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STUDY ON THE ANALYSIS METHOD OF BROMINATED AND ORGANOPHOSPHORUS FLAME RETARDANTS IN INDOOR AIR AND DUST

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SUMMARY OF CHEMICAL DOCTORAL THESIS

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INTRODUCTION

1. The necessary of the thesis

Flame retardants (FRs) are a group of chemicals widely used as additives in various materials to reduce flammability as well as meet fire safety standards and regulations. Brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) have been used extensively over the past decades. However, these compounds are persistent, potentially bioaccumulative, and highly toxic, so the widespread use of PBDEs has resulted in a rapid increase of these pollutants in the environment and adverse effects on human health as well as the ecosystem. As a result, the manufacturing and use of PBDEs have been restricted or banned in many countries. This has led to increased production and usage of alternative flame retardants such as organophosphorus flame retardants (OPFRs) which have increased rapidly in recent years. The increasing use of OPFRs in consumer products and building materials has resulted in their widespread release in the environment, resulting in the exposure of animals and humans to these chemicals. Many studies have demonstrated that OPFRs also cause negative effects on aquatic organisms, animals as well as humans. In particular, chlorinated organophosphorus flame retardants may pose comparable health risks as brominated flame retardants.

Most of the brominated and organophosphorus flame retardants are semi-volatile organic compounds. They are mainly used as additive chemicals and are not chemically bonded to the material, so they easily get out of products and release into the environment through volatilization and abrasion from FRs-containing products and materials during use and disposal. According to a report by the US Environmental Protection Agency, in today's modern life, the majority of human

activities take place indoors (80-90% of the time). Therefore, the quality of the indoor environment is an important factor, that has a great influence on human health as well as the quality of life.

In Vietnam, the research on air quality, especially concerning emerging compounds such as brominated and organophosphorus flame retardants remains limited. Accurately determining the concentrations of these compounds in the environment, particularly in the air, requires intricate sampling techniques and sample handling, as well as quantitative analysis equipment with high sensitivity. Hence, it is necessary to study analytical procedures for monitoring and evaluating the pollution levels of PBDEs and OPFRs in indoor air and dust, thereby assessing exposure levels as well as human health risks associated with these compounds in the indoor environment.

Therefore, the selection of the thesis project "*Study on the analysis method of brominated and organophosphorus flame retardants in indoor air and dust*" is necessary and deeply practical.

2. The objects of the thesis

- Study and develop the simultaneous analysis method of brominated and organophosphorus flame retardants using gas chromatography coupled with mass spectrometry (GC-MS).
- Evaluation of the distribution and estimation of the risk of exposure to brominated and organophosphorus flame retardants in indoor air and dust to human health through air inhalation, dust ingestion, and dermal absorption for both children and adults.

3. The main contents of the thesis

1 – Investigation of the optimal conditions of simultaneous extraction and analysis method for brominated and organophosphorus

flame retardants in indoor air and dust using gas chromatography coupled with mass spectrometry (GC-MS).

2 - Validation of analytical procedures for brominated and organophosphorus flame retardants in indoor air and dust samples.

3 - Determination of the concentrations of brominated and organophosphorus flame retardants in air and samples dust collected from houses in the urban districts of Hanoi city using gas chromatography coupled with mass spectrometry (GC-MS).

4 - Estimate the exposure and assess health risks for both adults and children from exposure to brominated and organophosphorus flame retardants in the indoor environment through air inhalation, dust ingestion, and dermal absorption.

CHAPTER 1. OVERVIEW

1.1. Overview of brominated and organophosphorus flame retardants

1.2. Emission sources and distribution of brominated and organophosphorus flame retardants in the environment

1.3. Toxicity of brominated and organophosphorus flame retardants

1.4. Human exposure to brominated and organophosphorus flame retardants

1.5. Analytical method for brominated and organophosphorus flame retardants in air and dust

1.5.1. Sample collection and preservation methods

1.5.2. Sample preparation method for the analysis of brominated and organophosphorus flame retardants

1.5.3. Analytical method for brominated and organophosphorus flame retardants

1.6. Overview of the study in Vietnam and worldwide

CHAPTER 2. SUBJECTS AND RESEARCH METHODS

2.1. Research subjects

Legacy brominated flame retardants belong to the group of polybrominated diphenyl ethers (PBDEs) and organophosphorus flame retardants belong to the group of phosphate esters in indoor air and settled dust.

2.2. Chemicals, tools, and equipment

2.3. Sample collection and preservation

Indoor air and dust samples were collected from apartments and individual houses in the urban districts of Hanoi city.

2.4. Research method

2.4.1. Investigation of quantitative conditions for PBDEs on GC-MS

Investigation of measurement conditions for PBDEs on GC-MS. Evaluate the stability of the PBDEs analysis signal on GC-MS. Determine the limit of detection (LOD) and limit of quantification (LOQ) of PBDEs on GC-MS. Investigation of the construction of calibration curves.

2.4.2. Investigation of quantitative conditions for OPFRs on GC-MS

Investigation of measurement conditions for OPFRs on GC-MS. Evaluate the stability of the OPFRs analysis signal on GC-MS. Determine the limit of detection (LOD) and limit of quantification (LOQ) of OPFRs on GC-MS. Investigation of the construction of calibration curves.

