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A Revisit to Effervescence-Assisted Microextraction of Non-Polar Organic Compounds Using Hydrophobic Magnetic Nanoparticles: Application to the Determination of UV Filters in Natural Waters

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Τμήμα Χημείας

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Declaration / Statement of Originality

I hereby declare that this thesis, entitled "A Revisit to Effervescence-Assisted Microextraction of Non-Polar Organic Compounds Using Hydrophobic Magnetic Nanoparticles: Application to the Determination of UV Filters in Natural Waters" is the result of my own independent work and investigation, except where otherwise stated. All sources of information and data have been acknowledged. This thesis has not been submitted, either in whole or in part, for a degree or diploma to this or any other institution.

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Abstract

In this work, we revisited the method of effervescence-assisted microextraction, aiming to assess the effect of the process of effervescence on the extraction efficiency of organic compounds. We used a magnetic nano sorbent material composed of stearic acid coated cobalt-ferrite magnetic nanoparticles as an adsorbent and dispersed it in water using 12 combinations of acid and base mixtures at two different mass ratios. The solution pH; the ionic strength; and the duration of effervescence were calculated and correlated to the extraction efficiency of nonpolar UV filters from aqueous samples as model organic compounds. Our findings provide a general perspective on the influence of the process of effervescence on extraction efficiency. Based on these findings, we developed and optimized a new analytical method for extracting UV filters from water samples using HPLC-UV as a detector. The method was found to afford good linearity in the calibration curve, expanding by two orders of magnitude; satisfactory reproducibility and repeatability (1.8-11.1%), and high recoveries (78.4-127.1%). This *research* provides a new perspective on the influence of the process of effervescence on the extraction efficiency of nonpolar organic compounds and introduces a new method for extracting UV filters from aqueous media.

Περίληψη

Σε αυτήν την εργασία επανεξετάστηκε η μέθοδος της εκχύλισης με αναβρασμό (effervescence-assisted microextraction), με στόχο να αξιολογηθεί η επίδραση της διαδικασίας του αναβρασμού στην αποδοτικότητα εκχύλισης οργανικών ενώσεων. Για αυτόν τον σκοπό χρησιμοποιήθηκε ένα μαγνητικό νανοϋλικό, αποτελούμενο από μαγνητικά νανοσωματίδια κοβαλτίου-σιδήρου επικαλυμμένα με στεαρικό οξύ, ως ροφητικό μέσο, και έγινε διασπορά στο νερό χρησιμοποιώντας 12 συνδυασμούς μειγμάτων οξέος και βάσης σε δύο διαφορετικούς λόγους μάζας. Το pH του διαλύματος, η ιοντική ισχύς και η διάρκεια του αναβρασμού υπολογίστηκαν και συσχετίστηκαν με την αποδοτικότητα εκχύλισης μη πολικών αντηλιακών φίλτρων από υδατικά δείγματα, τα οποία χρησιμοποιήθηκαν ως πρότυπες οργανικές ενώσεις. Τα ευρήματά παρέχουν μια γενική εικόνα για την επίδραση της διαδικασίας του αναβρασμού στην αποδοτικότητα της εκχύλισης. Βάσει αυτών των αποτελεσμάτων, αναπτύχθηκε και βελτιστοποιήθηκε μια νέα αναλυτική μέθοδος για την εκχύλιση αντηλιακών φίλτρων από δείγματα νερού, χρησιμοποιώντας ανίχνευση με HPLC-UV. Η μέθοδος παρουσίασε καλή γραμμικότητα στην καμπύλη βαθμονόμησης (εύρος δύο τάξεων μεγέθους), ικανοποιητική αναπαραγωγιμότητα και επαναληψιμότητα (1,8–11,1%), καθώς και υψηλές αποδόσεις (78,4–127,1%). Η έρευνα αυτή προσφέρει μια νέα προοπτική σχετικά με την επίδραση της διαδικασίας του αναβρασμού στην αποδοτικότητα εκχύλισης μη πολικών οργανικών ενώσεων και εισάγει μια νέα μέθοδο για την εκχύλιση αντηλιακών φίλτρων από υδατικά μέσα.

