PeCDD	355.8546	M+2	355.8546	M+2
	1,2,3,7,8-PeCDF	339.8597	M+2	341.8568	M+4
	2,3,4,7,8-PeCDF	339.8597	M+2	341.8568	M+4
	1,2,3,4,7,8-HxCDD	389.8157	M+2	391.8127	M+4
	1,2,3,6,7,8-HxCDD	389.8157	M+2	391.8127	M+4
	1,2,3,7,8,9-HxCDD	389.8157	M+2	391.8127	M+4
	1,2,3,4,7,8-HxCDF	373.8207	M+2	375.8178	M+4
	1,2,3,6,7,8-HxCDF	373.8207	M+2	375.8178	M+4
	1,2,3,7,8,9-HxCDF	373.8207	M+2	375.8178	M+4
	2,3,4,6,7,8-HxCDF	373.8207	M+2	375.8178	M+4
	1,2,3,4,6,7,8-HpCDD	423.7767	M+2	425.7737	M+4
	1,2,3,4,6,7,8-HpCDF	407.7818	M+2	409.7788	M+4

	1,2,3,4,7,8,9-HpCDF	407.7818	M+2	409.7788	M+4
	OCDD	457.7377	M+2	459.7348	M+4
	OCDF	441.7428	M+2	443.7398	M+4
	$^{13}C_{12}$-2,3,7,8-TCDD	331.9368	M	333.9339	M+2
	$^{13}C_{12}$-2,3,7,8-TCDF	315.9419	M	317.9389	M+2
	$^{13}C_{12}$-1,2,3,7,8-PeCDD	367.8949	M+2	367.8949	M+2
	$^{13}C_{12}$-1,2,3,7,8-PeCDF	351.9000	M+2	353.8970	M+4
	$^{13}C_{12}$-2,3,4,7,8-PeCDF	351.9000	M+2	353.8970	M+4
	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	401.8559	M+2	403.8530	M+4
	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	401.8559	M+2	403.8530	M+4
	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	385.8610	M+2	387.8580	M+4
	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	385.8610	M+2	387.8580	M+4
	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	385.8610	M+2	387.8580	M+4
	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	385.8610	M+2	387.8580	M+4
	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	435.8169	M+2	437.8140	M+4
	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	419.8220	M+2	421.8191	M+4
	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	419.8220	M+2	421.8191	M+4
	$^{13}C_{12}$-OCDD	469.7780	M+2	471.7750	M+4
	$^{37}Cl_4$-2,3,7,8-TCDD	327.8847	M	-	-
	$^{13}C_{12}$-1,2,3,4-TCDD	331.9368	M	333.9339	M+2
	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	401.8559	M+2	403.8530	M+4

2.4.2. Research on sample preparation procedure

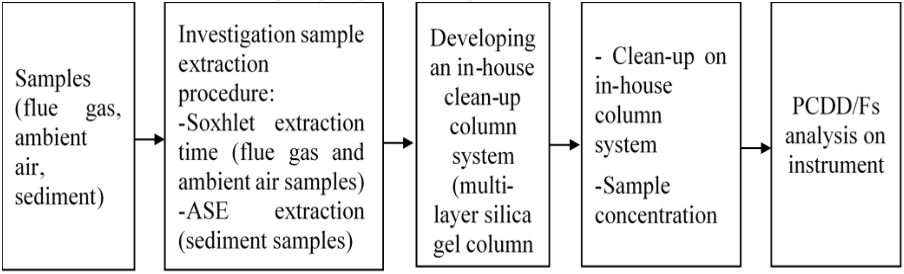


Figure 2.2. Experiments to optimize sample preparation procedure

- ❖ Investigation sample extraction procedure

- Investigation of Soxhlet extraction time for air samples

The extraction times of 10, 12, 16, 18, and 20 hours were investigated with blank samples spiked labeled standard solution by Soxhlet extraction using 300 ml of a mixture of hexane: DCM (4:1).

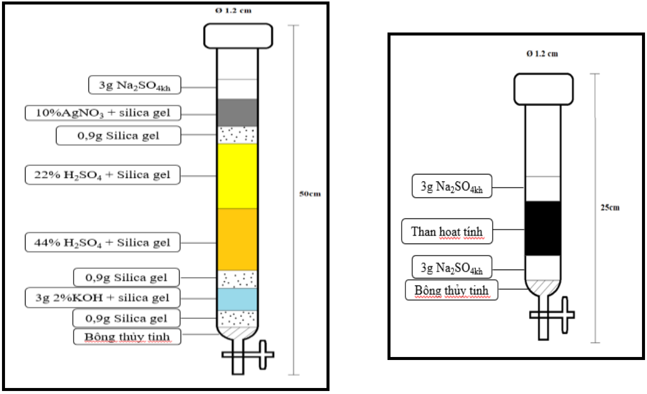
- Investigation of extraction methods for sediment samples

