VIETNAMESE ACADEMY OF SCIENCE AND TECHNOLOGY

GRADUATE UNIVERSITY OF SCIENCE AND TECHNOLOGY

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STUDY ON ANALYTICAL METHODS FOR TRICLOSAN, TRICLOCARBAN, PARABENS, AND BISPHENOLS IN THE ENVIRONMENT IN HA NOI

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INTRODUCTION

1. Necessity of the Thesis

Triclosan, triclocarban, parabens, and bisphenols are extensively utilized in consumer goods for their antimicrobial and plasticizing properties. However, these substances are identified as endocrine-disrupting chemicals (EDCs) with high environmental persistence and bioaccumulation potential, posing severe threats to human health and ecological integrity.

Despite international and national regulatory frameworks established by Vietnam to limit or prohibit their use, effective management is currently hindered by methodological gaps in chemical analysis, a lack of comprehensive monitoring data, and limited public awareness.

In Hanoi, the contamination of lakes and rivers by these compounds has emerged as a critical research priority. This thesis aims to characterize the occurrence and evaluate the ecological risks of these pollutants in Hanoi's surface waters, thereby providing a robust scientific basis and analytical framework for environmental management.

2. Research Objectives

- To develop advanced and high-precision analytical methodologies for the determination of TCS, TCC, parabens, and bisphenols in aqueous environments.

- To apply standardized methods for analyzing the target compounds in various water matrices collected across Hanoi’s inner-city areas.

- To conduct a preliminary ecological risk assessment regarding the accumulation of TCS, TCC, parabens, and bisphenols in the aquatic environment.

3. Scientific and Practical Significance

This research aims to advance analytical frameworks and provide a comprehensive assessment of pollution levels and ecological risks posed by the accumulation of TCS, TCC, parabens, and bisphenols in lakes, rivers, and swimming pool water.

CHAPTER 1. LITERATURE REVIEW

1.1. Overview of TCS, TCC, Parabens, and Bisphenols

1.1.1. Overview of Triclosan (TCS) and Triclocarban (TCC)

Triclosan (TCS): Triclosan is a multifunctional organic compound characterized by a molecular structure containing three chlorine atoms, aromatic rings, a phenolic group, and an ether linkage (Figure 1.1). According to IUPAC nomenclature, TCS is identified as 5-chloro-2-(2,4-dichlorophenoxy)phenol. Other systematic names include 2,4,4'-trichloro-2'-hydroxydiphenyl ether and 5-chloro-(2,4-dichlorophenoxy)phenol. It is also marketed under various trade names, such as CH-3565, Lexol 300, and Irgasan DP 30.

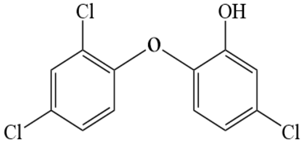


Figure 1.1.Structure of TCS

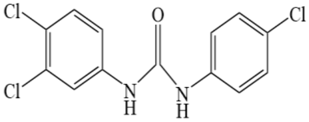


Figure 1.2. Structure of TCC

Triclocarban (TCC): Triclocarban (trichlorocarbanilide, TCC, Solubacter) is a chemical compound with the molecular formula $C_{13}H_{9}Cl_{3}N_{2}O$. Its IUPAC name is 3-(4-Chlorophenyl)-1-(3,4-dichlorophenyl) urea. The molecular structure of TCC is illustrated in Figure 1.2.

1.1.2. Overview of Parabens

Parabens (p-hydroxybenzoates) are esters of p-hydroxybenzoic acid, characterized by a general molecular structure as shown in Figure 3. The structural framework consists of a benzene ring with a hydroxyl group and an ester group substituted at the para-position. Within this structure, the "R" group in the ester substituent can be an alkyl radical (ranging from methyl to heptyl) or an aryl radical (such as benzyl or phenyl). Based on the configuration of the R-chain, parabens are classified into short-chain parabens (including MeP, EtP, PrP, and iPrP) and long-chain parabens (including BuP, iBuP, BBzP, HepP, and PheP). The molecular structures of these parabens are detailed in Figure 1.3

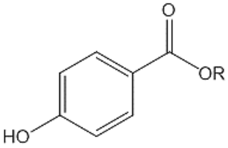
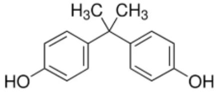
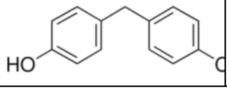


Figure 1.3. The structural formulas of paraben

1.1.3. Overview of bisphenols

Bisphenols are a group of chemical compounds that molecular structure containing two phenolic rings (-C_6H_4OH). Due to their diverse structural configurations and physicochemical properties, these compounds are extensively utilized across various industrial sectors and consumer products. Among them, bisphenol A (BPA) is the most prevalent compound, alongside structural analogues used as substitutes, such as bisphenol F (BPF)

Table 1.1. Structural formulas of BPA and BPF.

Analytes	Structural	Molecular formula	Molecular weight (g/mol)	Solubility in water
Bisphenol A (BPA)		$C_{15}H_{16}O_2$	228,3	
Bisphenol F (BPF)		$C_{13}H_{12}O_2$	200,2	

1.2. Current usage status of triclosan, triclocarban, parabens, and bisphenols

Triclosan (TCS) and Triclocarban (TCC) are antimicrobial agents extensively utilized in personal care products, including soaps, toothpastes, and detergents. Additionally, TCS is incorporated into textiles and household goods, typically entering the environment via domestic wastewater.

Parabens have been widely employed as preservatives and fragrance components since the 1920s. Due to their effective antibacterial and antifungal properties, they are prevalent in a broad range of cosmetics, pharmaceuticals, and other consumer goods.

Bisphenol A (BPA), first synthesized in 1891, is primarily used in the production of polycarbonate plastics and epoxy resins. Owing to its plasticizing properties, BPA also serves as an intermediate in the manufacturing of paints, textiles, and flame retardants. The ubiquitous industrial application of bisphenols has led to their widespread environmental release and subsequent human and ecological exposure.