Contents

List of abbreviations

Chapter 1: Microextraction Methods

- **LPE** – Liquid-Phase Extraction
- **LPME** – Liquid-Phase Microextraction
- **DLLME** – Dispersive Liquid-Liquid Microextraction
- **HF-LPME** – Hollow Fiber Liquid-Phase Microextraction
- **SDME / SD-LPME** – Single-Drop Microextraction / Single-Drop Liquid-Phase Microextraction
- **SPE** – Solid-Phase Extraction
- **SPME** – Solid-Phase Microextraction
- **SBSE** – Stir Bar Sorptive Extraction
- **TFME** – Thin-Film Microextraction
- **DSPME / D-m-SPE** – Dispersive Solid Phase Microextraction
- **EAME** – Effervescent-Assisted Microextraction
- **MEPS** – Microextraction in a Packed Syringe
- **HS-SPME** – Headspace Solid-Phase Microextraction
- **DI-SPME** – Direct Immersion Solid-Phase Microextraction
- **IT-SPME** – In-Tube Solid-Phase Microextraction
- **SPME-Tips** – In-Tip Solid-Phase Microextraction

Sorbent Materials

- **ILs** – Ionic Liquids
- **DESs / NADES** – Deep Eutectic Solvents / Natural Deep Eutectic Solvents
- **MOFs** – Metal-Organic Frameworks
- **COFs** – Covalent Organic Frameworks
- **MIPs** – Molecularly Imprinted Polymers

- **MWCNTs** – Multi-Walled Carbon Nanotubes
- **CNTs** – Carbon Nanotubes
- **GO** – Graphene Oxide
- **CDs / CQDs / GQDs / BCDs** – Carbon Dots / Carbon Quantum Dots / Graphene Quantum Dots / Biogenic Carbon Dots
- **SWCNTs** – Single-Walled Carbon Nanotubes
- **PDA** – Polydopamine
- **PDMS** – Polydimethylsiloxane
- **PEG / PES** – Polyethylene Glycol / Polyether Sulfone
- **POFs** – Porous Organic Frameworks
- **PILs** – Polymeric Ionic Liquids
- **MILs** – Magnetic Ionic Liquids
- **TSILs** – Task-Specific Ionic Liquids

UV Filters

- **UVFs** – Ultraviolet Filters
- **OMC** – Octyl Methoxycinnamate
- **OCR** – Octocrylene
- **BP-3, BP-4, BP-8** – Benzophenone derivatives
- **EHMC** – 2-Ethylhexyl-4-methoxycinnamate
- **4-MBC** – 4-Methylbenzylidene Camphor
- **PABA / OD-PABA** – Para-aminobenzoic Acid / Octyldimethyl PABA
- **IMC** – 3-Methylbutyl-(2E)-3-(4-methoxyphenyl)-acrylate
- **BDM** – 4-tert-butyl-4'-methoxydibenzoylmethane
- **BT** – Benzotriazole

- **PAHs / PCBs / PFAS / VOCs** – Polycyclic Aromatic Hydrocarbons / Polychlorinated Biphenyls / Per- and Polyfluoroalkyl Substances / Volatile Organic Compounds
- **CDOM / DOM** – Chromophoric Dissolved Organic Matter / Dissolved Organic Matter
- **ROS** – Reactive Oxygen Species

Analytical & Technical Terms

- **GC / LC / GC-MS / LC-MS / LC-MS/MS** – Gas Chromatography / Liquid Chromatography / GC–Mass Spectrometry / LC–Mass Spectrometry / Tandem LC–MS
- **ECD** – Electrochemical Detection
- **ICP-OES** – Inductively Coupled Plasma Optical Emission Spectrometry
- **LOD / LOQ / RSD** – Limit of Detection / Limit of Quantification / Relative Standard Deviation
- **Kow** – Octanol-Water Partition Coefficient
- **MRI** – Magnetic Resonance Imaging
- **SML** – Sea Surface Microlayer
- **EDCs** – Endocrine Disrupting Chemicals
- **API** – Active Pharmaceutical Ingredient

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PART I

THEORETICAL BACKGROUND

1. Microextraction methods

1.1. Introduction to Microextraction Methods

In the field of Green Analytical Chemistry, microextraction methods have developed as potent tools in analytical chemistry. These methods reduce the size of the samples, simplify the analytical procedures, and reduce the amount of toxic solvents that are used.

Microextraction methods have transformed analytical chemistry by providing several advantages over conventional extraction procedures. Their main benefit is miniaturization since they need only tiny quantities of liquids and sample sizes. This not only makes them more affordable but also environmentally benign, in line with the ideas of green chemistry [1], [2]. These methods also effectively remove trace analytes, so they are suitable for analyzing complex sample matrices [3], [4]. Another major benefit is that many microextraction methods are straightforward and don't call for costly equipment [5]. They are also rather versatile since they can be easily integrated with analytical instruments such as liquid chromatography (LC) and gas chromatography (GC). A smooth and effective analysis is made possible because of this [6], [7].

Microextraction methods have become vital in many other scientific fields because of their efficacy and flexibility. Environmental monitoring has benefited from them as they enable the identification of organic pollutants, heavy metals, and novel contaminants in soil and water, hence enabling pollution control and regulatory compliance [8], [9]. In the food sector, these methods are applied for the determination of bioactive compounds, pesticides, and other contaminants. Microextraction methods are also important in bioanalysis for examining medicines, metabolites, and biomolecules in biological samples, supporting drug development and medical research [10], [11].