2.4.3. Investigation of the simultaneous extraction method for PBDEs and OPFRs in indoor air samples

- *Conduct a survey to select operating parameters and extraction solvents for the extraction of PBDEs and OPFRs from indoor air samples using accelerated solvent extraction (ASE)*

Table 2.4. ASE system operating parameters for extraction of PBDEs and OPFRs in indoor air samples

Parameters of the ASE system	Values
Cell pressure (psi)	1500
Cell temperature (^{0}C)	100
Preheat time (mins)	1
Heat time (mins)	5
Cycles	2
Static time (mins)	10
Flush volume (%)	60

❖ *Investigation of the separation and purification conditions of the extract through the solid phase extraction column*

Investigation of the selection of a solid phase extraction column and eluent solvent to separate and clean the extract.

2.4.4. Determination of methods for the simultaneous extraction of PBDEs and OPFRs in indoor dust samples

- Investigation of the selection of extraction solvent and parameters for the extraction process of PBDEs and OPFRs in indoor dust samples using the ultrasonic extraction method.

Table 2.6. Parameters of the extraction process of PBDEs and OPFRs in dust samples by ultrasonic extraction method

Parameters	Values
The volume of extraction solvent (mL)	10
The temperature of an ultrasonic chamber (^{o}C)	25 - 28
Ultrasound time (minutes)	10
Centrifugation time (minutes)	2
Centrifugal speed (rpm)	3000
The number of repetitions (times)	3

- After simultaneous extraction of PBDEs and OPFRs in indoor dust samples, indoor dust sample extracts were fractionated and cleaned similarly to the indoor air sample extracts investigated in section 2.4.3.

2.4.5. Validation of the analytical method for PBDEs and OPFRs in indoor air samples

After optimizing the extraction conditions for PBDEs and OPFRs in air samples and the analysis conditions on the GC-MS, the analysis procedure for PBDEs and OPFRs in indoor air samples was developed. The method was validated to assess the quality and reliability of the analysis results through the following parameters: calibration curves, limit of detection and limit of quantification of the method, accuracy, repeatability, and reproducibility of the method, and measurement uncertainty.

2.4.6. Validation of the analytical method for PBDEs and OPFRs in indoor dust samples

Validation of procedures for analysis of PBDEs and OPFRs in indoor dust samples through parameters: calibration curve, limit of detection and limit of quantitation of the method, precision, repeatability, and reproducibility of the method, and measurement uncertainty.

2.4.7. Determination of PBDEs and OPFRs in indoor air and dust samples

Processing and analyzing the levels of PBDEs and OPFRs in indoor air and dust samples collected from 10 urban districts of Hanoi according to the established and evaluated procedures.

2.4.8. Exposure risk assessment of PBDEs and OPFRs in indoor air and dust

2.4.8.1. Estimation of daily intake of PBDEs and OPFRs through exposure pathways

Based on guidance from the United States Environmental Protection Agency (US EPA, 2011), the estimated daily intakes (EDI, ng/kg/day)

of PBDEs and OPFRs through three exposure pathways (including air inhalation - EDI_{inha}, dust ingestion - EDI_{inges}, and dermal absorption - EDI_{dermal}) were calculated according to the following equations:

$$EDI_{inha} = \frac{C_{air} \times IR_{air} \times AF_{inha} \times FT}{BW} \quad (2.19)$$

$$EDI_{inges} = \frac{C_{dust} \times IR_{dust} \times AF_{inges} \times FT}{BW} \quad (2.20)$$

$$EDI_{dermal\ (from\ air)} = \frac{C_{air} \times K_{p-g/p} \times SA \times f_{SA} \times FT}{BW} \quad (2.21)$$

$$EDI_{dermal\ (from\ dust)} = \frac{C_{dust} \times DAS \times SAD \times AF_{dermal} \times FT}{BW} \quad (2.22)$$

$$EDI_{dermal} = EDI_{dermal\ (from\ air)} + EDI_{dermal\ (from\ dust)} \quad (2.23)$$

$$EDI_{total} = EDI_{inha} + EDI_{inges} + EDI_{dermal} \quad (2.24)$$

2.4.8.2. Non-carcinogenic risk assessment

The hazard quotient (HQ) is used to describe the non-carcinogenic risks of individual PBDEs and OPFRs through air inhalation, dust ingestion, and dermal absorption. The hazard index (HI) was calculated to represent the total non-carcinogenic risk posed by PBDEs and OPFRs.

$$HQ = \frac{EDI_{tông}}{RfD} \quad (2.25)$$

$$HI = \Sigma HQ_i \quad (2.26)$$

If the HI value is ≥ 1, exposure to PBDEs and OPFRs in indoor air and dust is likely to have adverse health effects. Conversely, if the HI value is < 1, the potential adverse effects on human health from exposure to PBDEs and OPFRs in indoor air and dust are considered negligible.

2.4.8.3. Carcinogenic risk assessment

The carcinogenic risk was assessed based on the lifetime cancer risk (LCR) estimated according to the equation:

$$LCR = CDI_{inha} \times CPF + CDI_{inges} \times CPF + CDI_{dermal} \times CPF \quad (2.27)$$

$$CDI_i = (EDI_i \text{ x } EF \text{ x } ED) / AT \quad (2.28)$$

According to EPA guidelines, the potential carcinogenic risk to humans occurs when the LCR value is $\geq 10^{-6}$. Conversely, the carcinogenic risk is negligible if the LTCR value is $< 10^{-6}$.

2.4.9. Statistical analysis

Statistical analysis were performed using Microsoft Excel 2016 and IBM SPSS 22.0 statistical software. PBDEs and OPFRs concentrations that were below the limit of detection (< LOD) were considered zero.

CHAPTER 3. RESULTS AND DISCUSSION

3.1. The investigated results of the analysis conditions for PBDEs on GC-MS

3.1.1. Conditions for analyzing PBDEs on GC-MS

The investigated results of the optimal conditions for the quantification of PBDEs on GC-MS are presented in Tab 3.1 and Tab 3.2.