1.3. Origins and Environmental Dissemination of Compounds

1.3.1. Environmental Release of TCS and TCC

Triclosan (TCS) and Triclocarban (TCC) are ubiquitous antimicrobial agents found in a wide range of personal care and household products, such as soaps, toothpastes, and toys. Due to their extensive application, these compounds are readily dispersed into the environment, leading to human exposure through various pathways, including direct dermal contact, inhalation of contaminated dust, or consumption of tainted water and food sources.

1.3.2. Environmental Release of Parabens

1.3.2.1. Parabens in the Aquatic Environment

Parabens enter aquatic systems primarily through domestic wastewater discharge or atmospheric deposition, leading to their ubiquitous presence in various water bodies. Although some studies indicate that wastewater treatment plants can achieve high removal efficiencies—ranging from 96% to 99.9%—parabens are still consistently detected in surface water and groundwater at concentrations spanning from ng/L to μg/L. This persistent presence poses significant risks to aquatic organisms and raises substantial concerns regarding human health.

1.3.2.2. Parabens in Food and Other Environmental Matrices

Global research has confirmed the detection of parabens in water, air, and dust. A study conducted between 2006 and 2012, analyzing 158 indoor dust samples across cities in the United States, China, South Korea, and Japan, found that two specific compounds predominated the total paraben profile: Methylparaben (MeP) accounted for 42–73% (ranging from 226 to 1,670 ng/g), while Propylparaben (PrP) constituted 12–46% (ranging from 123 to 761 ng/g). Analytical data indicated that South Korea recorded the highest paraben concentrations in dust (2,320 ng/g), followed by Japan (2,300 ng/g), the United States (1,390 ng/g), and China (418 ng/g). Parabens and their metabolites have been identified in marine organisms, mangroves, and other environmental compartments such as soil, sludge, and sea sediments. High concentrations have been documented in environmental samples (dust, air, water, and sewage sludge) in numerous countries, including China, the U.S., France, and Greece. Indoor air and dust have been identified as primary media for direct exposure to these emerging endocrine-disrupting chemicals (EDCs).

1.3.3. Environmental Dissemination of Bisphenols

Bisphenols are anthropogenic compounds extensively utilized in the production of plastics, coatings, and paper, entering the environment through multiple pathways. They contaminate aquatic systems via industrial wastewater discharge and leaching from consumer products; atmospheric environments as vapors or by adhering to indoor fine particulate matter; and terrestrial systems through wastewater irrigation, sewage sludge application, and atmospheric deposition. Currently, bisphenol concentrations in sediments and sewage sludge across Asia have reached alarmingly high levels.

1.4. Risks of Target Compounds to Human Health and Ecosystems upon Exposure

1.4.1. Risks of TCS and TCC to Human Health and Ecosystems

TCS: Acts as an endocrine disruptor, interfering with thyroid hormones, stimulating cancer cell proliferation, and adversely affecting the nervous system. Furthermore, TCS may induce skin irritation, allergic reactions, and contribute to the proliferation of antibiotic-resistant bacteria.

TCC: Enhances sex hormones such as estrogen and testosterone, potentially linking it to cancers such as breast and prostate cancer. Similar to TCS, TCC also promotes the development of antibiotic resistance.

1.4.2. Risks of Paraben Exposure

Although parabens have been utilized for nearly a century, their full impact on human health has yet to be completely elucidated. Recent studies focus on the endocrine-disrupting potential of parabens in both humans and animals. Parabens can enter the body via dermal absorption, inhalation, or ingestion. Once absorbed, they are rapidly metabolized by the liver and excreted through urine within 24–48 hours. Other documented effects include endocrine disruption, carcinogenic potential, and adverse impacts on reproductive health, alongside ecological risks to the environment.

1.4.3. Risks of Bisphenol Exposure

Bisphenol A (BPA) is incorporated into numerous daily products, including toys, food packaging, and thermal paper receipts. Upon the environmental release of these products, BPA can enter the human body through dermal, respiratory, or gastrointestinal pathways. Despite its short half-life in soil (approximately 10 days), BPA remains a pollutant of significant concern due to its ubiquitous presence across air, water, and soil matrices.

1.5. Regulatory Frameworks for the Use of TCS, TCC, Parabens, and Bisphenols

1.5.1. Regulations by International Organizations

1.5.1.1. Regulations for TCS and TCC

Safety concentration limits for Triclosan (TCS) and Triclocarban (TCC) vary depending on the product type and target age group:

Triclosan (TCS): Deemed safe at a concentration of 0.3% in toothpaste for adults and children over 0.5 years old when used individually. For mouthwash, a concentration of 0.2% is considered safe only for adults when used individually. Triclocarban (TCC): Permitted at a maximum concentration of 0.2% in topical cosmetics and 1.5% in rinse-off cleansing products. However, TCC is not recommended for use in toothpaste for children under 6 years old (at the 0.2% level) and is deemed unsafe for use in mouthwash.

1.5.1.2. Regulations for Parabens

Numerous countries and international bodies have enacted regulations to restrict the use and monitor the environmental release of parabens (US EPA, 2011; US FDA, 2017; EU Regulation (EU) No 358/2014, 2014; SCCS/1348/10, 2011; SCCS/1514/13, 2013).

1.5.1.3. Regulations for Bisphenols

The management of TCS and TCC is governed by the regulations of the Ministry of Health. Regarding Parabens, the Drug Administration of Vietnam issued Official Dispatch No. 6577/QLD-MP, which stipulates the requirements for paraben use in cosmetics. For Bisphenols, the oversight of cosmetic products is implemented according to Ministry of Health regulations, aligned with the ASEAN Cosmetic Directive (ACD).