Table 2.2 Conditions for sediment sample extraction by Soxhlet and Accelerated solvent extraction (ASE) methods

Parameters	Soxhlet Extraction	Accelerated Solvent Extraction
Solvent	300 ml of hexane: DCM (4:1, v/v)	Toluen, 30 mL
Extraction Time	16-24h	17 mins with 1 extraction cycle (heating 5 mins, holding 10 mins)
Temperature	<111 °C	150 °C
Pressure	atmospheric pressure	1500 psi

❖ Investigation of environmental sample clean-up column system

The in-house packed clean-up column system was developed based on the clean-up system of Supelco, USA, including a multi-layer silica gel column combined with an activated carbon column with the size and composition parameters given in Figure 2.3.



Multi-layer silica gel column Activated carbon column

Figure 2.3. In-house packed clean-up column system

Experiments investigating the in-house packed clean-up system for environmental samples are shown in the diagram in Figure 2.4.

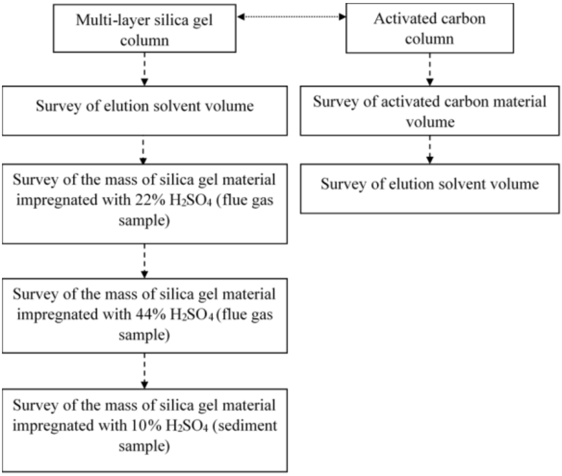


Figure 2.4 Diagram of experiments to investigate the optimization of in-house packed clean-up column system

2.4.3. Research on validation of the PCDD/Fs analytical method in environmental samples

After optimizing the sample processing procedure, the method detection limit (MDL), method quantification limit (MQL), accuracy, repeatability, and reproducibility parameters were evaluated to confirm the validity of the PCDD/Fs analysis method in sample matrices: flue gas, ambient air, and sediment according to criteria of AOAC.

2.4.4. Research on determination of PCDD/Fs in collected samples

❖ Research on determining PCDD/Fs concentration in flue gas, ambient air and sediment samples

The total toxicity equivalent (TEQ) of PCDD/Fs was calculated based on the concentrations of PCDD/Fs congeners (C) and the corresponding toxicity equivalent factor (TEF) of that congener issued by the World Health Organization (WHO) in 2005.

$$TEQ = \sum C_i \times TEF_i \qquad (2.1)$$

Concentrations of unquantifiable congeners were assigned a value of 0 when calculating TEQ.

- ❖ Estimation of PCDD/Fs emission levels from flue gas samples

The emission factors (EF) and annual emissions (EA) of PCDD/Fs in the flue gas samples from the investigated sites were calculated using the critical parameters of PCDD/Fs concentration C_{kt} (pgTEQ/Nm^3) as well as the parameters of flue gas flow rate F (Nm^3/h), capacity level C (ton/h), average operating time T (h/year):

$$\text{EF } (\mu\text{gTEQ/ton}) = \frac{C_{kt} \times F}{C \times 10^6} \tag{2.2}$$

$$\text{EA } (\text{gTEQ/year}) = \frac{EF \times C \times T}{10^6} \tag{2.3}$$

- ❖ Initial PCDD/Fs exposure risk from ambient air samples

The human health risks of PCDD/Fs are usually assessed through three main routes: inhalation, dermal contact, and food consumption. In this study, the risk of PCDD/Fs to human health was considered through the inhalation route of PCDD/Fs from ambient air samples. The daily inhalation dose for children and adults DID (pgTEQ/kg/day) = $\frac{C_{air} \times R \times T}{W}$ depends on C_{air} is the total $TEQ_{WHO2005}$ concentration in ambient air (pg TEQ/m^3), the hourly inhalation rate for adults and children (0.83 m^3/h and 0.4 m^3/h, respectively); T is duration of exposure (24 h), and W is the average weight of adults (70kg) and children (15kg).

In addition, the lifetime inhalation cancer risk (average 70 years) for residents of the study area was estimated using the chronic exposure factor (CE) and slope factor (SF) using the equation: Cancer risk (CR) = CE×SF.

2.4.5. Method to calculation and processing of data

The concentrations of the analytes were calculated and corrected according to the recoveries of labeled standards $^{13}C_{12}$ through the data processing software TargetQuan 3.0.