Table 3.1. Analytical conditions for PBDEs on GC-MS instrument

Parameters	Condition/setting values
Capillary GC column	DB-5ht (15 m × 0.25 mm × 0.10 µm)
Injection mode	Splitless mode,
Injection volume	2.0 µL
Injection port temperature	260°C
Carrier gas	Heli, flow rate 1.2 mL/min
Reagent gas	Metan (CH_4)
Oven temperature program	135°C (hold 1 min) → 215°C [10°C/min] → 275°C [5°C/min] → 295°C [20°C/phút, hold 0.5 min] → 310°C [20°C/min, hold 4 min]
Ion source temperature	250°C
Interface temperature	310°C
Ionization mode	Electron capture negative ionization (ECNI)
Monitoring mode	Selective ion monitoring – SIM

Table 3.2. Ions (m/z) were used for the qualitative and quantitative analysis of PBDEs and labeled compounds on GC-MS

Homolog	Compound	m/z
Tri-BDEs	BDE-28	**79**/81/159/161
Tetra-BDEs	BDE-47	**79**/81/159/161
Penta-BDEs	BDE-99, BDE-100	**79**/81/159/161
Hexa-BDEs	BDE-153, BDE-154	**79**/81/159/161
Hepta-BDEs	BDE-183	**79**/81/159/161
Octa-BDEs	BDE-196, BDE-197, BDE-203	79/81/407/**409**
Nona-BDEs	BDE-206, BDE-207	79/81/407/**409**
Deca-BDEs	BDE-209	79/81/**487**/489
Surrogate standard	FBDE-99, FBDE-183	**79**/81
	FBDE-208	79/81/**427**/429
	$^{13}C_{12}$-BDE-209	79/81/**497**/499
Internal standard	FBDE-154	**79**/81

* The bolded m/z values represent the quantitation ions

3.1.2. The stability of the analytical signal of PBDEs on GC-MS

The investigated result showed that the GC-MS instrument used for PBDEs analysis gives good signal analysis and high stability.

3.1.3. The limit of detection and the limit of quantification of the instrument for the analysis of PBDEs on GC-MS

LOD and LOQ of the GC-MS instrument for the analyzed PBDEs were in the ranges of 0.08-0.51 ng/mL (BDE-209 was 3.6 ng/mL) and 0.25-1.7 ng/mL (BDE-209 was 12 ng/mL), respectively. These values meet the requirements for quantification of PBDEs in environmental samples.

3.1.4. Calibration curve of PBDEs on GC-MS

Calibration curves of PBDEs were built by the internal standard method, with good linearity and correlation coefficients $R^2 > 0,999$.

3.2. The investigated results of the analysis conditions for OPFRs on GC-MS

3.2.1. Conditions for analyzing OPFRs on GC-MS

The investigated results of the optimal conditions for the

quantification of OPFRs on GC-MS are presented in Tab 3.6 and Tab 3.7.

Table 3.6. Analytical conditions for OPFRs on GC-MS instrument

Parameters	Condition/setting values
Capillary GC column	DB-5ms (30 m × 0.25 mm × 0.25 μm)
Injection	Splitless mode, Injection volume 1.0 μL
Injection port temperature	250^{o}C
Carrier gas	Heli, flow rate 1.0 mL/min
Oven temperature program	40^{o}C (hold 2 min), increased to 310^{o}C (8^{o}C/min, hold 4 min)
Ion source temperature	250^{o}C
Interface temperature	310^{o}C
Ionization mode	Electron ionization (EI)
Monitoring mode	Selective ion monitoring – SIM

Table 3.7. The selected ions (m/z) of OPFRs and labeled compounds

Compounds	Ion (m/z) for qualitative analysis	Ion (m/z) for quantitative analysis
TnBP	**99** / 155 / 211	**99**
TCEP	**249** / 251 / 205	**249**
TCIPP(1)	**125** / 99 / 201	**125**
TCIPP(2)	**99** / 157 / 201	**99**
TCIPP(3)	**99** / 157 / 175	**99**
DBPP	**175** / 94 / 174	**175**
TDCIPP	**99** / 191 / 209	**99**
TPhP	**326** / 325 / 215	**326**
TBOEP	**85** / 101 / 125	**85**
EHDPP	**251** / 94 / 170	**251**
TEHP	**99** / 113 / 71	**99**
TOCP	**165** / 179 / 368	**165**
TMCP	**368** / 165 / 243	**368**
TPCP	**368** / 165 / 261	**368**
Chất chuẩn đồng hành		
TnBP-d27	**103** / 167 / 231	**103**
TCEP-d12	**261** / 131 / 196	**261**
TPhP-d15	**341** / 243 / 180	**341**
IS (Phenanthrene-d10)	**188 / 184 / 160**	**188**

3.2.2. The stability of the analytical signal of OPFRs on GC-MS

The investigated result showed that the GC-MS instrument used

for OPFRs analysis gives good signal analysis and high stability.

3.2.3. The limit of detection and the limit of quantification of the instrument for the analysis of OPFRs on GC-MS

LOD and LOQ of the GC-MS instrument for the analyzed OPFRs were in the ranges of 0.8-3.3 ng/mL and 2.6-11 ng/mL, respectively. These values meet the requirements for quantification of PBDEs in environmental samples.

3.2.4. Calibration curve of OPFRs on GC-MS

Calibration curves of OPFRs were built by the internal standard method, with good linearity and correlation coefficients $R^2 > 0,999$.