Within the following chapter, we will conduct an analysis of the fundamental microextraction methods. We will focus on the fundamentals, as well as the advantages and disadvantages. Each strategy will be evaluated in terms of the extraction method, the efficiency of the extraction, and the applicability of the strategy for various matrices and analytes. Included in this discussion will be their contributions to the disciplines of bioanalysis, food analysis, and environmental monitoring, as well as their practical applications in other areas of scientific research. Understanding the advantages and disadvantages of every approach helps one to fully grasp their relevance and possibility for future success.

1.1.1. Liquid-phase micro-extraction (LPME) methods

Over the past two decades, liquid-phase microextraction (LPME) methods have emerged as powerful tools for sample pretreatment. They are offering various advantages, such as high preconcentration factors, minimal solvent consumption, and simplified procedures. This section presents an in-depth overview of commonly used LPME methods, such as dispersive liquid-liquid microextraction (DLLME), hollow fiber liquid-phase microextraction (HF-LPME), and single-drop microextraction (SDME) (Figure 1)(Table 1). These methods make use of the partitioning of analytes between a small volume of extraction solvent and the sample matrix. This partitioning is frequently improved by dispersion, membrane barriers, or droplet interfaces.

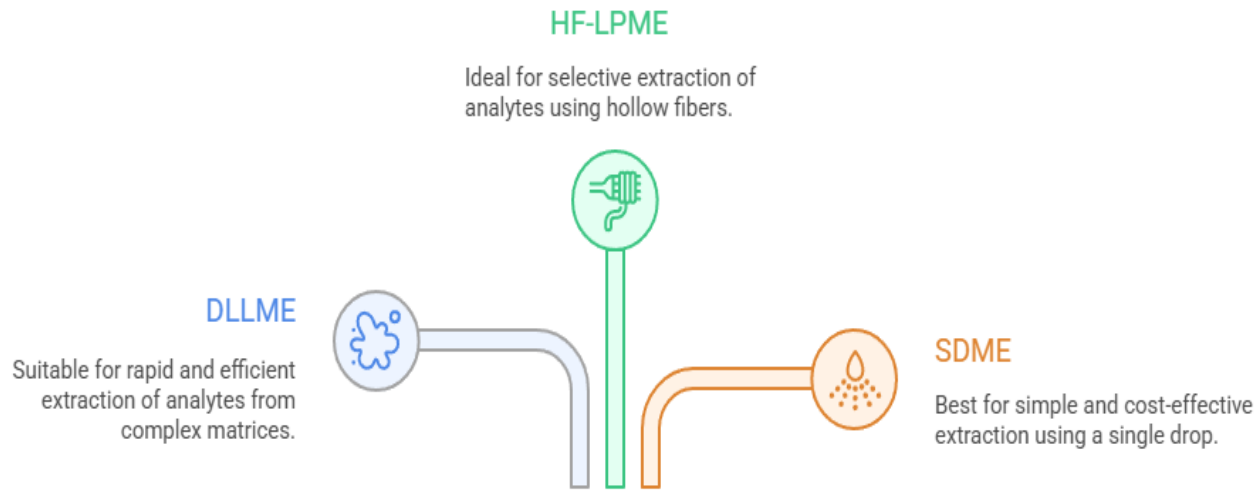

Figure 5: Commonly used LPME methods [12]

Table 1: Comparison of liquid phase extraction methods

Method	Key Features	Applications
DLLME	Rapid dispersion of extraction solvent, high surface contact, fast equilibrium	Trace analysis of pesticides, drugs, and metals in environmental, biological, and food samples
HF-LPME	Membrane-supported solvent interface, enhanced selectivity, low solvent use	Extraction of polar and non-polar analytes in complex matrices
SD-LPME	Single microliter-scale droplet, simple setup, solventless or low-solvent	Fast screening of volatile and semi-volatile compounds in water and urine

1.1.2. Solid-phase microextraction (µSPE) methods

Over the years, solid-phase microextraction (µSPE) methods have developed considerably, providing effective and eco-friendly alternatives for sample preparation in many analytical domains. This section provides an in-depth review of the most commonly used solid-phase microextraction (SPME) methods, including dispersive solid-phase microextraction (DSPME), stir-bar sorptive extraction (SBSE), solid-phase microextraction (SPME), thin-film microextraction (TFME), effervescent-assisted microextraction, and variants such as in-tip SPME, in-syringe SPME, and in-tube SPME (Figure 2). The concepts, benefits, uses, and current developments of each method are covered. Their main characteristics are summed up in Table 2.