Data processing and statistical analysis were performed using Microsoft Excel 2019, Minitab 21.4.2.0, and SPSS 20 statistical softwares.

CHAPTER 3: RESULTS AND DISCUSSION

3.1. Research results of the analytical method evaluation on HRGC-HRMS instrument

3.1.1. Chromatograms and retention times of PCDD/Fs congeners on HRGC-HRMS instrument

The retention times of PCDD/Fs congeners increased with increasing chlorination levels in the molecular. The retention time differences of 15 analyte–labeled standard pairs at the lowest point of the calibration curve (MCS1) ranged from 0.6–3 s (<6 s), meeting the requirements of the standard method. The signal/noise ratios of all compounds were more significant than 3, ensuring the detection of PCDD/Fs congeners. The the ion abundance ratios for the signal peaks were evaluated to match the theoretical ratios, and the variation in response factors for the reference standard solutions within a run was limited to 15%.

Table 3.1 Chromatographic retention times of analytes and labeled standards $^{13}C_{12}$

No.	Compound	Retention time (Min)	S/N	Ion abundance ratios
1	$^{13}C_{12}$-1,2,3,4-TCDD	24.03	948	0.83
2	2,3,7,8-TCDF	24.35	12	0.69
3	$^{13}C_{12}$-2,3,7,8-TCDF	24.34	301	0.84
4	2,3,7,8-TCDD	25.16	7	0.66
5	$^{13}C_{12}$-2,3,7,8-TCDD	25.12	174	0.81
6	1,2,3,7,8-PeCDF	30.04	46	1.45
7	$^{13}C_{12}$-1,2,3,7,8-PeCDF	30.02	244	1.65
8	2,3,4,7,8-PeCDF	32.04	87	1.47
9	$^{13}C_{12}$-2,3,4,7,8-PeCDF	32.00	948	1.60
10	1,2,3,7,8-PeCDD	32.41	48	1.70

No.	Compound	Retention time (Min)	S/N	Ion abundance ratios
11	$^{13}C_{12}$-1,2,3,7,8-PeCDD	32.36	121	1.63
12	1,2,3,4,7,8-HxCDF	37.76	43	1.27
13	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	37.71	226	0.49
14	1,2,3,6,7,8-HxCDF	37.98	47	1.32
15	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	37.96	273	0.57
16	2,3,4,6,7,8-HxCDF	39.58	35	1.22
17	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	39.53	234	0.53
18	1,2,3,4,7,8-HxCDD	39.78	29	1.36
19	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	39.76	153	1.25
20	1,2,3,6,7,8-HxCDD	40.00	27	1.32
21	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	39.96	149	1.23
22	1,2,3,7,8,9-HxCDD	40.71	40	1.31
23	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	40.69	151	1.30
24	1,2,3,7,8,9-HxCDF	41.44	45	1.35
25	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	41.40	151	1.31
26	1,2,3,4,6,7,8-HpCDF	44.95	36	0.94
27	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	44.94	211	0.47
28	1,2,3,4,6,7,8-HpCDD	47.33	31	1.01
29	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	47.30	194	1.05
30	1,2,3,4,7,8,9-HpCDF	48.25	25	1.17
31	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	48.22	151	0.47
32	OCDD	53.47	42	0.89
33	$^{13}C_{12}$-OCDD	53.45	211	0.90
34	OCDF	53.69	19	0.91

3.1.2. Results of calibration curve equation, detection limit, quantification limit of PCDD/Fs on HRGC-HRMS instrument

The standard curves had high linearity (R2>0.999), indicating a linear relationship between the measured signal and the substance concentration in the investigated concentration range. The LOD values of PCDD/Fs congeners on the HRGC-HRMS instrument ranged from 0.035 pg/µL to

0.577 pg/µL, corresponding to LOQ values ranging from 0.107 to 1.75 pg/µL.

3.2. Results of the survey environmental sample preparation procedure

3.2.1. Results of sample extraction optimization

❖ Investigation of Soxhlet extraction time for air samples

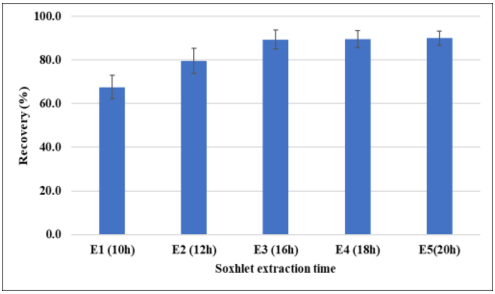


Figure 3.1 Average recoveries of labeled standards corresponding to different Soxhlet extraction times

In general, when the extraction time increased, the recovery of labeled standards tended to increase and reached the optimum when the extraction time was 16 hours, with an average recovery value of 89.4% and a standard deviation of 4.4%.

