

**FORENSIC SCREENING OF PHTHALATE COMPOUNDS IN PERFUMES
USING GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS)
AND CHEMOMETRIC ANALYSIS**

By

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Science

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CERTIFICATE

This is to certify that the dissertation entitled “**Forensic Screening of Phthalate Compounds in Perfumes using Gas Chromatography-Mass Spectrometry (GC-MS) and Chemometric Analysis**” is a bona fide record of research work carried out by NUR FAQIHAH BINTI MOHD FADZIL. During the period of October 2025 to February 2025 under my supervision.

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DECLARATION

I hereby declare that this thesis is the result of my own investigation, except where otherwise stated and duly acknowledge. I also declared that it has not been previously or concurrently submitted as a whole for any other degrees at University Sains Malaysia or other institutions. I grant University Sains Malaysia the right to use the dissertation for teaching and promotional purposes.

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LIST OF SYMBOLS

%	Percent
μL	Microliter
$^{\circ}\text{C}$	Degree Celcius
m/z	Mass-to-charge-ratio
v/v	Volume per volume
Log K_{ow}	Octanol–water partition coefficient
R_t	Retention time
TIC	Total Ion Chromatogram
EIC	Extract Ion Chromatogram

LIST OF ABBREVIATIONS

BBP	Benzyl Butyl Phthalate
DBP	Dibutyl Phthalate
DEHP	Di(2-ethylhexyl) Phthalate
DEP	Diethyl Phthalate
DMP	Dimethyl Phthalate
EDC	Endocrine Disrupting Chemical
EDT	Eau de Toilette
EDP	Eau de Parfum
EIC	Extracted Ion Chromatogram
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
GCMS	Gas Chromatography Mass Spectrometry
HMW	High Molecular Weight
LMW	Low Molecular Weight
MS	Mass Spectrometry
NIST	National Institute of Standards and Technology
PCA	Principal Component Analysis

ABSTRAK

Penggunaan formulasi pewangi sintetik yang semakin meluas telah meningkatkan penggunaan sebatian ester berasid, terutamanya ester ftalat, dalam minyak wangi komersial sebagai pelarut dan bahan pengikat bau (fixative). Walaupun berfungsi meningkatkan kestabilan dan ketahanan bau, ftalat dikenali sebagai bahan pengganggu sistem endokrin (endocrine-disrupting chemicals, EDC) dan selalunya tidak dinyatakan secara jelas pada label produk. Keadaan ini menimbulkan kebimbangan dari sudut toksikologi, peraturan serta siasatan forensik berkaitan pendedahan pengguna. Kajian ini bertujuan menjalankan saringan forensik sebatian ester berasid dalam minyak wangi menggunakan Kromatografi Gas–Spektrometri Jisim (GC–MS). Sebanyak 45 sampel minyak wangi yang mewakili pelbagai kategori kepekatan (minyak wangi, *extrait de parfum*, *eau de parfum* dan *eau de toilette*) telah dikumpulkan dari pasaran tempatan. Sampel dianalisis menggunakan GCMS bagi mengesan kehadiran ftalat pada aras surih. Pengenalpastian tentatif sebatian yang dikesan dilakukan melalui perbandingan spektrum jisim dengan pustaka NIST, dengan penekanan kepada ion serpihan diagnostik yang mencirikan ftalat. Penggunaan Kromatogram Ion Terekstrak (Extracted Ion Chromatogram, EIC) meningkatkan kekhususan pengesanan. Analisis kemometrik, khususnya Analisis Komponen Utama (Principal Component Analysis, PCA), diaplikasikan terhadap data GC–MS untuk membezakan sampel minyak wangi berdasarkan profil kimia masing-masing. Hasil kajian menunjukkan bahawa GC–MS merupakan teknik yang sensitif dan boleh dipercayai untuk pengesanan forensik sebatian ester berasid dalam matriks pewangi yang kompleks. Kehadiran ftalat dalam pelbagai jenis minyak wangi menekankan keperluan pemantauan analitik berkala, pelabelan yang telus serta penguatkuasaan peraturan. Integrasi teknik kemometrik turut menyokong pembezaan sampel dan mengukuhkan tafsiran

forensik. Secara keseluruhannya, kajian ini menyediakan asas saintifik bagi penilaian keselamatan kimia dan penyiasatan forensik utk produk formulasi minyak wangi.