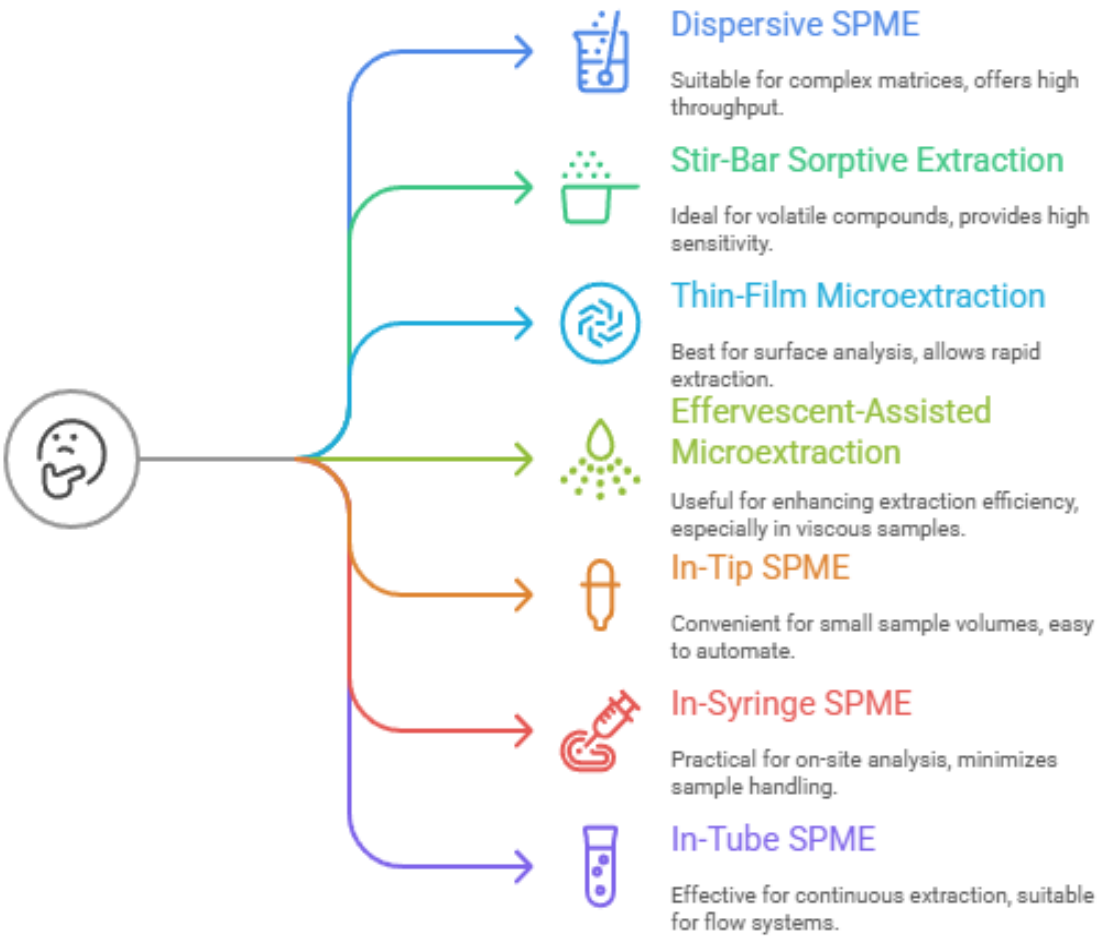

Figure 6: SPME methods comparison

Table 2: Comparison of Solid-Phase Extraction Methods

Method	**Key Features**	**Applications**
DSPME	Sample distribution, high surface area, rapid kinetics	Analysis of environmental and food samples, extraction of organic contaminants
SBSME	Sorbent-coated stir bar, high sensitivity, GC/LC compatibility	Removing semi-volatile and volatile organic chemicals
SPME	High selectivity, solventless, on-line coupling with analytical tools	Analysis of biological, environmental, and food samples
TFME	Minimal solvent use, large surface area, thin sorbent layer	Food analysis, metabolomics, and extraction of polar and non-polar chemicals
Effervescent-Assisted ME	Low cost, improved mass transfer, and use of effervescent tablets	Extraction from complicated matrices, environmental and food analysis

1.2.Liquid phase microextraction

Liquid phase microextraction (LPME) has shown many effective results in analytical chemistry. This is due to the various advantages that LPME presents as a method, which include low solvent consumption, small scale, and great extraction efficiency. Over the course of its existence, LPME has been through many changes that have led to its development in different sectors. Biological research, food safety, pharmaceutical analysis, and environmental monitoring are just some of its fields of application.