❖ Investigation of extraction methods for sediment samples

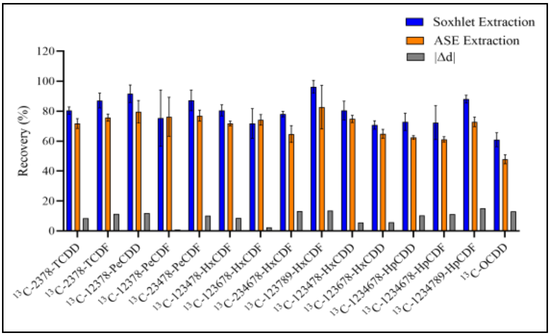


Figure 3.2 Recovery of $^{13}C_{12}$ standard in sediment samples with Soxhlet and ASE extraction methods (n=3)

The ASE extraction method has the advantage over Soxhlet extraction in that it significantly reduces the amount of solvent used and sample extraction time, while the recovery values of the PCDD/Fs isotope standards obtained are all within the reference range of the US EPA 1613 and EN 1948-2 standard methods.

From the results of the experiments to optimize the sample extraction process, the extraction method applied to air samples (ambient air, flue gas) was the Soxhlet extraction method using 300 mL of a solvent mixture of hexane: DCM (4;1) for 16 hours. The optimal extraction method with sediment samples was the ASE method using toluene solvent.

3.2.2 Investigation of environmental sample clean-up column system

❖ Results of experiments to optimize activated carbon columns

Optimum results of activated carbon mass: The mass of activated carbon material with 4 packed columns was investigated as 0.6g, 0.8g, 1.0g, and 1.2g, respectively. The recovery of labeled standards obtained in column A2 (equivalent to 0.8g of activated carbon) reached the optimal value, ranging from 62.5% to 103%

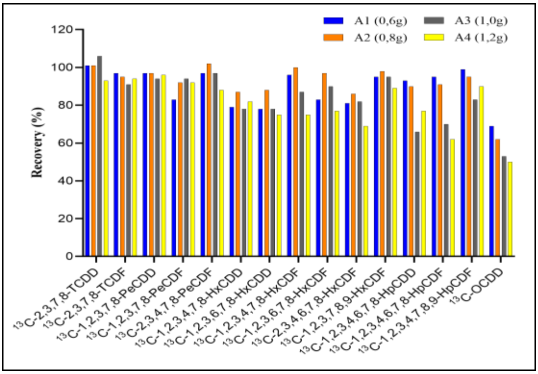


Figure 3.3 Comparison of recovery of labeled standards for activated carbon column mass survey

Optimum results of activated carbon column elution solvent volume:

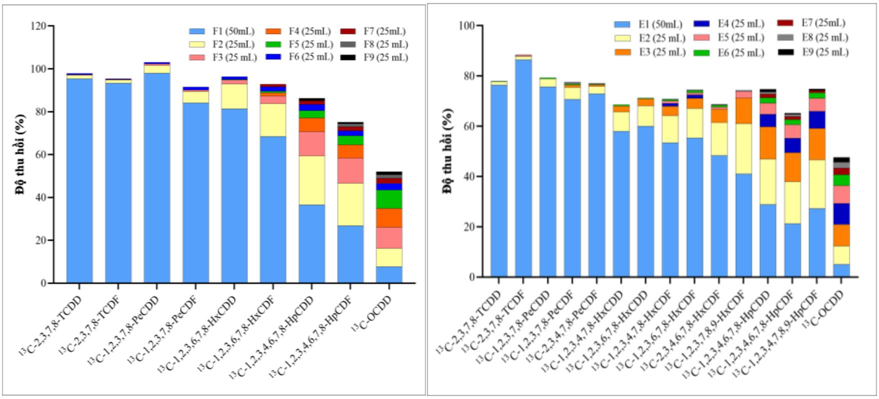


Figure 3.4 Comparison of recovery of $^{13}C_{12}$ M23 and M1613 standards from activated carbon column elution fractions

Investigation of 9 elution fractions on activated carbon column using toluene solvent. The results obtained from two standard methods, US EPA M1613 and M23, were similar due to the optimal recovery of the labeled standards when the elution solvent volume used was 150 mL.

The results of the investigation of the optimization of cleaning conditions on the activated carbon column show that the composition of the activated carbon column, including glass wool layers, 3g Na2SO4, 0.8g activated carbon, 3g Na2SO4, and 150 mL toluene was used to elute PCDD/Fs compounds from activated carbon column in the environmental sample clean-up procedure.

❖ Results of experiments to optimize multi-layer silica gel columns

<u>Results of the investigation of the elution solvent volume of the multilayer silica gel column</u>: The solvent used for the elution of PCDD/Fs compounds from the multilayer silica gel column was a mixture of hexane: dichloromethane (95:5, v/v) with an optimal volume of 50 mL because the labeled standards were eluted almost wholly, with efficiencies ranging from 81% to 111% (M23) and from 70.3% to 110% (M1613).