1.6. Overview of Current Analytical Methods

1.6.1. Sampling Methods

1.6.2. Sample Preparation Methods

Sample preparation is a critical stage that directly influences the accuracy of analytical results. The primary objectives of this process are to eliminate matrix interferences and maximize the recovery of target analytes. The selection of an appropriate preparation technique depends on the research objectives, the sample matrix (solid, liquid, or gas), and the specific laboratory conditions**.**

1.6.3. Analytical Techniques for TCS, TCC, Parabens, and Bisphenols

Modern analytical methods for the determination of above 4 compounds typically employ chromatographic techniques coupled with high-sensitivity detectors. The most prevalent methods include:

- High-Performance Liquid Chromatograph*y (HPLC):* HPLC coupled with various detectors: HPLC-UV/PDA (Ultraviolet/Photodiode Array).
- *Gas Chromatography-Mass Spectrometry (GC-MS) and GC-MS/MS (Tandem Mass Spectrometry).*

Literature Review Summary

TCS, TCC, parabens, and bisphenols are ubiquitous synthetic chemicals that are widely dispersed in aquatic environments. They are classified as emerging endocrine-disrupting chemicals (EDCs) due to evidenced toxicity in experimental animals. However, the effective management of these compounds remains constrained by several factors: A lack of high-precision analytical methodologies for aqueous samples. Insufficient data regarding pollution levels and ecological risks. Limited analytical capacity within existing laboratory facilities.

Inconsistent analytical standards and protocols, despite established concentration limits or total bans in certain countries.

Consequently, research dedicated to developing analytical methods for triclosan, triclocarban, parabens, and bisphenols in Hanoi’s surface waters is essential, carrying significant scientific and practical value.

CHAPTER 2. MATERIALS AND METHODS

2.1. Research Objects

- Triclosan (TCS) and Triclocarban (TCC).

- Paraben group: Methylparaben (MeP), Ethylparaben (EtP), Propylparaben (PrP), Isopropylparaben (iPrP), Butylparaben (BuP), Benzylparaben (BzP), and Heptylparaben (HepP).

- Bisphenol group: Bisphenol A (BPA) and Bisphenol F (BPF).

- Surface Water Samples: Collected from two rivers and several major lakes in Hanoi, including: To Lich River, Kim Ngưu River, West Lake (Ho Tay), Thuyen Quang Lake, Hoan Kiem Lake, Ngoc Khanh Lake, and Yen So Lake.

- Swimming Pool Water Samples: Samples from indoor swimming pools distributed across various districts of Hanoi, such as Thanh Xuan, Cau Giay, Long Bien, and Bac Tu Liem.

2.2. Chemicals and Equipment

2.2.1. Apparatus and Equipment

Analytical System: LC-MS/MS 8040 (Shimadzu, Japan) equipped with a Kinetex C18 column (150 × 2.1 mm, 2.6 µm; Sigma-Aldrich, Germany). Analytical balance (0.1 mg precision) and technical balance (Sartorius, Germany). Ultrasonic bath (S 100H, Elma, Germany). pH meter (HI2215 pH/ORP, Hanna, Romania). Centrifuge, vortex mixer. Milli-Q Integral 3 ultrapure water system (Merck Millipore, Germany). Temperature-controlled nitrogen evaporation system (N_2 blowdown evaporator). Solid-phase extraction (SPE) manifold (Newaskin 30, CAMI, Italy) with a maximum vacuum of -0.8 bar, equipped with a Buchner funnel vacuum filtration set.

SPE Cartridges: Oasis HLB 60 mg/3 mL and Oasis HLB 500 mg/5 mL (Waters, Milford, MA, USA).

Micropipettes: Eppendorf (10-100 µL, 100-1000 µL; Cyberlab, USA).

Glassware: 100 mL round-bottom flasks; 100 mL graduated cylinders; 250 mL Erlenmeyer flasks; volumetric flasks (50 mL, 100 mL, 1000 mL); Pasteur pipettes; 20 mm filter paper.

2.2.2. Chemicals

The following analytical standards and surrogate standards (internal standards) were utilized in the experiments for this thesis:

TCS$^{-13}C_{12}$ ($C_{12}H_7Cl_3O_2$): ^{13}C-labeled isotope of TCS, used as a surrogate standard for both **TCS** and **TCC**.

MeP$^{-13}C_6$ and BuP$^{-13}C_6$: ^{13}C-labeled isotopes of methylparaben and butylparaben, used as surrogate standards for the paraben group.

BPA$^{-13}C_{12}$: a ^{13}C-labeled isotope used as a surrogate standard for BPA.

BPF-d10: A deuterated isotope used as a surrogate standard for BPF.

2.3. Research Methodology and Content

In this study, an LC-MS/MS 8040 (Shimadzu) system was employed to investigate and determine the three target compound groups. For the separation of TCS and TCC, a Zorbax C8 column (2.1m x 100 mm}, 3.5 µm; Sigma-Aldrich, USA) was used. For parabens and bisphenols, an XDB-C18 column (100 x 4.6 mm, 3 µm particle size, 120 Å pore size, and 170 m^2/g surface area was utilized.

2.3.1. Optimization of Analytical Conditions for Triclosan and Triclocarban

Analytical parameters for the LC-MS/MS system, including carrier gas flow rate, collision energy (CE), and precursor/product ions, were optimized. This was achieved by direct infusion of 10 µL of a 1000 ng/mL mixed standard solution into the system. Each parameter was systematically adjusted until the maximum peak intensity was reached, which was then selected as the optimal value.

2.3.2. Optimization of Analytical Conditions for Parabens

The LC-MS/MS parameters, including flow rate, collision energy, and precursor ion identification, were optimized by direct injection of 10 µL of a 100 ng/mL paraben standard solution. Each parameter was varied to achieve the maximum peak signal. Following this, the 100 ng/mL standard solution was analyzed in full-scan mode. The resulting spectra were compared with the NIST spectral library and relevant literature to identify the two most characteristic multiple reaction monitoring (MRM) transitions for each compound.

2.3.3. Optimization of Analytical Conditions for Bisphenols

The study investigated voltage settings ranging from 10.0 V to 25 V and collision energies (CE) from 10.0 to 30.0 eV to determine the optimal conditions for the analytes and surrogate standards, while simultaneously optimizing sensitivity and selectivity. Subsequently, measurements were conducted in both positive (+) and negative (-) ionization scan modes, with a mass-to-charge ratio (m/z) range of 50–500 over a 2-minute duration to identify the characteristic fragment ions and optimal potentials for the target analytes.