ABSTRACT

Acid ester compounds, especially phthalate esters, are now more frequently used as fixatives and solvents in commercial perfumes due to the extensive use of synthetic fragrance compositions. Phthalates are rarely disclosed in formulations despite known as endocrine-disrupting chemicals (EDCs). Concerns about consumer exposure are raised from a toxicological, regulatory, and forensic perspective. This work aims to use gas chromatography–mass spectrometry (GCMS) to perform a forensic screening of acid ester chemicals in perfumes. From the local market, 45 perfume samples of various concentration categories (perfume oil, extrait de parfum, eau de parfum, and eau de toilette) were gathered. GCMS was used to screen and find traces of phthalates in the samples. By comparing mass spectrum data with the NIST library and concentrating on diagnostic fragment ions typical of phthalates, the discovered chemicals were tentatively identified. To improve detection specificity, Extracted Ion Chromatograms (EICs) were employed. To separate perfume samples according to their chemical profiles, GCMS data was subjected to chemometric analysis, specifically Principal Component Analysis (PCA). The study shows that GCMS is a sensitive and trustworthy method for identifying acid ester chemicals in intricate scent matrices. Phthalates are present in many types of perfumes, which emphasises the significance of regular analytical monitoring, clear labelling, and regulatory enforcement. Forensic interpretation is strengthened, and sample discrimination is further supported through the inclusion of chemometric techniques. All things considered, this work offers a solid foundation for assessing chemical safety and conducting forensic analysis of scent mixtur

CHAPTER 1

INTRODUCTION

1.1 Background of the study

The perfume industry has evolved dynamically due to advancement of synthetic fragrances, which is chemically related to a class of chemicals known as esters. These adaptable organic compounds vital to the fragrance industry are created when acids and alcohols react, and they are prized for their capacity to recreate a variety of scents. Esters special quality has made them essential in the perfumery industry, giving innumerable scents depth, complexity, and a classic appeal (Koh, 2024). Phthalate esters, (shown in Figure 1.1) such as diethyl phthalate (DEP), dimethyl phthalate (DMP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), and di(2-ethylhexyl) phthalate (DEHP), are often employed as synthetic fixatives to stabilise volatile scent molecules. These substances generally improve the overall olfactory experience by slowing evaporation and prolonging the scent.

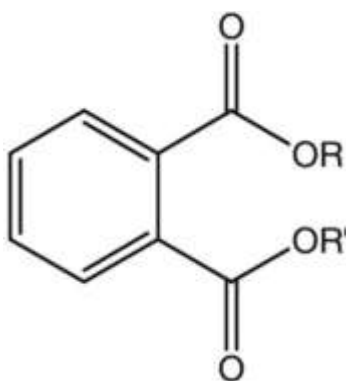


Figure 1.1 General chemical structure of phthalate esters (Savoca et al., 2023).

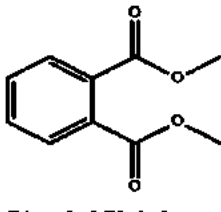
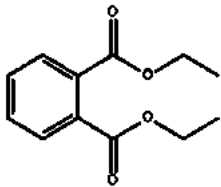
Depending on their molecular weight, phthalates display a variety of chemical and physical characteristics (Table 1.1). Due to their smaller molecular structures and weaker intermolecular interactions, low-molecular-weight (LMW) phthalates like DMP, DEP, and DBP typically have lower boiling temperatures and higher volatility. Because of these characteristics, they are more suited for usage in fragrance and cosmetic formulations where aroma diffusion requires a modest level of volatility. For example, DEP ($\text{Log } K_{ow} = 2.47$) and DMP ($\text{Log } K_{ow} = 1.6$) evaporate more easily, making them useful as fixatives and solvents in perfumes and personal care items (Huang et al., 2021).

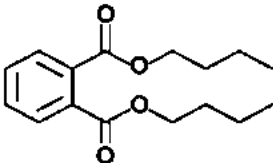
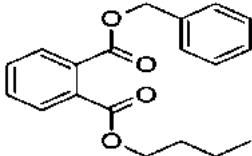
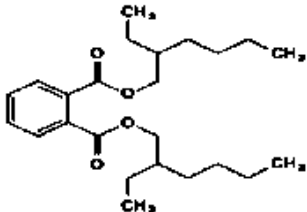
On the other hand, high-molecular-weight (HMW) phthalates, such as DEHP and BBP, have lesser volatility and higher boiling temperatures. Because of their higher molecular size and stronger van der Waals forces, they have lower vapour pressures, which makes them more heat-resistant and stable. Because of these qualities, HMW phthalates are perfect as plasticisers in PVC materials, where long-term performance, flexibility, and durability are more important than volatility. For instance, DEHP ($\text{Log } K_{ow} = 7.5$), a popular HMW phthalate, is widely used in industrial and medical products such as flooring and tubing since it is essentially non-volatile (Huang et al., 2021).