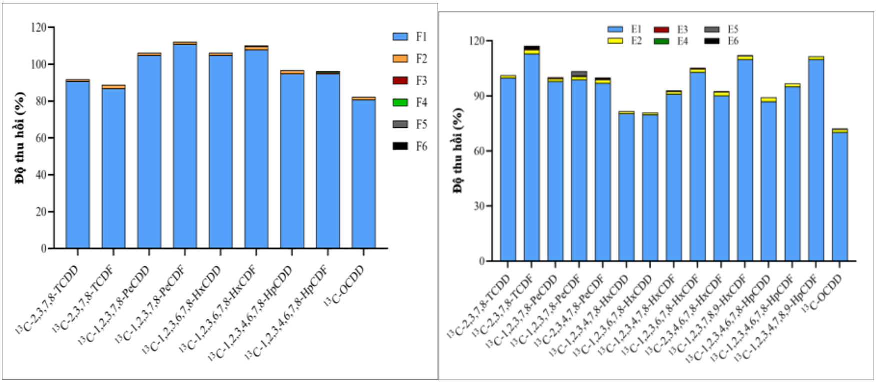
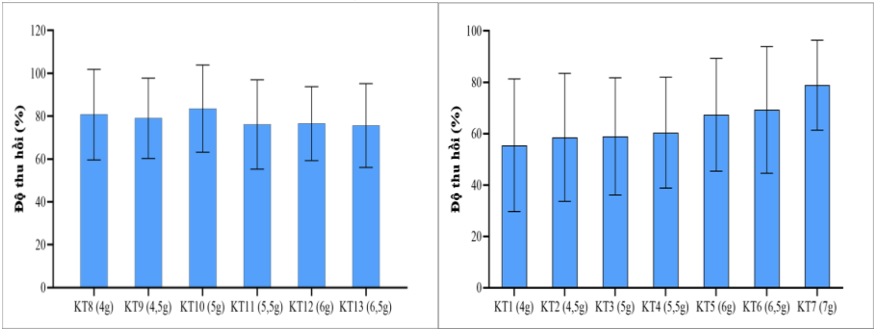


Figure 3.5 Recovery of $^{13}C_{12}$ M23 and M1613 standards through 6 elution fractions of multi-layer silica gel columns

<u>Results of investigation of the H_2SO_4+silica gel mass</u>: When the mass of 22% H_2SO_4+Silica gel was 7g, the recoveries of the labeled standards were within the allowable range of the EN 1948-2 standard method, ensuring the analysis requirements. When the mass of 44%H_2SO_4+Silica gel was 5g, the average recovery value of the labeled standards was the highest (83.5%), so this value was chosen to add to the multi-layer silica gel column for further investigations.



22% H_2SO_4+ silica gel 44% H_2SO_4+ silica gel

Figure 3.6 Average recovery values of $^{13}C_{12}$ standards added to flue gas samples in investigation of H_2SO_4+Silica gel mass

<u>Results of investigation of the 10% $AgNO_3$+silica gel mass</u>:

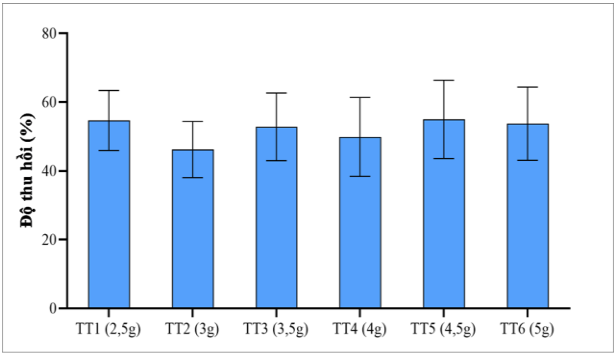


Figure 3.7 Average recovery values of $^{13}C_{12}$ standards added to sediment samples** in **investigation of 10%$AgNO_3$+Silica gel mass

For the sediment sample cleaned on the column of 2.5g of 10%$AgNO_3$+Silica gel material, the recovery of $^{13}C_{12}$ standards was optimal and ensured that these recovery values were within the reference range of the US EPA 1613 standard method.

Conclusion: The results of the survey of the mass of three material layers on the column and the elution volume of the multilayer silica gel column show that the mass of the surveyed layers includes 7g of 44%H_2SO_4+Silica gel material, 5g of 22%H_2SO_4+Silica gel material, 2.5g of 10%$AgNO_3$+Silica gel material with the selected elution solvent volume being 50mL of hexane: DCM solvent mixture (95:5).