1.2.1. Principles and Modes of LPME

LPME is based on the principle of liquid-liquid extraction, where analytes are transferred from a donor phase to an acceptor phase. The method has several modes, and each has distinct operational principles and advantages:

1. **Dispersive Liquid-Liquid Microextraction (DLLME)**: In this method, a mixture of extraction solvent and disperser is injected into the sample. This produces a cloudiness in the solution. DLLME is well-known for its speed and efficiency, but it requires a careful ratio of the disperser to the solvent [13], [14].

2. **Hollow Fiber Liquid Phase Microextraction (HF-LPME)**: The method uses a porous hollow fiber, which is submerged in the sample solution. The organic solvent fills its pores to create a supported liquid membrane (SLM). Then the analytes are collected into the lumen. HF-LPME is known for its stability and suitability for complex matrices [14], [15].

3. **Single-Drop Microextraction (SDME)**: One drop of liquid is fixed in place at the syringe's tip. It is a simple and inexpensive method, but it is quite vulnerable to external factors [14], [15].

1.2.2. Advancements in LPME Methods

The development of LPME requires a greener approach with more sustainable solvents. For this reason, natural deep eutectic solvents (NADES) and deep eutectic solvents (DESs) have become popular due to their biodegradable nature and low toxicity. Also, their great solubility makes them a suitable candidate for several LPME modes, like hollow fiber LPME (HF-LPME) and dispersive liquid-liquid microextraction (DLLME). These methods are both sustainable and efficient, which explains their wide application [16], [17], [18].

Another key development is the automation and downsizing of LPME, which has significantly enhanced analytical accuracy and repeatability. LPME is an effective tool for high-throughput applications in clinical and environmental research, and it is also employed in flow-based systems, robotic platforms, and column-switching methods. It has overall simplified sample preparation and analysis [19], [20].

Analytical capability has been further improved by combining LPME with electrochemical detection (ECD). Also, it can be used instead of standard chromatographic methods and is easier to carry around. Methods such as cyclic voltammetry and stripping voltammetry help researchers to do direct post-extraction detection of analytes. They are therefore especially useful for the study of ions, medications, and other bioactive compounds [21].

Moreover, the LPME process's better selectivity and efficiency have come from including chemical processes. Derivatization, complexation, and phase transfer catalysis are among the methods that increase the target chemicals' extractability. At the same time, they guarantee fit with detection methods. These methods have expanded the field of LPME by allowing the extraction of labile or reactive compounds. It is therefore a flexible analytical method [22].

1.2.3. Applications of LPME

Liquid-phase microextraction can detect even the smallest traces of organic pollutants in water and soil. Magnetic ionic liquids and deep eutectic solvents have the potential to make the process even more accurate and efficient. LPME is consequently an essential method in environmental analysis [23].

Aside from its applications in the environment, LPME is also an essential component in pharmaceutical research. The analysis of drugs is one area in which it is extremely useful. For instance, it is utilized for chiral compounds, in which the separation of enantiomers is necessary. Additionally, the method aids in understanding drug metabolism and pharmacokinetics. This supports therapeutic drug monitoring with reliable results [24], [25].

In the food and beverage industry, LPME is widely used to detect additives, contaminants, and bioactive compounds. It is a suitable method for analyzing cinnamic acids in traditional Chinese medicines, or even for identifying organic pollutants in food [26], [27]. Its efficiency and ease of use make it an indispensable tool for ensuring food safety.

LPME is also useful in biomedical and forensic sciences. It allows for the analysis of biological samples such as blood, urine, and tissues. As far as the analytes are concerned, it is particularly

used for detecting drugs of abuse, toxicants, and other bioactive substances. Its exceptional sensitivity and selectivity make it a go-to method for forensic investigations and toxicology studies [24], [28].

1.2.4. Future Trends and Challenges in LPME

Despite significant advancements in LPME, challenges that need to be addressed remain. For example, there is limited compatibility of some extraction solvents with analytical instruments. Also, further miniaturization and automation are needed. Future research should focus on the development and application of novel green solvents. Moreover, the integration of LPME with advanced detection methods is quite important. These features could assist LPME in exploring emerging fields such as nanotechnology and biomedicine [20], [29], [30].

Table 3 highlights the key modes of LPME, their advantages, and typical applications.