2.3.4. Determination of Recovery, IDL, IQL, and Calibration Curves

2.*3.4.1. Stability and Recovery*

The precision of the analytical method was evaluated based on the Relative Standard Deviation (RSD%). According to the standards of the Association of Official Agricultural Chemists (AOAC), the RSD% of the analytical signal should be less than or equal to 15% at a concentration of 50 ng/mL.

Method repeatability and accuracy were investigated by processing standardized samples with 10 replicates. The results obtained from these experiments were used to determine the recovery of the method.

2.*3.4.2. Instrument Detection Limit (IDL) and Instrument Quantification Limit (IQL)*

Standard solutions were injected in increasing concentrations to determine the IDL and IQL:

Instrument Detection Limit (IDL): The lowest concentration of the analyte in the solvent that yields a signal-to-noise ratio of approximately 3 (S/N ≈ 3).

Instrument Quantification Limit (IQL): The lowest concentration of the analyte in the solvent that yields a signal-to-noise ratio of approximately 10 (S/N ≈ 10).

The S/N ratio was determined using the instrument's data processing software. The IDL and IQL were calculated based on the analysis of the lowest concentration standards, which for both TCS and TCC was 1 ng/mL.

2.3.4.3. Construction of Calibration Curves

Working calibration curves in this thesis were constructed using the external standard method, with the concentration levels specified in Table 2.

Table 2. Calibration curves of the groups of substances.

	Cal 1	**Cal 2**	**Cal 3**	**Cal 4**	**Cal 5**	**Cal 6**	**Cal 7**	**Solvent**
Triclosan, triclocarban (C ng/ mL)								
C_{NS}	0,5	1	5	10	20	50	100	ACN
Paraben (C ng/ mL)								
C_{NS}	1	2	5	10	20	50	100	MeOH
Bisphenol (C ng/ mL)								
C_{NS}	1	5	10	50	100	200	500	MeOH

2.4. Optimization of Sample Preparation Procedures

2.4.1. Blank Sample Treatment

A blank sample (procedural blank) is defined as a matrix identical to the real sample but devoid of the target analytes. However, since TCS, TCC, parabens, BPA, and BPF are ubiquitous in industrial applications and present in most wastewater, river, and lake environments, selecting an ideal blank matrix is challenging. Within the scope of this thesis, Milli-Q water (resistivity $> 18\text{ M}\Omega\cdot\text{cm}$) was utilized as the blank matrix for all experimental investigations. Blank samples were processed sequentially, following the exact protocol used for river and lake water samples.

2.4.2. Water Sample Treatment

2.4.2.1. Procedure for Triclosan and Triclocarban Determination

To optimize the water treatment process, several parameters were systematically investigated, including the selection of Solid-Phase Extraction (SPE) cartridges, elution solvents, and solvent ratios. Based on the recovery rates obtained from these experiments, the most effective extraction solvent was identified to establish the optimal sample preparation procedure for both analytes in surface water matrices.

2.4.2.2. Procedure for Paraben Determination

To optimize the analytical protocol, two primary investigations were conducted:

Effect of pH: The study was performed using six spiked water samples. Three samples were acidified to pH 3 using formic acid, while the remaining three were maintained at their original pH. After loading the samples onto Oasis SPE cartridges, they were washed and eluted. The recovery results at both pH levels were compared to determine the optimal pH condition.

Optimization of Elution Volume: The sample treatment followed the same protocol as the pH investigation, but the elution solvent volume was varied between 3 mL and 5 mL. The recovery efficiency and Relative Standard Deviation (RSD%) were calculated to determine the optimal volume for the analytical procedure.

Dưới đây là bản dịch tiếng Anh chuyên ngành cho quy trình xử lý mẫu Bisphenol, được trình bày dưới dạng các bước kỹ thuật (step-by-step) thường thấy trong các bài báo khoa học:

2.4.2.3. Procedure for Bisphenol Determination in Water Samples

Sample Preparation**:** 100 mL of water is acidified to pH 3 (formic acid), spiked with 200 µL surrogate standard, and equilibrated for 30 minutes.

SPE Clean-up**:** A cartridge is conditioned with 5 mL each of MeOH and deionized water. After loading the sample, interferences are washed away with 10 mL of 5% MeOH.

Elution & Analysis: Analytes are eluted with 5 mL MeOH, nitrogen-evaporated to 1 mL, and filtered (0.45 µm) for LC-MS/MS analysis.

2.4.2.4. Investigation of Solid-Phase Extraction (SPE) Cartridges

Three SPE cartridges (Oasis HLB, CHROMABOND C18, and CNWBOND HC-C18) were evaluated in triplicate. Deionized water (100 mL) was spiked with 200 ng of surrogate standards ($BPA-^{13}C_{12}$ and $BPF-d_{10}$), acidified to pH 3, and equilibrated. After conditioning with MeOH and water, samples were loaded, washed with 5% MeOH, and eluted with 7 mL MeOH. Eluates were nitrogen-concentrated to 1 mL, filtered (0.45 µm), and analyzed via LC-MS/MS. The optimal cartridge was selected based on recovery rates (R%).

2.4.2.5. Optimization of Elution Solvent Volume

To optimize elution, 100 mL of acidified ultrapure water (pH 3) was spiked with 200 ng of surrogate standards and processed using the optimized SPE cartridge. Following conditioning (5 mL MeOH/water) and washing (10 mL 5% MeOH), analytes were eluted with 3, 5, or 10 mL of MeOH in triplicate. Eluates were concentrated to 1 mL under N_2, filtered (0.45 µm), and analyzed. The optimal volume was selected based on maximum recovery efficiency.

2.4.3. Evaluation of the Analytical Procedures for TCS, TCC, Parabens, and Bisphenols

Sample preparation is the most critical stage of the analytical process, directly impacting analyte recovery, precision, and reliability. Optimization ensures the removal of matrix interferences and enhances overall method efficiency. Based on these preliminary studies, a refined 8-step procedure is proposed for the determination of TCS, TCC, parabens, and bisphenols in river and lake water.