- Results of evaluating the in-house packed column systen

Comparison of analysis results of two flue gas samples and two sediment samples using two clean-up column systems: Supelco column system and in-house column system. Comparison results by the Wilcoxon test showed that the cleaning efficiency of two clean-up column systems was equivalent. Therefore, the in-house packed clean-up column system was optimized to meet the requirements of PCDD/Fs analysis in air samples (including flue gas and ambient air) and sediment samples.

3.2.3. PCDD/Fs analysis procedure in environmental samples

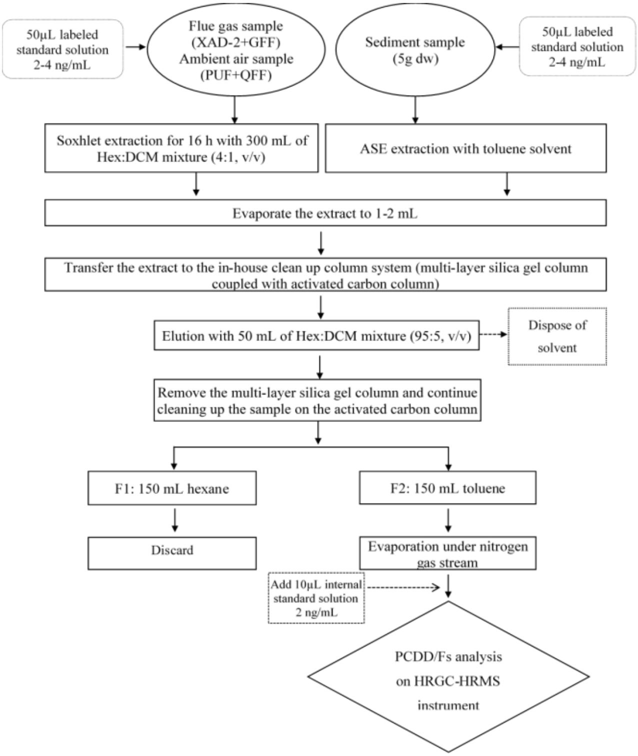


Figure 3.8 Flowchart of PCDD/Fs analysis in environmental samples

3.3. Results of validation of PCDD/Fs analytical method in environmental sample matrices

3.3.1. Results of validation of PCDD/Fs analytical method in flue gas

The results of the validation of the method for the analysis of PCDD/Fs in flue gas samples showed that the detection limit (MDL) and the quantification limit (MQL) were low, with the MDL ranging from 0.04 to 0.34 pg/Nm^3 and the recovery of the $^{13}C_{12}$ standard ranging from 73.4% to 86.5%. The method showed high precision with the relative standard deviations of 17 PCDD/Fs congeners in the replicate and reproducible experiments ranging from 2.4% to 4.9% and 3.7% to 6.2%, respectively. Therefore, this method fully met the requirements of the standard methods and was suitable for the analysis of PCDD/Fs in flue gas samples with guaranteed accuracy.

3.3.2. Results of validation of PCDD/Fs analytical method in ambient air

The results of the validation of the PCDD/Fs analysis method in ambient air samples with the method detection limit at 0.2-1.7 fg/m^3, method quantification limit from 0.5 to 5.8 fg/m^3 for 17 PCDD/Fs congeners, high recovery from 62.7%-83.6% and good precision (RSD of repeatability from 2.5% to 8.3% and RSD of repeatability from 4.5% to 11.2%) showed that the method met the requirements and could be applied to the analysis of ambient air samples with high reliability.

3.3.3. Results of validation of PCDD/Fs analytical method in sediment

The parameters confirming the validation of the PCDD/Fs analysis method in sediment samples showed that the MDL for 17 congeners was low, ranging from 0.01-0.08 pg/g, the recovery was in the range of 62.5-91.1% and good precision (RSD of repeatability and reproducibility were in the range of 1.1% to 3.7% and from 3.8% to 10.1%, respectively). The PCDD/Fs evaluation results in certified reference material were within the manufacturer's published range, and the international proficiency test sample had z-score results from -1 to 1. The results demonstrated that the PCDD/Fs analysis procedure in sediment samples in this thesis was highly accurate and can be applied to sediment sample analysis.

3.4. Results of PCDD/Fs concentration in environmental samples

3.4.1. PCDD/Fs concentration in flue gas samples

The results showed that 17 PCDD/Fs congeners were detected and quantified in the flue gas samples at levels more significant than the quantification limit of the method.