Table 3: Comparison of Key LPME Modes

Mode	**Advantages**	**Applications**	**Citation**
Dispersive LLME (DLLME)	Rapid, high efficiency	Environmental, food, and pharmaceutical	[14], [15]
Hollow Fiber LPME (HF-LPME)	Stable, suitable for complex matrices	Pharmaceutical, biomedical analysis	[14], [15]
Single-Drop Microextraction (SDME)	Simple, cost-effective	Environmental, food analysis	[14], [26]

1.3.Dispersive liquid-liquid microextraction (DLLME)

Dispersive liquid-liquid microextraction (DLLME) has come a long way to make extraction more effective while leaving less of an environmental impact. This method includes the dispersion of an extraction solvent in an aqueous sample. As a result, one can achieve the selective extraction of analytes. Modern developments have made DLLME a more environmentally friendly choice for a range of uses.

1.3.1. Fundamentals of DLLME

The idea of dispersive liquid-liquid microextraction (DLLME) came from Rezaee et al. [31]. It is a new way of performing liquid-liquid extraction (LLE) that uses a ternary solvent system with an extraction solvent, a disperser solvent, and an aqueous phase [32]. In this approach, the analyte-containing sample solution is swiftly mixed with a small volume of extraction solvent and disperser solvent. This ensures compatibility with both the organic and aqueous phases. Water, disperser solvent, and extraction solvent all come together in a hazy mixture due to the high turbulence caused by this rapid injection. Rapid equilibrium is enabled by the large surface area between the aqueous phase and the extraction solvent. This drastically cuts down the extraction time. Once the extracted phase has been centrifuged and gently mixed, it will sink to the bottom of a conical tube as a small droplet enriched with the target analytes. This droplet may then be separated and tested using the proper methods [33]. The extraction and disperser solvent volumes and types are the most important variables affecting DLLME efficiency.

1.3.2. Extraction Solvents in DLLME

A decent DLLME extraction solvent must have certain qualities. It must first be selective while also strongly attractive to the target analytes. The solvent must be incompatible with water, have low solubility in the aqueous phase, and be readily separable from the aqueous phase by centrifugation [34]. Additionally, the ability to mix with the disperser liquid and have a different density than the water sample will assist in separating the phases. Also, the solvent should be suitable for chromatography and the testing tools employed in the experiment. Last but not least, it is highly encouraged to use environmentally friendly, non-toxic solvents [35].

1.3.3. Disperser Solvents in DLLME

DLLME requires a disperser solvent with outstanding miscibility both with the extraction solvent and the aqueous phase [36]. Thorough mixing depends on the disperser solvent being able to assist the extraction solvent in forming small droplets in the aqueous sample, hence optimizing the extraction process. Disperser solvents like methanol (MeOH), ethanol (EtOH), acetone, and acetonitrile (ACN) are frequently used in DLLME. This is because they are

affordable, have a low level of toxicity, and mix well with both the extraction solvent and the aqueous phase [34].

1.3.4. Variations of DLLME

DLLME has evolved greatly from its inception. This has led to the evolution of several approaches enhancing its environmental sustainability and efficiency. Analytical performance has been raised and the ecological effect has been lowered using several dispersion methods, solvent choices, and integration with other extraction processes.

1.3.4.1. Variations in Dispersion Methods

Vortex-assisted dispersive liquid-liquid extraction (VA-DLLME) is a new method where vortex agitation distributes the extraction solvent into microscopic droplets. This method allows for improved interaction with the target chemicals. This method allows a better interaction with the target molecules. VA-DLLME has successfully extracted chemicals from food matrices, traditional medicines, and environmental components, proving its flexibility [37], [38].

Ultrasound-assisted extraction utilizes ultrasonic waves to create cavitation bubbles in the solvent, which improves mass transfer and extraction efficiency. This method nowadays is mainly implemented as an innovative method that enhances the extraction of bioactive compounds from various plant materials [39], [40], [41]. The key advantage of UAE-DLLME is its ease of usage. One significant benefit of this procedure is the use of ultrasonics to properly disperse the extraction solvent throughout the solution.

Microwave-assisted extraction (MAE) is another method used to improve the separation of bioactive chemicals from a variety of plant materials [42], [43]. This technology has gained popularity since it is more efficient, requires less processing time, and has a lesser environmental impact than traditional extraction methods.

1.3.4.2. Solvent Innovations in DLLME

In solvent-terminated dispersion liquid-liquid microextraction (ST-DLLME), low-density extraction solvents are mainly used. This method removes the centrifugation step, and therefore, the extraction time is reduced. For SD-DLLME, having alcohols as extraction solvents is quite important. Some of the most used alcohols are undecanol, 1-octanol, and 1-dodecanol. Usually, these alcohols are less harmful than the solvents used in traditional DLLME, which are chlorinated [44].

One efficient and environmentally friendly method is ionic liquid-dispersive liquid-liquid microextraction (IL-DLLME). Compared to traditional organic solvents, these are safer for the environment and have lower volatility. Ionic liquids have unique physicochemical properties due to the electrostatic interactions between the organic cations and inorganic or organic anions in these liquids [35]. Ionic liquids are perfect for creating highly selective analytical methods due to their characteristics. This explains the rise in their use as an extraction step in DLLME procedures.