2.5. Determination of Method Detection Limits (MDL) and Method Quantification Limits (MQL)

Once the optimal chromatographic conditions and sample preparation protocols were established, the method detection limits were determined based on the Instrument Detection Limits (IDL) and the sample preparation factors (dilution, pre-concentration, etc.).

Method Detection Limit (MDL): The lowest concentration of an analyte in the original sample that, after undergoing the entire analytical procedure, yields a signal-to-noise ratio of approximately 3 (**S/N ≈ 3**).

Method Quantification Limit (MQL): The lowest concentration of an analyte in the original sample that, after undergoing the entire analytical procedure, yields a signal-to-noise ratio of approximately 10 (**S/N ≈ 10**).

Within the scope of this thesis, the **MDL** is determined at **S/N ≈ 3**, adjusted for the recovery of the corresponding surrogate standard, multiplied by the final volume, and divided by the initial sample volume or sample mass:

$$\mathrm{MDL} = \frac{\mathrm{C}_{\text{tại S/N= 3}} \text{ x } \mathrm{V}_{\text{đm}}}{\mathrm{R}(\%) \text{ x } \mathrm{V}_{\text{mẫu}}}$$

MDL: Method Detection Limit (ng/L).

2.6. Sampling and Analysis

Surface water samples for the study of triclosan, triclocarban, parabens, and bisphenols were collected from the To Lich River (11 samples). Lake water samples were obtained from Thien Quang Lake (7 samples), Hoan Kiem Lake (7 samples), Ba Mau Lake (6 samples), West Lake (20 samples), and Yen So Lake (12 samples) during August 2024. All samples were collected in amber glass bottles, preserved in a refrigerator at 4°C, and analyzed within 48 hours.

2.7. Ecological Risk Assessment

This thesis selected three aquatic species commonly found in freshwater ecosystems across Asia and Europe: the freshwater crustacean (Daphnia magna), green algae, and common carp. The Risk Quotient (RQ) was employed to assess the environmental impact of target compounds on sensitive aquatic organisms. The RQ values are categorized into three risk levels: Low risk: $RQ < 0.1$,Medium risk: $0.1 < RQ < 1$, High risk: $RQ > 1$

This quotient is calculated as folllows:

$$\mathrm{RQ} = \sum_{i=1}^{n} \frac{\mathrm{MEC_i}}{\mathrm{PNEC_i}} \qquad \mathrm{RQ} = \sum_{i=1}^{n} \frac{\mathrm{MEC_i}}{\mathrm{PNEC_i}}$$

$$\mathrm{PNEC_{ct}} = \frac{\mathrm{LC_{50}}}{\mathrm{AF_{ct}}} = \frac{\mathrm{EC_{50}}}{\mathrm{AF_{ct}}} \qquad \mathrm{PNEC_{mt}} = \frac{\mathrm{NOEC}}{\mathrm{AF_{mt}}}$$

Where: n: Number of compounds, MEC_i: Measured Environmental Concentration of compound I, $PNEC_i$: Predicted No-Effect Concentration of compound i (safety threshold), LC_{50}: Median lethal concentration (lethal to 50% of the test population), EC_{50}: Half-maximal effective concentration, NOEC: No Observed Effect Concentration, AF: Assessment Factor (or Uncertainty Factor), assigned values of 1000 or 100 for acute and chronic toxicity, respectively.

CHAPTER 3. RESULTS AND DISCUSSION

3.1. Determination of Chromatographic Conditions for the Target Compounds

3.1.1. Analytical Conditions for TCS and TCC

3.1.1.1. Chromatographic Conditions for TCS and TCC Analysis

The survey of mobile phase flow rates in this study indicated that a flow rate of 0.3 mL/min provided the optimal signal intensity, peak shape, and peak area. Furthermore, this flow rate offered a short analysis time and was therefore selected for subsequent studies.

3.1.1.2. Results of Stability, Repeatability, Reproducibility, and Calibration Curve

The RSD values for the analytical signals were 4.3% (repeatability) and 6.2% (reproducibility) for TCS, and 3.8% and 5.6% for TCC, respectively. These values fall within the regulated limits.

3.1.1.3. Evaluation of SPE Cartridges

Testing three types of cartridges—Poly Sery HLB, Copure HLB, and Oasis HLB—showed high recovery rates for both TCS and TCC across all three types. However, the Oasis HLB (60 mg) cartridge was selected for the experiments as it yielded the highest recovery efficiency.

3.1.1.4. Investigation of Elution Solvents and Solvent Volume

Recovery rates of TCS and TCC based on solvent ratio (%) investigation When using MeOH as the elution solvent, TCS and $^{13}C_{12}$-TCS were eluted more effectively from the SPE cartridge. Conversely, when using ACN as the elution solvent, TCC (which contains two –NH groups) showed better compatibility with the ACN solvent. Consequently, TCC was eluted more efficiently, leading to a very high recovery rate. Therefore, the research group selected a MeOH:ACN (1:1, v/v) solvent system for the elution of both TCS and TCC from the SPE cartridges.

3.1.1.2. Method Detection Limits (MDL), Method Quantification Limits (MQL), and Recovery (Re%)

The analytical results demonstrate that the method achieves high reliability. Peak signals were well-identified with a signal-to-noise (S/N) ratio ≥ 3. The Method Detection Limit (MDL) values ranged from 0.04 to 0.29 ng/L, indicating the ability to detect analytes at ultralow concentrations. The recovery rates for Triclosan (TCS) and Triclocarban (TCC) were within the acceptable limits defined by the Association of Official Analytical Chemists (AOAC). Specifically, TCS recovery fluctuated between 72.8% and 105.7%, while TCC ranged from 71.8% to 103.1%, depending on the concentration level. The MDL and Method Quantification Limit (MQL) values for both substances are suitable for trace analysis in river and lake water samples, providing clear signals and high precision ($S/N \geq 10$).