3.3. The investigated results of the extraction method for PBDEs and OPFRs in air samples

3.3.1. The investigated results of solvents used to extract PBDEs and OPFRs in indoor air samples

Four extraction solvent systems including Hex:DCM (1:1, v/v), DCM, Hex:Ace (1:1, v/v) and Hex:Ace (1:3, v/v) were selected to investigate the extraction efficiencies of PBDEs and OPFRs in air samples by accelerated solvent extraction method. The investigated results are shown in Figure 3.5.

The results showed that extraction efficiencies of two solvent mixtures Hex:Ace (1:1, v/v) and Hex:Ace (1:3, v/v) are better than those of solvent mixture Hex:DCM (1:1, v/v) and solvent DCM with high average recoveries of analytes, ranging from 84.3% to 97.1 % for PBDEs and from 83.6% to 97.8% for OPFRs. However, the solvent mixture of Hex:Ace (1:3, v/v) has a higher polarity than the mixture of Hex:Ace (1:1, v/v), which means that many interfering compounds in the sample matrix will also be extracted more easily, making the clean-

up process after extraction more complicated. Therefore, the Hex:Ace (1:1, v/v) mixture has been selected for the extraction of PBDEs and OPFRs in air samples using accelerated solvent extraction (ASE).

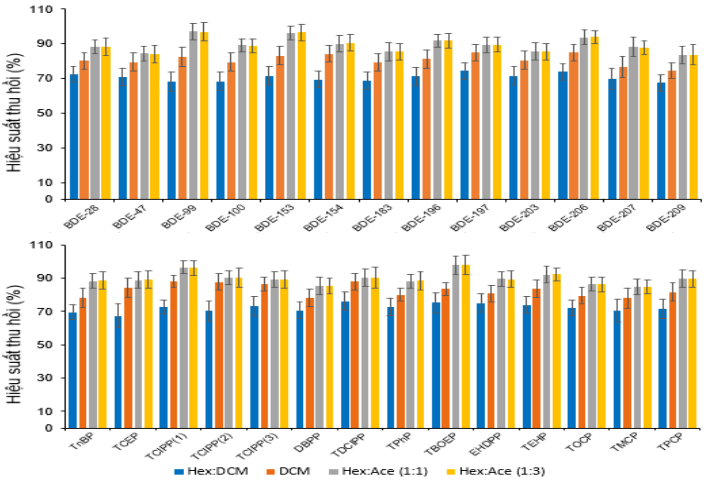

Figure 3.5. Extraction efficiencies of PBDEs and OPFRs in indoor air samples when using different solvent systems

3.3.2. The investigated results of separation and purification conditions of the extract on solid phase extraction column

This study used a Florisil solid-phase extraction column and an acidified silica gel column for the separation and purification of the extract prior to analysis on GC-MS. The Florisil column was selected to clean up and separate PBDEs (Fraction 1) and OPFRs (Fraction 2). Then, an acidified silicagel column was used to further clean up Fraction 1 in the next purification step to avoid the degradation of less chemically stable OPFR compounds while still removing interfering compounds before analyzing PBDEs on GC-MS.

The results showed that using 8 mL Hex followed by 10 mL EtAc was enough to completely elute PBDEs (Fraction 1) and OPFRs

(Fraction 2) from the Florisil column. For the next cleaning step on the 44% acidified silica gel column, complete elution of the PBDEs from the column required 10 mL Hex:DCM (1:1, v/v).

3.3.3. Procedure for the analysis of PBDEs and OPFRs in indoor air

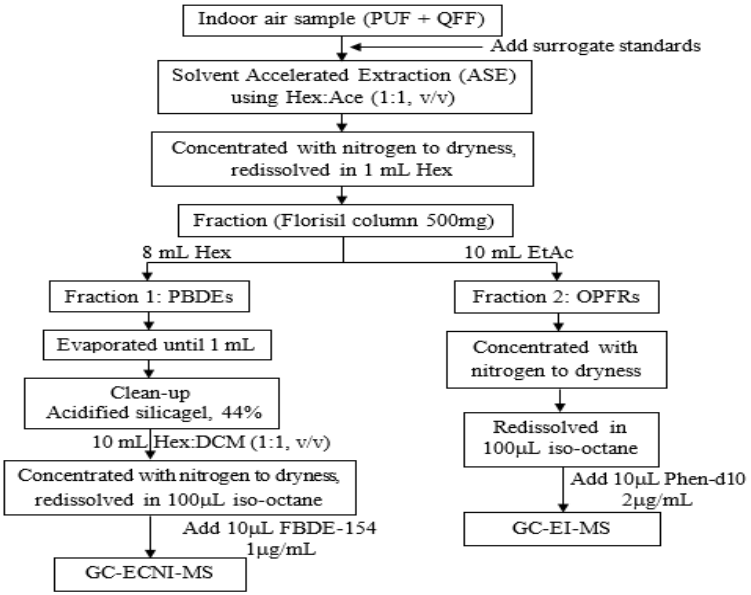

Figure 3.6. Procedure for the analysis of PBDEs and OPFRs in air samples

3.4. The investigated results of the extraction method for PBDEs and OPFRs in dust samples

3.4.1. The investigated results of solvents used to extract PBDEs and OPFRs in indoor dust samples

The investigated results of the extraction efficiencies of PBDEs and OPFRs in indoor dust samples using different solvent systems are presented in Figure 3.7. The results showed that solvent mixtures Hex:Ace (1:1, v/v) and Hex:Ace (1:3, v/v) have significantly better extraction efficiencies than Hex:DCM (1:1, v/v) mixture and DCM

solvent. This can be explained because the analyte compounds have strong interactions with the sample matrix, so the use of more polar solvents will increase the extraction efficiency better.