The TEQ content in the exhaust gas samples at the 4 incinerators KT01, KT02, KT03, and KT04 ranged from (176±19.0) pgTEQ/Nm^3 to (2488±174) pgTEQ/Nm^3. Samples KT01, KT02, KT04 had similar TEQ profiles, the average percentage (± SD) of PCDD/Fs for TEQ decreased in the following order: 1,2,3,7,8-PeCDD (29 ± 4.5%) > 2,3,4,7,8-PeCDF (22 ± 1.6%) > 1,2,3,4,7,8-HxCDF (8.0 ± 1.9%) ≈ 1,2,3,6,7,8-HxCDF (8.2 ± 1.3%)≈2,3,4,6,7,8-HxCDF (8.0 ± 2.1%) > 2,3,7,8-TCDF (3.7 ± 0.5%) ≈ 2,3,7,8-TCDD (5.3 ± 0.5%) 2.1%). For sample KT03, the TEQ profile was mainly contributed by the 1,2,3,7,8,9-HxCDF congener (32%), followed by 2,3,7,8-TCDF and 2,3,4,6,7,8-HxCDF with a proportion of 11%.

3.4.2. PCDD/Fs concentration in ambient air samples

Most of the 17 PCDD/Fs congeners were detected in all samples, except for 2,3,7,8-TCDD congener, which was not detected in sample KXQ03 in the aluminum recycling village. The total PCDD/Fs concentration in the 15 ambient air samples ranged from 989 pg/m3 to 17634 fg/m^3 (average 7224 fg/m^3). The TEQ-PCDD/Fs concentration in the 15 ambient air samples ranged from 40.2 fgTEQ/m^3 to 453 fgTEQ/m^3 (average 258 fgTEQ/m^3) and decreased in the craft villages in the following order: Bronze casting village 1 > Bronze casting village 2 > Steel recycling village > Paper recycling village > Aluminum recycling village.

OCDD is the congener that contributes the most significant proportion to the total PCDD/Fs content in most ambient air samples collected in craft villages, ranging from 13.8% to 78.6%. Except for bronze casting village 1, OCDF is the congener that contributes the most to the total PCDD/Fs concentration. 1,2,3,4,6,7,8-HpCDF congener accounted for the second largest proportion of the total PCDD/Fs content in the two bronze casting villages, with average values of 12.5% and 17.1%, respectively.

3.4.1. PCDD/Fs concentration in sediment samples

The total PCDD/Fs concentrations ranged from 8.34 to 698 pg/g in 15 sediment samples. The average TEQ-PCDD/Fs concentrations in the five craft villages ranged from 0.821 pgTEQ/g to 66.8 pgTEQ/g. Among the five craft villages, the sediment samples collected in the paper recycling craft village had the highest PCDD/Fs and TEQ concentrations. The total PCDD/Fs concentration profile in the sediment samples showed that OCDD congeners accounted for the highest proportion (19% to 52%), the most toxic isomer, 2378-TCDD, only contributed a small proportion to the total PCDD/Fs concentration in the sediment samples, averaging about 0.4%.

PCDFs were the main contributors to the TEQ values in the sediment samples in the steel recycling craft village (93%) and the bronze casting craft village 1 (65%). Meanwhile, PCDDs contributed the most to the TEQ value of sediment samples in the aluminum recycling village. For sediment samples taken from the paper recycling village and bronze casting village 2, the contribution of PCDDs and PCDFs to the total TEQ was similar, in which the two congeners with the highest proportion were 1,2,3,7,8-PeCDD (35-41%) and 2,3,4,7,8-PeCDF (19-24%).

3.5. Results of the initial assessment of emission levels and risks to human health due to PCDD/Fs

3.5.1. Results of the initial assessment of PCDD/Fs emission levels from flue gas samples

Table 3.3 Estimation of EF and EA of PCDD/Fs in flue gas samples

Incinerator Type	Sample Code	EF (µgTEQ/ton)	EA (gTEQ/year)
Industrial waste incinerator	Incinerator No. 1, KT01 (n=3)	34.3 ± 5.3	0.074 ± 0.011
	Incinerator No. 1, KT02 (n=3)	1.37 ± 0.15	0.010 ± 0.001
Municipal waste incinerator	Incinerator No. 1, KT03 (n=3)	33.2 ± 2.4	0.199 ± 0.014
	Incinerator No. 1, KT04 (n=3)	8.35 ± 1.75	0.040 ± 0.008

The average EF values ranged from 1.37 to 34.3 µg TEQ/ton, with significant variation between incinerators of the same type. The highest EF value was estimated for an industrial waste incinerator KT01 (average 34.3 µg TEQ/ton), followed by a domestic waste incinerator KT03 (average 33.2 µg TEQ/ton). While the KT01 incinerator had the highest emission factor, the KT03 incinerator had the largest annual emissions (average 0.199 gTEQ/year).