3.1.2. Determination of Analytical Conditions for Parabens

3.1.2.1. Chromatographic Conditions for Paraben Analysis

The retention times for the seven parabens (MeP, EtP, PrP, iPrP, BuP, BzP, and HepP) were 8.3, 10.6, 12.7, 13.2, 15.3, 15.5, and 20.2 minutes, respectively. For the two internal standards, $MeP^{13}C_6$ and $BuP^{13}C_6$, the retention times were 8.2 and 14.4 minutes. Two compounds with closely eluting peaks were BzP (15.3 min) and BuP (15.5 min). Although the two isomers, PrP and iPrP, share the same m/z fragment of 179, they can be distinguished based on their retention times of 12.7 minutes (PrP) and 13.2 minutes (iPrP). This confirms that the method is reliable for the analysis of seven types of parabens in water samples.

3.1.2.2. Selection of Solid Phase Extraction (SPE) Cartridges

The Oasis HLB (500 mg) cartridge provided the best recovery for the target analytes. Consequently, HLB-SPE (500 mg) was selected for the extraction of parabens in swimming pool water samples.

3.1.2.3. Calibration Curves for Paraben Determination

The calibration curves for the parabens were constructed over a concentration range of 1 ng/mL to 200 ng/mL. All curves exhibited a correlation coefficient (R^2) greater than 0.997, demonstrating a strong linear relationship between the peak area and the analyte concentration.

3.1.2.4. Determination of MDL, MQL, and Recovery Rates

The Method Detection Limits (MDL) for the target compounds in water samples ranged from 0.05 ng/mL to 0.28 ng/mL, while the Method Quantification Limits (MQL) ranged from 0.14 ng/mL to 0.83 ng/mL. These results indicate that the method achieves high efficiency in terms of detection and quantification limits, making it suitable for determining paraben concentrations at trace levels within the sample matrix.

The recovery rates for parabens in water samples ranged from 76.9% to 94.6%, with RSD values between 1.3% and 4.7%. These values fall well within the permissible limits (the acceptable range for paraben recovery is 40%–120%, with an RSD of 30%). The results obtained are consistent and provide acceptable reliability for an analytical method targeting organic compounds at trace levels.

3.1.3. Determination of Analytical Conditions for Bisphenols

3.1.3.1. Chromatographic Conditions

Voltages ranging from 10.0 V to 25 V and collision energies from 10.0 to 30.0 eV were investigated. The optimal potential and collision energy for each analyte and internal standard were selected to optimize sensitivity and selectivity. Collision energies of 22, 23, and 20 eV were assigned to the three analytical channels, respectively.

3.1.3.2. Investigation of Flow Rate and Mobile Phase Solvents

The investigation showed that a flow rate of 0.3 mL/min yielded the best signal intensity, peak area, and peak shape. Consequently, 0.3 mL/min was determined to be the optimal flow rate for the bisphenol analysis method and was selected for subsequent evaluations.

3.1.3.3. Determination of Instrument Detection Limit (IDL) and Instrument Quantification Limit (IQL)

The IDL value for the bisphenol group was 0.0002 ng, corresponding to an IQL of 0.0006 ng for both target analytes, BPA and BPF.

3.1.3.4. Evaluation of Solid Phase Extraction (SPE) Cartridges

All three types of cartridges—Oasis HLB, CHROMBOND-C18, and CNWBOND-C18—demonstrated the capability to extract bisphenols from the sample matrix.

Investigation of Elution Solvent Volume Determining the appropriate volume of elution solvent is essential to minimize waste and protect the environment. An elution volume of 5 mL provided high recovery rates for both bisphenols while remaining solvent-efficient, reducing environmental impact, and simplifying the evaporation process. Therefore, an elution volume of 5 mL was selected for further studies.

Method Detection Limit (MDL) and Method Quantification Limit (MQL) The Method Detection Limit (MDL) was 1.2 ng/L and the

Method Quantification Limit (MQL) was 3.6 ng/L for water samples. These results confirm that the method is suitable and acceptable for the quantitative analysis of bisphenols.

3.1.3.5. Determination of Recovery, Repeatability, and Reproducibility

The average recovery for bisphenols and internal standards in spiked blank water samples ranged from 83.99% to 91.56%, meeting AOAC requirements for recovery (60–115% at ppb levels). The repeatability of the method was also high, with RSD (%) values ranging from 2.9% to 4.05%, which satisfies the AOAC repeatability criteria of RSD < 21% at ppb concentrations.

3.2. Establishing procedures and conditions for water sample

3.2.1. Procedure for extracting water samples to determine triclosan and triclocarban

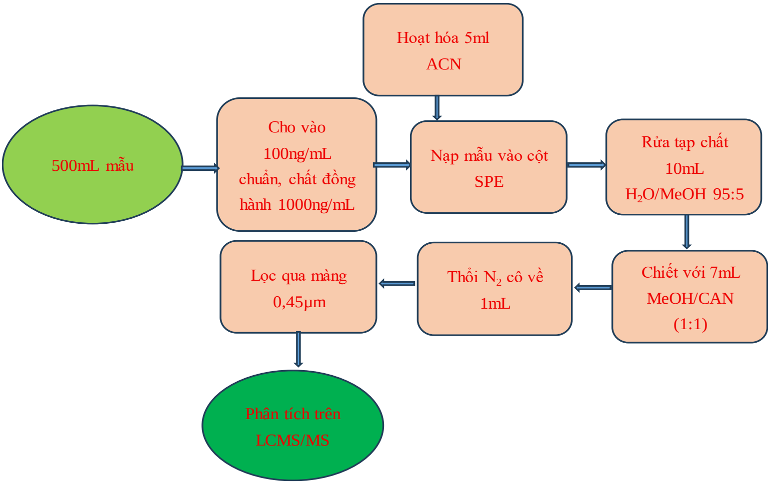


Figure 3.1. Sample processing procedure for triclosan and tricyclocarban analysis.