Overall, boiling point increases and volatility falls with increasing molecular weight and $\text{Log } K_{ow}$. The uses of each type of phthalate are directly influenced by this physicochemical relationship; HMW phthalates are used in durable plastic materials, while LMW phthalates are chosen in volatile consumer goods like perfumes (Huang et al., 2021).

Table 1.1 Summary of low- molecular-weight (LMW) and high-molecular-weight (HMW)

Phthalates, their properties, and applications (Huang et al., 2021)

No	Phthalate types	Classification (Molecular Weight)	Log K_{ow}	Typical Use and Applications
1	Dimethylphthalate (DMP), $C_{10}H_{10}O_4$ 	LMW (194.19 g/mol)	1.6	Perfumes, insect repellents, cellulose acetate plasticiser, solvents, and personal hygiene items
2	Diethyl phthalate (DEP), $C_{12}H_{14}O_4$ 	LMW (222.24 g/mol)	2.47	Fixative for cosmetics and fragrances, solvent to extend aroma
3	Di-n-4butyl phthalate (DBP), $C_{16}H_{22}O_4$	LMW (278.34 g/mol)	4.5	Printing inks, adhesives, nail

				polish, cellulose esters, and historically, plastics
4	<p>Butyl benzyl phthalate (BBP)</p> <p>$C_{19}H_{20}O_4$</p> 	<p>LMW–mid</p> <p>312.36</p>	4.7	<p>PVC</p> <p>plasticiser:</p> <p>adhesives,</p> <p>synthetic</p> <p>leather, and</p> <p>vinyl flooring</p>
5	<p>Di(2-ethylhexyl) phthalate (DEHP),</p> <p>$C_{24}H_{38}O_4$</p> 	<p>HMW 390.56</p>	7.5	<p>PVC</p> <p>plasticiser:</p> <p>waterproofing</p> <p>materials,</p> <p>flooring, wires,</p> <p>and medical</p> <p>tubing</p>

1.2 Problem statement

Mostafa and Shaaban (2023) have discovered an increasing prevalence of unreported phthalate esters in scent goods. Despite regulatory requirements that all chemical contents be disclosed, phthalates are frequently left off of ingredient lists and hidden under broad phrases like "fragrance" or "parfum." Phthalates may not be listed on the product packaging, so users may be unaware of the exposure. This lack of transparency raises serious toxicological and regulatory problems, as consumers may unknowingly be exposed to potentially dangerous compounds (Al-Saleh & Elkhatib, 2016).

These findings studied products from other regions. Nonetheless, it highlights the relevance of undeclared additives as concealed sources of chemical exposure, with important forensic and toxicological implications. Therefore, it is important to study similar samples from the local market. Given that phthalates are well-known endocrine disrupting chemicals (EDCs) that interfere with hormonal function and have an impact on reproductive and developmental health, their undisclosed presence in perfumes highlights the critical need for stricter analytical monitoring, transparent labelling practices, and harmonised international regulatory standards to protect consumer health (Al-Saleh & Elkhatib, 2016).

1.3 Objective

In general, this study aims perform a forensic screening analysis using GC_MS to screen and detect phthalates in perfumes sold in local markets.

1.3.1 Specific Objectives

The study is directed to the following particular goals in order to accomplish the main objective:

i. **To screen and detect the presence of phthalates in various perfume samples**

This goal entails a preliminary analysis of particular perfume goods to identify the presence of phthalates. GC-MS was used in the screening procedure to examine each sample's volatile and semi-volatile components. The technique will enable the detection of these substances even at trace quantities by recognising distinctive mass spectral fragments and retention periods. This stage is crucial for determining how common these chemicals are across various brands, formulations, and price points, providing information on consumer exposure and industry practices.

ii. **To tentatively identify the detected phthalates using targeted mass spectral analysis**

The next goal is to potentially identify the individual compounds found after the presence of phthalates has been confirmed. Comprehensive mass spectral data from GC-MS can be compared to recognized NIST spectral libraries and reference standards. This identification procedure will assist in differentiating between various phthalates (such as diethyl phthalate, dibutyl phthalate, and dimethyl phthalate). For the purpose of evaluating possible health hazards and comprehending the chemical diversity present in perfume formulations, accurate identification is essential.

iii. **To discriminate the various perfume samples using chemometric method**

The goal is to use chemometric approaches, which allow for the interpretation of complex analytical data from experimental techniques like GC-MS, to distinguish and categorise different perfume samples. Principal Component Analysis (PCA), a

multivariate statistical tool, is used in this method to find patterns, similarities, and differences in the chemical compositions of various types of perfumes. Chemometric analysis offers a deeper understanding of the chemical profile and quality differentiation of perfume samples by successfully differentiating changes related to fragrance concentration, formulation, or the presence of chemicals such as phthalates.