Two solvent systems Hex: Ace (1:1, v/v) and Hex: Ace (1:3, v/v) both gave good extraction efficiencies with average recoveries ranged 83.2% - 97.4% for PBDEs and 84.6% - 96.5% for OPFRs. Additionally, Hex: Ace mixtures used as extraction solvents have the advantage of good phase separation between dust and the extract after centrifugation, making sample processing easier and reducing the loss of compounds compared to using DCM solvent. However, using the Hex: Ace (1:3, v/v) mixture as extraction solvent will result in many impurities from the sample matrix, making the later clean-up process more difficult. Therefore, the Hex: Ace (1:1, v/v) mixture was selected as the preferred solvent for the simultaneous extraction of PBDEs and OPFRs in the dust sample using the ultrasonic extraction method.

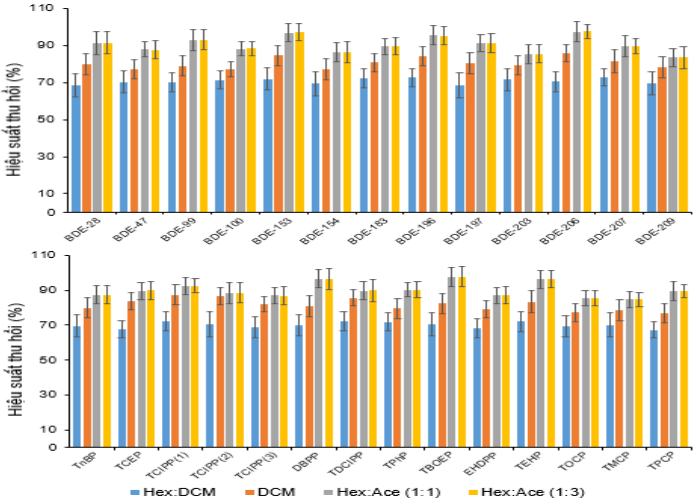

Figure 3.7. Extraction efficiencies of PBDEs and OPFRs in indoor dust samples when using different solvent systems

3.4.2. Procedure for the analysis of PBDEs and OPFRs in indoor dust

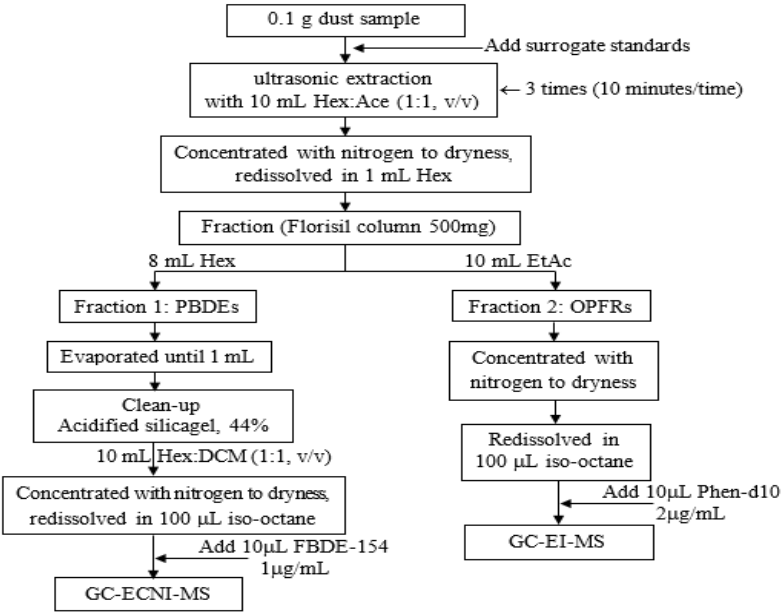

Figure 3.8. Procedure for the analysis of PBDEs and OPFRs in dust samples

3.5. The results of analytical method validation

3.5.1. The results of analytical method validation for PBDEs and OPFRs in indoor air

3.5.1.1. The limit of detection and the limit of quantification of the analytical method for PBDEs and OPFRs in indoor air

The MDL and MQL for the studied PBDEs ranged from 0.003-0.013 ng/m^3 (for BDE-209 was 0.136 ng/m^3) and 0.009-0.043 ng/m^3 (for BDE-209 was 0.453 ng/m^3), respectively. The MDL and MQL values for OPFRs ranged from 0.025-0.141 ng/m^3 and 0.082-0.469 ng/m^3, respectively, and all R values are between 4 and 10, complying with the AOAC requirements. The method meets the requirements for the analysis of trace amounts of PBDEs and OPFRs in air samples.

3.5.1.2. Accuracy/recovery of analytical methods for PBDEs and OPFRs in indoor air

The accuracy of the analytical method for PBDEs and OPFRs in air samples was determined by performing 8 repeated analyses of spiked samples (K-TC1, K-TC2, and K-TC3) at three concentration levels (low, medium, and high) following the surveyed procedure in Figure 3.6. The result showed that average recoveries of PBDEs and OPFRs at the three investigated levels ranged from 80.2% - 98.4% and 81.4% - 102%, respectively. The average recoveries of surrogate standards for the analysis of PBDEs and OPFRs also ranged from 80.6% - 102% and 80.2% - 101%, respectively.

The obtained values are within the allowable limits recommended by AOAC and are similar to the research results in the world. Therefore, the analytical method for the determination of PBDEs and OPFRs in indoor air samples using solvent accelerated extraction (ASE) method combined with GC-MS has high accuracy and is suitable for analyzing and quantifying the levels of PBDEs and OPFRs in indoor air samples..