Switchable-hydrophilicity solvents (SHSs) are an important development in ecologically friendly chemistry. They are capable of switching between hydrophobic and hydrophilic states often. Their reversibility responds to changes in pH or CO_2 in the environment. This makes them useful for microextraction and environmental remediation. Secondary and tertiary amines, such as N,N-dimethylcyclohexylamine (DMCHA) and N-methylcyclohexylamine (MCHA), are effective in the chemical extraction [45].

Supramolecular solvents (SUPRASs) are new materials that enhance extraction processes through non-covalent interactions. They are particularly useful in the fields of food and environmental studies. Their variable polarity and various binding sites make them intriguing alternatives to standard solvents [46]. Since they are sensitive to low levels of pollutants, SUPRASs have been effectively used to extract perfluoroalkyl acids from aquatic products [47]. The DLLME method has also been utilized to extract dangerous polycyclic aromatic hydrocarbons from various water sources, with interesting recovery rates [48].

Deep eutectic solvents (DESs) are currently being developed as alternatives to conventional solvents. The combination of a hydrogen bond donor and an acceptor in a specific molar ratio results in the formation of DESs [35]. This means that they are eutectic mixtures. Their low toxicity, configurable characteristics, and low cost make them perfect for many uses. This addresses methods of extraction and enhancement of drug solubility [49].

1.3.4.3.Coupling with other methods

A major advance in sample preparation is electromagnetic extraction (EME) coupled with dispersive liquid-liquid microextraction (DLLME). It is applied particularly for the charged analyte extraction from complex matrices. EME uses an electric field to help analytes pass through a liquid membrane. At the same time, DLLME improves the efficiency of extraction

with the distribution of a small amount of organic liquid to the water sample. EME has recovered ionic target analytes from complex biofluids [50] and identified antidepressants in blood, breast milk, and wastewater [51].

DLLME packed syringe microextraction is an approach that combines the principles of dispersive liquid-liquid microextraction (DLLME) with methods that are based on syringes. Simple use and phase separation without the need for centrifugation are both made possible by the utilization of commercially available syringes [52]. It has been demonstrated that DLLME-packed syringe microextraction is a successful method for extracting metal ions from food samples and phthalate esters from water [52], [53].

Dispersive liquid-liquid microextraction (DLLME) is widely used in combination with other extraction and pre-concentration methods, including stir bar sorptive extraction (SBSE) and solid-phase extraction. One effective way to remove PAHs and active pharmaceutical chemicals is to combine DLLME with Stir Bar Sorptive Extraction (SBSE) [54], [55]. SPE-DLLME has been successfully used in food analysis to remove phthalates from hot beverages and polycyclic aromatic hydrocarbons (PAHs) from cosmetics [56], [57]. In the context of environmental analysis, it has also been used to identify pesticide residues in soil samples and sugar samples, respectively [58]. DLLME is occasionally used with hollow-fiber liquid-phase microextraction HF-LPME to get even greater phase dispersion and extraction efficiency during the process.

1.3.5. Advantages and limitations of DLLME

Many benefits of dispersive liquid-liquid microextraction (DLLME) make it appropriate in many different fields. DLLME is efficient for trace-level analysis because it boosts detection sensitivity [26], [59]. Using deep eutectic solvents (DESs) for extraction results in a process even more ecologically friendly. DESs are greener than solvents since they are biodegradable and are nontoxic [60]. DLLME also saves costs and environmental impact by using fewer solvents and chemicals [59], [60]. Furthermore, the method significantly speeds up the sample preparation.

DLLME has many problems that must be addressed despite its many benefits. Since one is required to test some parameters of the experiment, including the kind of solvent and its concentration, it might be difficult to determine the optimal conditions for extraction [61], [62]. Furthermore, even though DLLME is highly adaptable, it might not work especially well with

some materials or analytes (for example, polar) [26]. Another problem is that interferences might occur, which means that other chemicals in complex sample matrices could make extraction less effective and analysis less accurate[62]. So, the method development in DLLME requires both precision and matrix-effect considerations.

1.3.6. Applications of DLLME

Due to its low detection limits, excellent recovery rates, and appropriateness for routine analysis, DLLME is widely used to extract a wide range of environmental pollutants. It has been used to accurately identify sulfonylurea herbicides in polluted water sources and remove them from environmental water sources [63]. It can also extract organophosphorus pesticides using nonhalogenated solvents, which is necessary for environmental monitoring [64]. The method can simultaneously extract PAHs and PCBs from natural waters with great accuracy and precision, making it useful for environmental evaluations [65]. A more environmentally friendly option to traditional solvents, deep eutectic solvents (DES) have increased the efficiency of PAH extraction even more [66]. The use of eutectic mixtures to improve recovery rates has also led to the successful use of DLLME to detect pollutants such as gemfibrozil and bisphenol A [67]. Additionally, a switchable solvent solution allows effective preconcentration and recovery of heavy elements like lead, making the approach versatile for environmental studies [68].