1.4 Research questions

- i. Is there undeclared phthalates present in perfumes sold in local market?
- ii. Can trace level phthalates detected using GCMS target screening method?
- iii. How to discriminate types of perfumes using the GCMS data?

1.5 Significance of the study

This work produce solid analytical data that can further knowledge of chemical safety in perfumes by utilising the sensitivity and specificity of GC-MS. The forensic method used in this study places a strong emphasis on tentative identification and trace-level detection. The study's ultimate goal is to offer a simple and effective method with scientific basis for evaluating scents' chemical makeup and support forensic and regulatory investigation in cosmetic chemistry

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

This chapter reviews the regulatory, chemical and analytical background relevant to the forensic screening of phthalate compounds in perfumes using gas chromatography–mass spectrometry (GC–MS). It begins with the Malaysian and ASEAN regulatory framework governing cosmetic safety and restricted ingredients, followed by a concise overview of perfumes, making showing perfumes as complex chemical matrices where phthalates may occur as functional additives or contaminants. The chapter then summarises the chemistry of phthalate esters and their significance as endocrine disrupting chemicals. Next, analytical approaches for phthalate detection are compared, with emphasis on GC–MS identification features, quality considerations, and recent studies that motivate the present work and to identify the research gap addressed by this study.

2.1 Regulatory and Safety Framework for Cosmetics in Malaysia

In Malaysia, perfumes are regulated as cosmetic products under the Control of Drugs and Cosmetics Regulations 1984 (CDCR 1984) enacted pursuant to the Sale of Food and Drugs Act 1952. The regulatory framework aims to ensure product safety, quality and consumer protection through a notification system, labelling requirements and post-market surveillance. Regulatory oversight is administered by the Drug Control Authority (DCA) with operational support from the National Pharmaceutical Regulatory Agency (NPRA) and the Director of Pharmaceutical Services. Enforcement actions may include inspection, compliance directives, product seizure and recall when non-compliance or safety risks are identified (Ministry of Health Malaysia, 1984).

The National Pharmaceutical Regulatory Agency (NPRA) and the Director of Pharmaceutical Services assist the Drug Control Authority (DCA) in carrying out regulatory control. These organisations are in charge of enforcing CDCR 1984 compliance and regulating cosmetic items. Cosmetics, which also include perfumes, are defined by the Regulations as goods that are meant to be applied externally to the human body, including fragrances and perfumes, and they are not allowed to claim to be medicinal. Before being put on the market, cosmetics must be reported to the Director of Pharmaceutical Services under a notification procedure. The maker, importer, or person in charge of putting the goods on the market bears responsibility for compliance (Ministry of Health Malaysia, 1984). Regulation states that any cosmetics must be properly marked, prepared under suitable quality control circumstances, and free of prohibited substances.

2.1.1 Regulatory control of phthalates under CDCR 1984 and ASEAN Cosmetic Directive

Phthalates are not always explicitly listed as prohibited across all cosmetic categories in national legislation; however, cosmetics marketed in Malaysia must meet general safety as per requirements under CDCR 1984, including the prohibition of harmful, unauthorised or mislabelled products that may endanger consumer health. Malaysia also implements the ASEAN Cosmetic Directive (ACD), which harmonises ingredient restrictions across ASEAN member states. Under the ACD, specific high-risk phthalates associated with reproductive toxicity and endocrine disruption (e.g., dibutyl phthalate, benzyl butyl phthalate and di(2-ethylhexyl) phthalate) are restricted or prohibited via the relevant annexes. Consequently, forensic screening is important to verify compliance, particularly when ingredient disclosure is limited for ‘fragrance’ components (NPRA, 2024).

Table 2.1 Examples of phthalates of regulatory concern in cosmetic products.

Phthalate	Common use/role in products	Regulatory concern (general)
Diethyl phthalate (DEP)	Solvent/fixative in fragrances (historical/common)	Monitored due to exposure concerns; disclosure may be limited
Dimethyl phthalate (DMP)	Solvent/diluent; formulation aid	Monitored due to exposure concerns
Dibutyl phthalate (DBP)	Plasticiser; formulation aid	Restricted/banned in many cosmetic frameworks due to reproductive toxicity
Benzyl butyl phthalate (BBP)	Plasticiser	Restricted/banned in many cosmetic frameworks due to reproductive toxicity
Di(2-ethylhexyl) phthalate (DEHP)	Plasticiser; potential packaging migration	Restricted/banned in many cosmetic frameworks due to reproductive toxicity

Phthalates such as dimethyl phthalate (DMP) and diethyl phthalate (DEP) are frequently used in cosmetic formulations to increase product flexibility and aroma retention. Safety assessments have justified its usage at low concentrations due to the low toxicological risk under controlled exposure. Other phthalates, such as benzyl butyl phthalate (BBP), dibutyl phthalate (DBP), and di(2-

ethylhexyl) phthalate (DEHP), are known to be harmful to reproduction and development. As a result, these substances are strongly restricted by the ASEAN Cosmetic Directive (ACD), which has been implemented into Malaysia's regulatory framework by the National Pharmaceutical Regulatory Agency (NPRA) (ASEAN, 2021).