3.5.1.3. The repeatability and reproducibility of the analytical method for PBDEs and OPFRs in indoor air

The repeatability and reproducibility of the method were evaluated through the relative standard deviation of the repeated analysis results of spiked samples at three concentration levels (low, medium, and high) on the same day and on 8 different days. The results showed that, at all concentration levels, the relative standard deviation of the studied PBDEs and OPFRs ranged from 3.54% - 6.52% and 3.62% - 6.34%, respectively. Therefore, the analytical method for PBDEs and OPFRs in indoor air meets the acceptable requirements for repeatability and reproducibility.

3.5.1.4. The measurement uncertainty of the analytical method for PBDEs and OPFRs in indoor air

The expanded measurement uncertainty of the analytical method for PBDEs and OPFRs in indoor air samples is determined by spiked samples at three concentration levels (low, medium, and high), ranging from 13.2% - 21.5%, 11.7% - 20.3%, and 10.4% - 21.2% for PBDEs, and 12.5% - 22.8%, 11.4% - 21.6%, and 9.82% - 19.1% for OPFRs, respectively. These results are consistent with the analysis of trace amounts of these compounds in indoor air.

3.5.2. The results of analytical method validation for PBDEs and OPFRs in indoor dust

3.5.2.1. The limit of detection and the limit of quantification of the analytical method for PBDEs and OPFRs in indoor dust

The MDL values of PBDEs and OPFRs ranged from 0.10 - 0.54 ng/g (for BDE-209 was 5.00 ng/g), and 0.76 - 3.12 ng/g, corresponding to MQL values of 0.33 - 1.79 ng/g (for BDE-209 was 16.7 ng/g), and 2.53 - 10.4 ng/g for PBDEs and OPFRs, respectively. The analytical method fully meets the requirements for analyzing trace amounts of PBDEs and OPFRs in indoor dust samples.

3.5.2.2. Accuracy/recovery of analytical methods for PBDEs and OPFRs in indoor dust

The evaluation results showed that the analytical method has high recoveries with average recoveries of the PBDEs and OPFRs in dust samples at the three investigated concentrations ranging from 81.3% - 101% and 80.8% - 103%, respectively. The recoveries of surrogate standards for analysis of PBDEs and OPFRs ranged from 80.5% - 101% and 79.2% - 102%, respectively. These values are within the allowable limits recommended by AOAC and EPA 1614. Therefore,

the ultrasonic extraction method combined with analysis on GC-MS has good accuracy for analyzing and quantifying these compounds in indoor dust samples.

3.5.2.3. The repeatability and reproducibility of the analytical method for PBDEs and OPFRs in indoor dust

The repeatability and reproducibility of the method were evaluated by calculating the relative standard deviation of the results of the analysis repeated 8 times on the same day and on 8 different days of spiked samples at three concentration levels. The results showed that, at three concentration levels, the relative standard deviation of PBDEs and OPFRs ranged from 3.42% - 6.25% and 3.69% - 6.41%, respectively. The method for determining PBDEs and OPFRs in indoor dust samples meets the acceptable requirements for repeatability and reproducibility.

3.5.2.4. The measurement uncertainty of the analytical method for PBDEs and OPFRs in indoor dust

The expanded measurement uncertainty of the analytical method for PBDEs and OPFRs in indoor air samples is determined by spiked samples at three concentration levels (low, medium, and high), ranging from 12.7% - 22.4%, 11.0% - 20.9% and 11.3% - 19.5% for PBDEs, and 13.4% - 23.2%, 12.1% - 21.4% and 11.8% - 20.3% for OPFRs, respectively. These results are consistent with the analysis of trace amounts of these compounds in indoor dust.

3.5.2.5. Accuracy of analytical method for PBDEs and OPFRs in standard reference material samples

The results of repeated analysis of 5 times of the standard reference material SRM 2585 according to the analytical procedure in Figure 3.8 showed that the measured levels of PBDEs and OPFRs in SRM 2585 are within the acceptable ranges. The average recoveries

of PBDEs and OPFRs in SRM 2585 ranged from 85.8-105% and 87.8-103%, respectively, with the relative standard deviations ranging from 3.78-6.84% and 3.95-5.36%, respectively.

3.6. Concentrations of PBDEs and OPFRs in indoor air in Hanoi

3.6.1. Presence and distribution of PBDEs in indoor air in Hanoi

Six out of thirty target PBDEs were found in indoor air samples with detection frequencies (DF) of 11% - 75% and total concentrations of PBDEs (ΣPBDEs) ranging from < MDL - 1.14 ng/m^3 (mean 0.418 ng/m^3). BDE-209, BDE-207, and BDE-206 were the most frequently detected congeners, with detection frequencies ranging from 64% -75%. BDE-28, BDE-99, and BDE-47 were found in some samples, while BDE-100, BDE-153, BDE-154, BDE-183, BDE-196, BDE-197, and BDE-203 were not found in any indoor air samples.

BDE-209 was the predominant congener with BDE-209 concentrations ranging from < MDL - 0.904 ng/m^3 (mean 0.357 ng/m^3), accounting for 78.1% - 90.5% (mean 85.5%) of ΣPBDEs levels. The other congeners, such as BDE-206, BDE-207, BDE-99, BDE-28, and BDE-47, were detected at very low levels with concentrations of (mean ± SD) 0.024 ± 0.016 ng/m^3, 0.021 ± 0.018 ng/m^3, 0.010 ± 0.030 ng/m^3, 0.004 ± 0.006 ng/m^3, and 0.002 ± 0.005 ng/m^3, respectively, contributing (mean ± SD) 6.50 ± 2.71%, 4.75 ± 2.61%, 1.33 ± 3.11%, 1.02 ± 1.19%, and 0.45 ± 1.24% to the total PBDEs levels.