3.5.2. Results of the initial health risk assessment of PCDD/Fs from ambient air samples

Daily inhalation doses (DID) for adults in the five craft villages ranged from 0.004±0.001 to 0.042±0.002 pgTEQ/kg/day. DID values ranged from 0.010±0.002 đến 0.094±0.004 pgTEQ/kg/day for children. All values were lower than the WHO tolerable daily intake (TDI) by inhalation of 0.1-0.4 pgTEQ/kg/day. The estimated cancer risk values in the five craft villages ranged from 3.04×10^{-6} to 3.08×10^{-5}. The cancer risk values due to PCDD/Fs in ambient air samples in the scope of this thesis were all within the acceptable range of 10^{-6} to 10^{-4}, according to the US EPA.

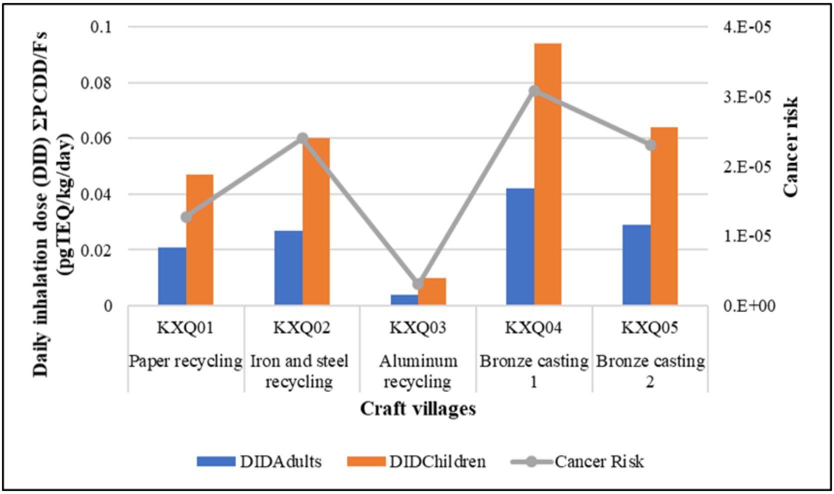


Figure 3.9 Health risk assessment parameters: daily (DID), lifetime (cancer risk) from PCDD/Fs in ambient air samples

CONCLUSIONS

1. Development and optimization of an in-house packed clean-up column system in the laboratory, including a multilayer silica gel column coupled with an activated carbon column applicable to environmental sample matrices.

2. The parameters confirming the validity of the PCDD/Fs analysis method in flue gas, ambient air, and sediment samples, including the method detection limit, quantification limit, recovery, repeatability, and reproducibility met the analysis requirements of standard methods and criteria of AOAC. In addition, the analysis results of the certified reference material (CRM) sample are within the reference range of the manufacturer, and the proficiency test sediment samples have z-score values ranging from -1 to 1, demonstrating the accuracy of the PCDD/Fs analysis method in sediment samples in particular and environmental samples in general.

3. Applying the validated analytical procedure to analyze 17 toxic PCDD/Fs congeners in flue gas, ambient air, and sediment samples collected in Bac Ninh. TEQ levels in flue gas samples at 4 waste incinerators ranged from (176±19.0) pgTEQ/Nm3 to (2488±174) pgTEQ/Nm^3. TEQ-PCDD/Fs levels in ambient air samples at 5 craft villages ranged from 40.2 fgTEQ/m3 to 453 fgTEQ/m3, with the highest values obtained in two copper recycling/casting craft villages. However, among sediment samples in the same study area as the ambient air samples, the paper recycling craft village had a higher TEQ-PCDD/Fs level than other areas (66.8 pgTEQ/g).

4. Initial estimation of emission levels from flue gas samples and assessment of PCDD/Fs risks to human health from ambient air samples. Emission factor values ranged from 1.37 to 34.3 µg TEQ/ton, and annual emission values of 4 incinerators ranged from 0.010 to 0.199 gTEQ/year.

PCDD/Fs exposure risks from ambient air samples were estimated through inhalation. The results showed that the estimated daily exposure (DID) in children was approximately 2.5 times higher than that in adults. The DID values and estimated carcinogenic risks were below the maximum acceptable threshold, indicating that the health risk level of PCDD/Fs compounds in ambient air in craft villages in Bac Ninh is not a concern for residents living in these areas.

RECOMMENDATION

The study has investigated and optimized an in-house packed clean-up column system to analyze PCDD/Fs in environmental samples on a laboratory scale. It is necessary to expand the research direction to other POP compounds besides PCDD/Fs, such as coplanar PCBs or Dioxin-like compounds, to improve the simultaneous analysis process of these compounds.

The number of research samples in the thesis is still limited; therefore, to have more general and comprehensive assessments, it is necessary to expand the scope of research to other craft villages in the province and other samples, such as soil samples and food samples in these areas.

Regular monitoring and installation of emission and wastewater treatment systems that meet standards in craft villages, as well as promulgating regulations on the allowable emission concentration of PCDD/Fs, are necessary to minimize the risk of these substances affecting the environment and human health.