The ACD, enforced by NPRA, includes Annex II, (Table 2.2) listed compounds that are not permitted in cosmetic products. DBP, which was previously used as a plasticiser in nail polish and perfumes, is now banned due to its well-documented reproductive toxicity and endocrine disruptive effects. Malaysia's restriction on DBP indicates its commitment to consumer protection and the harmonisation of cosmetic safety standards throughout ASEAN member nations (ASEAN, 2021). Under this harmonised approach, cosmetics sold in Malaysia must meet ASEAN-wide safety standards to ensure that they are devoid of high-risk chemicals (NPRA, 2024).

2.2 Perfumes as a chemical matrix relevant to forensic screening

Table 2.2 Annex II List of substance which must not form part
of the composition of cosmetic products

Substances	CAS Number	Ref. No
1-Chloro-2,3-epoxypropane	106-89-8	657
R-1-Chloro-2,3-epoxypropane	51594-55-9	658
1,2-Epoxy-3-phenoxypropane	122-60-1	659
2,3-Epoxypropan-1-ol	556-52-5	660
R-2,3-Epoxy-1-propanol	57044-25-4	661
2,2'-Bioxirane	1464-53-5	662
(2RS,3RS)-3-(2-Chlorophenyl)-2-(4-fluorophenyl)-[1H-1,2,4-triazol-1-yl)methyl]oxirane; epoxiconazole	133855-98-8	663
Chloromethyl methyl ether	107-30-2	664
2-Methoxyethanol [Ethylene glycol monomethyl ether (EGMME)]	109-86-4	665
2-Ethoxyethanol [Ethylene glycol monoethyl ether (EGMEE)]	110-80-5	666
Oxybis[chloromethane]; bis (Chloromethyl) ether	542-88-1	667
2-Methoxypropanol	1589-47-5	668
Propiolactone	57-57-8	669
Dimethylcarbamoyl chloride	79-44-7	670
Urethane	51-79-6	671
2-Methoxyethyl acetate	110-49-6	672
2-Ethoxyethyl acetate	111-15-9	673
Methoxyacetic acid	625-45-6	674
Dibutyl phthalate	84-74-2	675

2.3 Perfume concentration categories (oil, extrait, EDP, EDT)

Commercial perfumes are often grouped by fragrance oil concentration: perfume oil, extrait de parfum, eau de parfum (EDP) and eau de toilette (EDT) (lower). Perfume oils, derived from natural or synthetic aromatic compounds, are the major source of fragrance in perfumes and give them

their distinct scent (Panda, 2010). They are the foundation of several perfume varieties, including Extrait de Parfum, which has the maximum oil content for a strong and long-lasting aroma. Eau de Parfum (EDP) has a somewhat lower concentration, which balances longevity with subtlety, but Eau de Toilette (EDT) has the lowest concentration, resulting in a lighter, more transient aroma. The concentration of fragrance oil impacts the strength and persistence of the aroma on the skin.

Differences in oil-to-solvent ratio also can influence matrix complexity and may affect analytical recovery, chromatographic behaviour and potential reliance on stabilisers. Therefore, method development should account for variability across different perfume categories.

2.4 Overview of perfumes chemistry

Perfumes are multi-component mixtures that typically contain aromatic compounds, a volatile carrier solvent (commonly ethanol) and fixatives that slow evaporation and stabilise the fragrance profile. From an analytical standpoint, perfume matrices can be complex, containing dozens to hundreds of volatile and semi-volatile components that may co-elute or contribute background signals (Panda, 2010).

Perfume formulation is a multidisciplinary process that combines chemistry and sensory research to create enticing, long-lasting smells. It is made up of three important components which are solvents, aromatic ingredients and fixatives (Panda, 2010).

First is the solvents, which work as transporters for aromatic molecules. Solvents most frequently used is ethanol, which act as carriers that dilute and disperse aromatic chemicals. Secondly, aromatic compounds, which offer the particular odours that distinguish each fragrance. Therefore, a thorough understanding of these ingredients' roles and interactions is essential for creating

balanced, stable, and long-lasting perfumes (Panda, 2010; Logan & Rumbaugh, 2012; Mostafa & Shaaban, 2023). The third important component is the fixatives.