3.2.2. Procedure and conditions for extracting water samples to determine paraben levels.

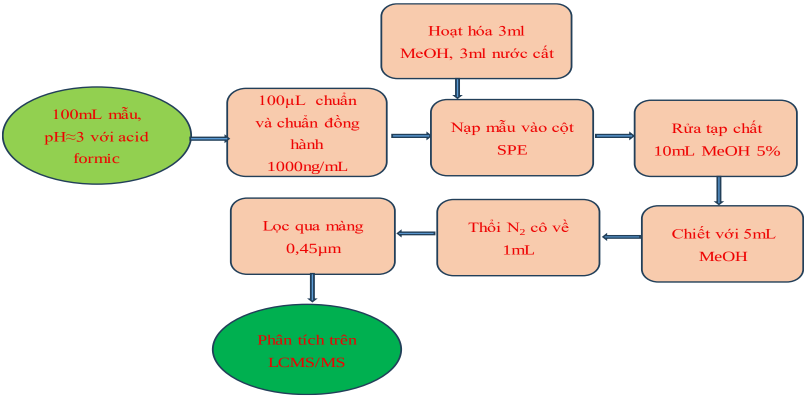


Figure 3.2. Sample processing procedure for paraben analysis.

3.2.3. Procedure for extracting water samples to determine bisphenol

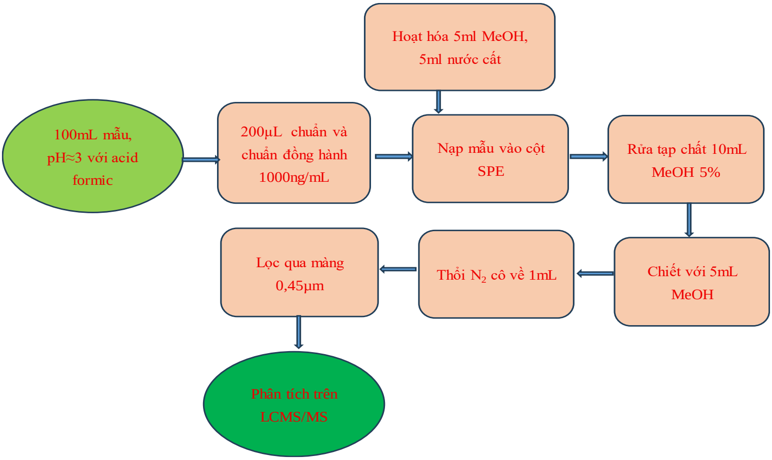


Figure 3.3. Sample processing procedure for bisphenol analysis.

3.3. Analytical Results of Target Compounds in Aqueous Environments

3.3.1. Analytical Results for TCS and TCC in Aqueous Environments

3.3.1.1. Results of TCS and TCC Analysis in Lake Water

TCS and TCC concentrations in Hanoi’s surface waters varied significantly by population density. Densely populated urban lakes (West, Hoan Kiem, Thien Quang, and Ba Mau) showed higher concentrations of TCS (98.5–237 ng/mL; mean 158 ng/mL) and TCC (36.1–94.4 ng/mL; mean 66.1 ng/mL). Conversely, less populated areas like Yen So Lake exhibited lower levels, with TCS and TCC means of 59.8 ng/mL and 30.8 ng/mL, respectively.

3.3.1.2. Results of TCS and TCC Analysis in River Water

Results for TCS and TCC levels in the To Lich River indicated that both compounds were detected in almost all samples. TCS concentrations reached a maximum of 199 ng/mL and a minimum of 53.8 ng/mL, with a mean of 165 ng/mL and a median of 175 ng/mL. TCC concentrations peaked at 121 ng/mL with a minimum of 42.4 ng/mL, a mean of 75.6 ng/mL, and a median of 75.6 ng/mL. Compared to global data, these TCS and TCC levels are relatively high, likely due to the ongoing use of products containing these two ingredients.

3.3.2. Analytical Results for Parabens

3.3.2.1. Paraben Levels in To Lich River Water

The analysis of 11 river water samples from the To Lich River showed that the concentrations of individual and total parabens were very low, ranging from 0.44 to 3.40 ng/mL. MeP remained the most frequently detected paraben, accounting for over 99% of the total paraben concentration.

3.3.2.2. Paraben Levels in Swimming Pool Water

Eight swimming pools, including both indoor and outdoor facilities across various districts in Hanoi, were sampled for paraben analysis. Three samples (a, b, and c) were collected from each pool. The total paraben concentration in the swimming pool water samples (1a–8c) ranged from 19.3 to 340 ng/L. MeP, EtP, and PrP constituted the majority of the paraben concentrations.

3.3.3. Analytical Results for Bisphenols

3.3.3.1. Bisphenol Levels in To Lich River Water

The results for total BPA and BPF in To Lich River water samples showed concentrations ranging from 0.01 ng/L to 3.73 ng/L. Specifically, BPF levels ranged from 0.11 ng/L to 0.54 ng/L. The total concentration of Bisphenols (BPs) at the sampling points along the To Lich River was 0.09 ng/L to 3.85 ng/L, with BPA accounting for the majority of the total bisphenol content. Samples TL-1 to TL-8 and TL-10 showed negligible or relatively low BP levels. In contrast, samples TL-9 and TL-11 yielded significantly higher BP concentrations at 3.85 ng/L and 1.63 ng/L, respectively.

3.3.3.2. Bisphenol concentration in Lake Water in Hanoi

The analytical results for bisphenols in lake water samples from the Hanoi area revealed that BPA and BPF were present in all samples, with a detection frequency of 100%. The mean concentration of BPA was 0.13 ng/mL (median: 0.09 ng/mL), while BPF had a mean concentration of 0.09 ng/mL (median: 0.05 ng/mL).

3.3.3.3. Bisphenol concentration in Swimming Pool Water

Bisphenols were detected in 5 out of 20 samples. BPA concentrations ranged from nd to 0.54 ng/mL (mean: 0.2 ng/mL; median: 0.15 ng/mL). BPF concentrations ranged from nd to 0.57 ng/mL (mean: 0.2 ng/mL; median: 0.18 ng/mL).