3.6.2. Presence and distribution of OPFRs in indoor air in Hanoi

The total concentration of OPFRs in indoor air samples ranged from 42.3 - 358 ng/m^3, with an average concentration of 144 ng/m^3.

TCIPP was the dominant compound, detected in all indoor air samples with the highest levels ranging from 17.2 - 316 ng/m^3 (mean 108 ng/m^3), accounting for 34.4% - 93.0% (mean 69.4%) of the total

OPFRs concentration. TBOEP was the second most abundant compound with an average concentration of 25.2 ng/m^3 (range 0.116 - 125 ng/m^3), accounting for an average of 19.9% (range 0.056 - 52.0%) of the total OPFRs concentration.

Other OPFRs compounds such as TDCIPP, TPhP, TBP, and TCEP were also detected in most samples (DF 75% - 86%) with relatively low concentrations of (mean ± SD) 4.33 ± 3.69, 2.89 ± 1.59, 1.80 ± 1.99, and 1.23 ± 2.67 ng/m^3, respectively, contributing (mean ± SD) 5.10 ± 5.67, 3.10 ± 2.62, 1.13 ± 0.93, and 0.72 ± 0.96% to the total OPFRs concentration. However, compounds EHDPP, DBPP, TOCP, and TMCP were only detected in a few samples at very low levels, with average concentrations of < 0.5 ng/m3, accounting for < 0.35% of the total OPFRs concentration.

3.7. Concentrations of PBDEs and OPFRs in indoor dust in Hanoi

3.7.1. Presence and distribution of PBDEs in indoor dust in Hanoi

Most of the studied PBDEs were detected in indoor dust samples with total PBDEs concentrations ranging from 39.6 - 460 ng/g (mean 186 ng/g). BDE-209 was the most dominant congener detected in all indoor dust samples, with concentrations ranging from 29.0 - 361 ng/g (mean 154 ng/g), accounting for 72.4% - 89.7% (mean 81.4%) of ΣPBDEs. The level of BDE-209 was much higher (1-3 orders of magnitude) than levels of other PBDE congeners, with a nearly absolute correlation between BDE-209 and ΣPBDEs concentration (Pearson's $r = 0.993$; $p < 0.001$). This indicated that deca-BDE is one of the most widely used PBDE mixtures in consumer products, electronic appliances, and furniture in Vietnam.

The low-brominated PBDE congeners contributed to a small proportion of the total concentration of PBDEs in indoor dust, with the

concentrations of BDE-206, BDE-207, BDE-99, BDE-28, and BDE-47 being (mean ± SD) 9.64 ± 5.01, 8.28 ± 3.77, 4.56 ± 11.8, 2.34 ± 1.48, and 1.83 ± 1.31 ng/g, respectively. The concentrations of the remaining PBDE congeners in indoor dust samples were very small, with average concentrations < 1 ng/g.

3.7.2. Presence and distribution of OPFRs in indoor dust in Hanoi

The total concentration of OPFRs detected in indoor dust samples ranged from 1290 - 17500 ng/g (mean 7850 ng/g). TCIPP and TBOEP were the dominant compounds detected in all indoor dust samples, with concentrations ranging from 442 - 8870 ng/g (mean 3640 ng/g) and 97 - 5920 ng/g (mean 2810 ng/g), respectively, contributing (mean ± SD) 45.7 ± 15.9% and 34.5 ± 17.0% to the total OPFRs concentration in indoor dust, respectively. These two compounds had significantly higher concentrations than other OPFRs, indicating their widespread use in consumer products and building materials in Vietnam.

The subsequent compounds that contributed relatively to the total concentration of OPFRs in indoor dust samples are TPhP and TDCIPP, with concentrations (mean ± SD) of 446 ± 319 ng/g and 290 ± 465 ng/g, respectively, accounting for (mean ± SD) 6.28 ± 3.35% and 4.84 ± 6.46% of the total OPFRs concentration.

3.8. Exposure risk assessment of PBDEs and OPFRs in indoor air and dust

3.8.1. Estimated daily intake and the contribution of exposure pathways

The total estimated daily intake (EDI_{total}) of ΣPBDEs for children in the mean and high exposure scenarios were 1.24 and 4.12 ng/kg/day, respectively. These values were approximately 4-5 times greater than those for adults in the same scenarios (0.262 and 1.16 ng/kg/day for the mean and high exposure scenarios, respectively). Similarly, the EDI_{total}

of ΣOPFRs for children in the mean and high exposure scenarios were 183 and 1020 ng/kg/day, respectively. These values were about 4 times greater than those for adults in the same scenarios (50.5 and 266 ng/kg/day for the mean and high exposure scenarios, respectively). These results indicated that children are exposed to higher levels of ΣPBDEs and ΣOPFRs than adults in the indoor environment.

The contribution of exposure pathways to PBDEs and OPFRs for children and adults are relatively different and are shown in Figure 3.23.