Fixatives serve to stabilise volatile compounds and extend fragrance longevity. Phthalate esters are among the most commonly utilised synthetic additives for improving performance and stability. Fixatives are also significant in perfume creation since they stabilise volatile chemicals and increase the scent's persistence on the skin. Traditional fixatives like musks, balsams, and resins anchor lighter top notes and balance the whole blend by slowing their evaporation. Synthetic fixatives are frequently used in modern perfumery to provide consistency, cost efficiency, and safety compliance while preserving the ideal olfactory balance (Logan & Rumbaugh, 2012).

2.5 Phthalate esters: structure, properties and occurrence

Phthalate esters (phthalic acid diesters) are produced via esterification of phthalic anhydride with alcohols. Their physicochemical properties are governed mainly by the length and branching of the alkyl side chains, influencing volatility, hydrophobicity and partitioning behaviour. Many phthalates are colourless, slightly oily liquids at room temperature and can persist in consumer product matrices. In fragrances, phthalates have been reported as fixatives that reduce evaporation of aromatic compounds and improve scent longevity and formulation stability. General chemical structure of phthalate esters are as shown in Section 1.1 earlier (Ashcroft et al., 2024).

2.6 Sources of phthalates in perfumes

Phthalates may be present in perfumes for two main reasons: (i) as discussed earlier, intentional use as functional additives such as fixatives or carrier solvents (particularly low-molecular-weight

phthalates like DEP and DMP), and (ii) unintentional contamination or migration from plastic packaging materials where phthalates act as plasticisers. These factors justify robust confirmatory methods for screening. Distinguishing between intentional use and contamination requires careful interpretation supported by concentration levels, product type, packaging information, and analytical quality controls.

2.6.1 Phthalates as endocrine disrupting chemicals

One of the many reasons for detection of phthalates in cosmetic product is that it is known to be an endocrine disrupting chemical (EDC). EDCs are exogenous substances that may interfere with hormonal signalling pathways and cause adverse biological effects. Phthalates are widely discussed as EDCs because they can influence endocrine function through multiple mechanisms, including receptor-mediated interactions and disruption of hormone synthesis, transport or metabolism. Their lipophilic nature can promote distribution into fatty tissues, raising concern for chronic exposure (Ashcroft et al., 2024).

In addition, a study by Parlett et al. (2013) found that perfume use was substantially related with higher urine levels of monoethyl phthalate (MEP), indicating exposure to diethyl phthalate (DEP) from fragranced personal care items. Their bivariate analysis found that women who used perfume, deodorant, hairspray, or conditioner had significantly greater MEP levels than non-users (Figure 1.4). Other metabolites, such as monocarboxyisooctyl phthalate (MCPP), mono-isobutyl phthalate (MiBP), mono-n-butyl phthalate (MnBP), and monomethyl phthalate (MMP), exhibited little fluctuation in urine levels.

Figure 2.1 shows that cumulative use of scented items increases exposure to DEP, as urine MEP concentrations increased proportionally with the number of personal care products (PCPs) utilised. However, the concentrations of MCPP, MiBP, MnBP, and MMP remained rather stable, indicating that these metabolites are less affected by successive PCP administrations.

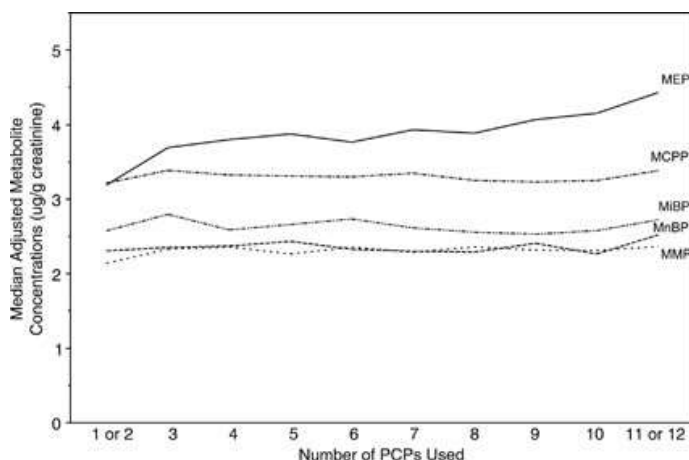


Figure 2.1 Median concentration changes of specific phthalate metabolites relative to the total number of PCPs consumed during the previous 24 hours.

Al-Saleh and Elkhatib (2016) found five major phthalate esters which are diethyl phthalate (DEP), dimethyl phthalate (DMP), benzyl butyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP), and dibutyl phthalate (DBP) in nearly all tested perfume samples, despite the fact that these compounds were not declared on product labels. The investigation found 100% detection frequency for DEP, DMP, and BBP, demonstrating their widespread and undocumented use in scent formulations. This toxicological context strengthens the forensic and public-health relevance of screening perfumes for phthalate residues.