3.4. Distribution Characteristics of Triclosan, Triclocarban, Parabens, and Bisphenols in the Aqueous Environment

TCS and TCC concentrations were significantly higher in the To Lich River (200–500 and 100–300 ng/L) than in lakes (<50 ng/L), with strong correlations suggesting a shared domestic wastewater origin. Conversely, BPA was more prevalent in lakes (80–200 ng/L) than rivers (30–70 ng/L), likely due to commercial plastic and packaging discharges. Paraben distribution also varied: MeP and PrP were higher in the river, whereas BuP was more common in lakes, likely linked to cosmetic wastewater

3.5. Ecological Risk Assessment

TCS and TCC: Studies indicate that these two compounds pose a significant risk to the aquatic ecosystem, particularly in lakes such as Thien Quang and Ba Mau, which exhibited high Risk Quotients (RQ). Other lakes, including West Lake and Hoan Kiem Lake, are also at high risk, while Yen So Lake presents the lowest ecological risk.

Parabens: Although some paraben types showed low RQ values—indicating moderate risk—Methylparaben (MeP) and Propylparaben (PrP) had RQ values greater than 1. This suggests a potential for significant adverse impacts on microorganisms.

CHAPTER 4: CONCLUSIONS AND RECOMMENDATIONS

The study successfully developed a suitable analytical method for the determination of TCS, TCC, parabens, and bisphenols in lake and river water. By utilizing Solid Phase Extraction (SPE) coupled with Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS), the method provided accurate and reliable results.

+ Triclosan (TCS): The Method Detection Limit (MDL) was 0.07 ng/mL, the Method Quantification Limit (MQL) was 0.2 ng/mL, and the recovery rate (Re) ranged from 89.4% to 96.5%.

+ Parabens: The MDL and MQL for various parabens (MeP, PrP, etc.) ranged from 0.05 to 0.28 ng/mL and 0.15 to 0.84 ng/mL, respectively. Recovery rates ranged from 83.1% to 89.5%.

+ Bisphenols: The MDL and MQL for BPA and BPF were 1.2 ng/L and 3.6 ng/L, respectively. Recovery rates reached 91.6% and 84.0%. *(Note: I have adjusted the units to ng/L as per the standard for Bisphenols mentioned in your previous sections; please verify if they should be ng/mL).*

+ The validated method was applied to analyze concentrations of TCS, TCC, parabens, and bisphenols in swimming pool, lake, and river water samples collected in the Hanoi area from 2023 to 2024.

+ Risk Assessment: The study estimated the ecological risks posed by the accumulation of these substances in water samples for three trophic levels: algae, crustaceans (Daphnia), and common carp.

RECOMMENDATIONS

Based on the research findings, the following recommendations are proposed:

- **Advanced Method Development:** Develop analytical techniques for the simultaneous determination of multiple EDC groups (TCS, TCC, parabens, and bisphenols) across diverse, complex matrices.
- **Expanded Monitoring:** Broaden environmental surveys to comprehensively assess pollution levels and conduct holistic risk assessments for human and aquatic health

NOVEL CONTRIBUTIONS OF THE THESIS

1. Standardized Analytical Methodology: The study has established highly accurate and efficient standardized analytical methods for determining emerging endocrine-disrupting chemicals (EDCs)—including TCS, TCC, parabens, and bisphenols—in aqueous matrices. This was achieved by utilizing Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS) in combination with traditional Solid Phase Extraction (SPE) techniques.

2. Baseline Data for Urban Hanoi: The research provides an original and comprehensive baseline dataset regarding the distribution levels of TCS, TCC, parabens, and bisphenols across various types of water samples collected within the urban districts of Hanoi.

3. Insights into Ecological Risks: The study offers new insights into the risks associated with the accumulation of TCS, TCC, parabens, and bisphenols in diverse water bodies in urban Hanoi. These findings serve as a critical scientific foundation for conducting specialized and in-depth environmental research in the future.

PUBLISHED WORKS RELATED TO THE THESIS

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2. **Nguyen Thuy Ta**, Vu Le, Anh Duy Dao, Anh Ngoc Nguyen, Cuc Kim Thi Pham, Yen Hai Dao, Mai Thi Dang, Ngoc Chau Chu, Huyen Thanh Thi Nguyen, Tri Manh Tran (2025), 'Study on the method for analysis of parabens in swimming pool water samples'', Tạp chí Phân tích Hóa, Lý và Sinh học, được Hội đồng Giáo sư Nhà nước tính 1,0 điểm từ năm 2025, NCS là tác giả đứng tên đầu.

3. **Nguyen Thuy Ta**, Anh Duy Dao, Anh Hong Duong, Ngoc Thuy Nguyen, Yen Hai Dao, Tri Manh Tran (2025) "Development of the method for determination of bisphenol A and bisphenol F in water samples", 78-86, Analytica Vietnam conference 2025. Hội nghị quốc tế có số ISBN: 978-604-43-4341-9, được Hội đồng Giáo sư Nhà nước tính 1,0 điểm, NCS là tác giả đứng tên đầu.

4. **Tạ Thủy Nguyên**, Đào Duy Anh, Chu Ngọc Châu, Đặng Văn Long, Hoàng Quốc Anh, Phạm Gia Bách, Từ Bình Minh, Trần Mạnh Trí (2025), 'Sự phân bố của các nhóm chất hữu cơ mới nổi trong nước mặt tại một số khu vực nội đô Hà Nội'', 400-408, Hội thảo về Thực trạng và giải pháp xử lý các vấn đề cấp bách trong công tác bảo vệ môi trường thủ đô Hà Nội.

5. Anh Duy Dao, **Nguyen Thuy Ta**, Ha My Nu Nguyen, Ngoc Chau Chu, Long Van Dang, Anh Quoc Hoang, Tu Binh Minh, Tri Manh Tran (2025), 'Development of an Effective method for the determination of p-Hydroxybenzoic Acid esters (Parabens) surface sediment in To Lich river', VNU Journal of Science