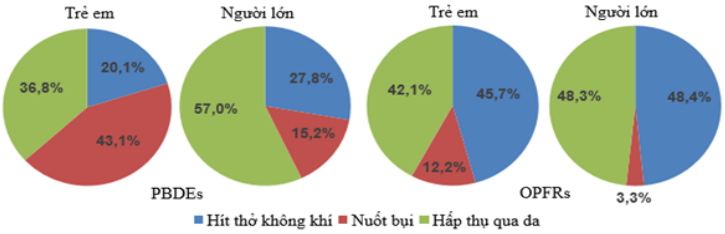

Figure 3.23. Contribution of exposure pathways

3.8.2. Non-carcinogenic risk assessment

The HI values of PBDEs and OPFRs for adults and children in both exposure scenarios ranged from 0.004 - 0.085, much lower than 1. Therefore, the non-carcinogenic risk from exposure to PBDEs and OPFRs through indoor air and dust is negligible for both adults and children..

3.8.3. Carcinogenic risk assessment

The LCR values of BDE-209 and 4 OPFRs for children and adults under the mean and high exposure scenario ranged between 5.31×10^{-11} - 4.13×10^{-11} and 4.55×10^{-11} - 1.84×10^{-7}, respectively. All these LCR values were much lower than the acceptable level for carcinogenic risk (LCR < 10^{-6}). Therefore, the carcinogenic risk of these compounds in indoor air and dust is negligible for both children and adults.

CONCLUSION

1. Successfully developed and validated a method for the simultaneous extraction of PBDEs and OPFRs in indoor air and dust samples and analysis on gas chromatography coupled with mass spectrometry (GC-MS).

2. The analytical procedure was applied to evaluate the distribution of PBDEs and OPFRs in indoor air and dust samples collected from the urban districts of Hanoi. The total concentration of PBDEs in indoor air and dust samples ranged from < MDL - 1.14 ng/m^3 (mean 0.418 ng/m^3) and 39.6 - 460 ng/g (mean 186 ng/g), respectively, with BDE-209 being the dominant compound. The total concentration of OPFRs in indoor air and dust samples ranged from 42.3 - 358 ng/m3 (mean 144 ng/m3) and 1290 - 17500 ng/g (mean 7850 ng/g), respectively, with TCIPP and TBOEP as the dominant compounds.

3. The risks of exposure to PBDEs and OPFRs in indoor air and dust were assessed through three exposure pathways for children and adults. The results showed that the estimated daily intake of PBDEs and OPFRs for children was about 4-5 times greater than those for adults. Dermal absorption was the major exposure pathway to PBDEs for adults, whereas dust ingestion was the major exposure pathway to these compounds for children. Meanwhile, air inhalation and dermal absorption were the major exposure pathways to OPFRs for both children and adults. Dust ingestion contributed only minimally to OPFRs exposure.

The HQ, HI, and LCR values for both adults and children are below acceptable levels even in the high-exposure scenario, indicating that the health risk from exposure to PBDEs and OPFRs via indoor air and dust is negligible for both adults and children.

RECOMMENDATION

This study initially assessed the presence and distribution of brominated and organophosphorus flame retardants in indoor air and dust in the urban districts of Hanoi as well as the potential health risks of exposure to these compounds in the indoor environment for the local residents. To obtain comprehensive assessments of exposure and health risks associated with brominated and organophosphorus flame retardants in the indoor environment for the Vietnamese population, further extensive research is required, including larger sample sizes, diverse study subjects, broader study area, and increased sampling frequency. In addition, more analytical studies are needed to determine the levels of these flame retardants in other objects such as food and drinking water to assess the overall exposure of the population.

NEW CONTRIBUTIONS OF THE THESIS

1. Successful development of the procedure for the simultaneous extraction of brominated and organophosphorus flame retardants in indoor air and dust and analysis on GC-MS. This is the first report in Vietnam on the standardization of extraction and analysis methods of these flame retardants in indoor air and dust.

2. Initial assessment of the presence and distribution of brominated and organophosphorus flame retardants in indoor air and dust in urban districts of Hanoi.

3. This is the first study to assess the exposure to brominated and organophosphorus flame retardants in indoor air and dust for adults and children through all three exposure pathways to obtain a comprehensive evaluation of the exposure and human health risks from exposure to these compounds in indoor environments in urban districts of Hanoi.

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2. **Minh Tue Thi Hoang**, Hanh Thi Duong, Giang Truong Le, Ha Thu Trinh (2020), *A pilot study of the determination of organophosphate flame retardants in indoor air*, Vietnam Journal of Science and Technology, vol 58 (5), p. 592-603.
3. **Minh Tue Thi Hoang**, Hoang Quoc Anh, Kiwao Kadokami, Hanh Thi Duong, Ha Mai Hoang, Tuyen Van Nguyen, Shin Takahashi, Giang Truong Le, Ha Thu Trinh (2021), *Contamination status, emission sources, and human health risk of brominated flame retardants in urban indoor dust from Hanoi, Vietnam: the replacement of legacy polybrominated diphenyl ether mixtures by alternative formulations*, Environmental Science and Pollution Research, vol. 28, pp. 43885-43896.
4. **Minh Tue Thi Hoang**, Giang Truong Le, Kadokami Kiwao, Hanh Thi Duong, Thang Quang Phan, Minh Quang Bui, Dung Anh Truong, Phuong Ha Doan, Ha Thu Trinh (2023), *Occurrence and risk of human exposure to organophosphate flame retardants in indoor air and dust in Hanoi, Vietnam*, Chemosphere, vol.328, 138597.
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6. **Minh Tue Thi Hoang**, Hanh Thi Duong, Thang Quang Phan, Ha Thu Trinh (2023), *Occurrence and human exposure risk assessment of brominated and organophosphate flame retardants in indoor dust in Hanoi, Vietnam*, Vietnam Journal of Science and Technology, vol 61 (4).