2.7 Analytical approaches for detecting phthalates in perfumes

Analytical techniques used for phthalate detection include spectroscopic screening (FTIR, UV–Vis) and chromatographic methods (HPLC–UV/DAD, LC–MS/MS, GC–MS). These advantages and disadvantages of the techniques are compared as listed in Table 2.3. Screening methods may provide rapid preliminary indication, but confirmatory identification in complex fragrance matrices generally requires chromatographic separation and compound-specific detection. GC–MS is widely used for volatile and semi-volatile phthalate esters because it provides both separation and mass spectral confirmation (Ashcroft et al., 2024; Mostafa & Shaaban, 2023).

Table 2.3 Comparison of analytical techniques commonly applied to phthalate detection

Technique	Principle	Strength	Limitation
GC–MS	Chromatographic separation with mass spectral identification	Confirmatory; high sensitivity and selectivity	Higher cost; requires skilled operation; contamination control needed
HPLC–UV/DAD	Liquid chromatographic separation with UV detection	Accessible and reasonably sensitive	Lower specificity than MS; solvent use and maintenance
LC–MS/MS	Liquid separation with tandem MS fragmentation	Very high sensitivity and	High capital/maintenance

		confirmation in complex matrices	cost; method complexity
FTIR	Infrared absorption (functional group information)	Rapid screening; minimal preparation	Limited selectivity for mixtures; not confirmatory alone
UV–Vis	UV absorbance by chromophores	Simple and low cost for screening	Low selectivity; usually requires extraction and confirmation

2.8 GC–MS identification of phthalates: diagnostic features and quality considerations

Under electron impact ionisation, phthalate esters yield characteristic fragment ions that support confirmatory identification. A common diagnostic ion is m/z 149, associated with the phthalate core fragment, while additional ions vary with side-chain structure and enable differentiation among individual phthalates. Reliable identification in perfume matrices requires adequate chromatographic resolution, appropriate acquisition mode (full scan and/or selected ion monitoring), and comparison against validated mass spectral libraries and reference standards (Mostafa & Shaaban, 2023).

Table 2.4 Examples of phthalates and common diagnostic ions in EI-GC–MS

(Source: Adapted from Mostafa and Shaaban (2023) and Kazemi et al. (2022).

Compound	Typical diagnostic ions (m/z)	Analytical note	Typical relevance in perfumes
DEP	149, 177	Often strong 149 ion; confirm with retention time and library match	Reported as solvent/fixative; frequently detected
DBP	149, 205	Side-chain fragments aid discrimination from DEP	Regulatory concern; may be present as contaminant/additive
DEHP	149, 167, 279	Higher-MW fragments; may show broader peaks if contamination present	Common plasticiser; potential packaging/lab contamination

2.9 Contamination control and quality assurance in GC–MS phthalate screening

Phthalates are ubiquitous laboratory contaminants (e.g., from plastic consumables, septa, tubing, solvents and ambient laboratory sources). Consequently, robust QA/QC is critical, including the use of solvent blanks, procedural blanks, glassware preference over plastics where feasible, validated cleaning procedures, and monitoring of carryover. Instrument maintenance (liner/septum

replacement, inlet cleaning, column trimming and controlled bake-out) may be required when high-boiling contaminants accumulate and cause broad peaks or elevated background.

2.10 Previous studies and research gap

International studies have repeatedly reported undeclared phthalates in commercial perfumes and personal care products. Population-level biomonitoring studies have also linked perfume use with increased urinary metabolites consistent with DEP exposure (Parlett et al., 2012) . Analytical surveys of branded fragrances have reported high detection frequencies for DEP and varying frequencies for DMP, DBP, BBP and DEHP, including occasional exceedances of regulatory thresholds in certain jurisdictions. These findings emphasise the need for routine analytical screening using confirmatory methods. However, phthalate profiles may differ across markets and product types; therefore, localised forensic screening using validated GC–MS conditions remains necessary to characterise the presence of phthalates in perfumes available to consumers within the study context (Al-Saleh & Elkhatab, 2016).

Table 2.5 Selected studies reporting phthalates in perfumes or related exposure indicators using GCMS method.

Study	Matrix	Key phthalates reported	Key takeaway
Mostafa & Shaaban (2023)	Commercial perfumes	DEP (high frequency), DEHP, BBP, DBP, DMP	Undeclared phthalates detected; supports need for GC–MS screening

Al-Saleh & Elkhatib (2016)	Branded fragrances	DEP, DMP, BBP, DEHP, DBP	High prevalence of several phthalates; labelling limitations noted
Parlett et al. (2013)	Biomonitoring (urine metabolites)	MEP (DEP metabolite)	Perfume use associated with higher DEP exposure indicators

In Al-Saleh & Elkhatib (2016) study, result reveals 100% detection frequency for DEP, DMP, and BBP, in all 47 perfume samples tested despite the fact that these compounds were not declared on product labels. The findings is as tabulated in Table 2.6. This demonstrated a widespread and undocumented use in scent formulations.

Table 2.6 Overview of Phthalate Identification in 47 Branded Fragrances
(Al-Saleh & Elkhatib, 2016)

Phthalate Compound	Function in Perfume	% Detected (n=47)	% Above Threshold	EU Regulation Status	Mean Concentration (ppm)	Maximum (ppm)
DEP (Diethyl phthalate)	Solvent, fixative	100%	68.1% (>1 ppm)	Not restricted	1621.6	23,649.2

Phthalate Compound	Function in Perfume	% Detected (n=47)	% Above Threshold	EU Regulation Status	Mean Concentration (ppm)	Maximum (ppm)
DMP (Dimethyl phthalate)	Solvent, film-former	100%	72.3% (>0.1 ppm)	Not restricted	30.2	405.2
BBP (Benzyl butyl phthalate)	Plasticizer	100%	85.1% (>0.1 ppm)	Banned (EU)	8.4	186.8
DEHP (Di(2-ethylhexyl) phthalate)	Plasticizer	97.9%	36.2% (>1 ppm)	Banned (EU)	5.9	147.5
DBP (Dibutyl phthalate)	Plasticizer	51.1%	6.7% (>0.1 ppm)	Banned (EU)	0.03	0.59

A more recent studies have revealed similar outcome and proved the widespread use of undocumented phthalate esters in consumer fragrance goods. Mostafa and Shaaban (2023) used gas chromatography-mass spectrometry (GC-MS) to analyse 40 commercial perfume samples for the presence of five common phthalates: dimethyl phthalate (DMP), diethyl phthalate (DEP),

dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), and di(2-ethylhexyl) phthalate (DEHP). None of these chemicals were listed on the product ingredient label (Mostafa & Shaaban, 2023).

According to the results (Table 2.7) the study found DEP in 100% of the perfume samples, with values ranging from 771.67 µg/mL to 5766 µg/mL. While DEHP, a forbidden cosmetic ingredient in many countries, was found in 95% of the samples, with a mean value of 55.92 µg/mL and a high of 377.67 µg/mL (Mostafa & Shaaban, 2023). DMP, DBP, and BBP were found in 20%, 27.5%, and 57.5% of the samples, with average values ranging from 4.13 to 20.50 µg/mL (Mostafa & Shaaban, 2023).

These findings highlight the ongoing use of phthalates as undeclared components in commercial fragrances, despite existing limits and bans. The continual identification of these chemicals emphasises the critical need for stricter quality control methods, more product transparency, and enhanced regulatory monitoring in the fragrance business to ensure consumer safety and compliance (Mostafa & Shaaban, 2023).

Table 2.7 Concentrations (µg/mL) of the detected phthalate esters in the analyzed fragrance samples.

Phthalate	Detection Frequency (out of 40)	Detection Rate (%)	Mean Concentration (µg/mL)	Max Concentration (µg/mL)
DMP	8	20.0 %	20.76	60.00
DEP	40	100 %	771.67	5766.00

Phthalate	Detection Frequency (out of 40)	Detection Rate (%)	Mean Concentration (µg/mL)	Max Concentration (µg/mL)
DBP	11	27.5 %	15.18	66.00
BBP	23	57.5 %	4.13	22.50
DEHP	38	95.0 %	55.92	377.67

Detection of phthalates using scan mode in GCMS analysis can sometimes become problematic because many phthalates share the same major fragment ion (m/z 149) and often co-elute. Therefore the extracted ion chromatogram (EIC) technique is suggested in many technical notes to provide solution when detecting similar compounds such as phthalates in complex matrices (freeman et al, n.d.). It is suggested that EIC greatly enhances selectivity by isolating diagnostic ions such as m/z 177 for DEP or m/z 205 for DBP, enabling clearer differentiation between structurally similar esters. However, the study using this approach was not reported in research studies elsewhere.

2.11 Research Gap

While international studies have documented undeclared phthalates in commercial fragrances, no Malaysian study has specifically investigated phthalate residues in locally available perfumes using validated GC–MS methods. Existing literature also lacks comparative analysis across perfume concentration categories (extrait, EDP, EDT) and does not relate findings to Malaysian regulatory expectations. This study fills these gaps by conducting systematic fast and simple GC–MS screening and evaluating diagnostic ions to increase the sensitivity of detection and contextualising results within national regulatory requirements.