DLLME is absolutely important for food safety as it helps to identify preservatives and pollutants in different food and drink samples. Its effectiveness in monitoring pesticide residue has been demonstrated by the successful application of succinate dehydrogenase inhibitors in water, juice, wine, and vinegar [69]. Moreover, this method can be used for removing pesticides from fruit juices [70]. This proves that it can manage complicated food matrices and improve food safety. DLLME has also been used to investigate the presence of preservatives such as benzoic and sorbic acids in drinks [71]. This emphasizes its usefulness for food quality control.

1.4.Hollow fiber extraction

Analytes can be selectively extracted and concentrated via hollow fiber extraction from a wide variety of matrices. This approach is well-suited for the study of pharmaceutical and pollutant traces because it uses hollow fiber membranes to improve extraction efficiency.

Hollow fiber membranes play a key role in liquid-liquid extraction (LLE). When two immiscible liquids, such as a sample and an extraction solvent, need to be separated, the membrane is used to separate the two liquid phases. This allows the analytes to diffuse selectively while preventing them from coming into physical touch with one another.

1.4.1. Fundamentals of HF-LPME

In HF-based Liquid Phase Microextraction (HF-LPME), the extraction phase is put in the lumen of a porous hollow fiber, while the acceptor phase is protected by a Supported Liquid Membrane (SLM), as shown in Figure 3. Before the hollow fiber is used, it is sonicated with acetone to eliminate contaminants. Then the fiber is submerged in an impregnating solution, which causes the pores of the membrane to fill. Excess solvent is washed away with distilled water. After that, the acceptor phase is introduced into the lumen. In the two-phase mode, the receiving phase can be an organic liquid that is identical to the SLM. In the three-phase mode, it can be an aqueous solution. The hollow fiber is submerged within the sample so that analytes may be extracted into the acceptor phase. Four designs of HF-LPME have been reported: a rod-like configuration, a U-shaped design, a hollow-fiber solvent bar configuration, and a knotted hollow-fiber configuration. Depending on the analytes and sample complexity, the method can be performed in two- or three-phase mode [72].

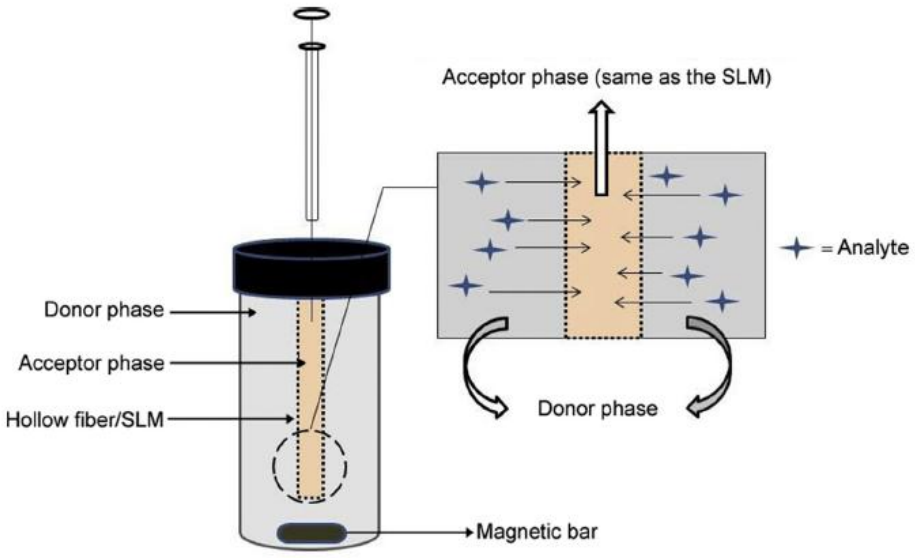

Figure 7: A schematic mechanism of the two-phase HF-LPME [72]

1.4.2. Advantages and challenges of HF-SPME

Hollow fiber membranes offer several advantages over flat sheet and inorganic membranes. This proves why they are the best choice for membrane modules. Some of these benefits are that they are self-supporting, flexible, and have a large specific surface area. All of these things contribute to simpler equipment and more efficient operations. These membranes' high packing density and large surface area make them more productive and energy-efficient. These unique properties also contribute to excellent mass-transfer characteristics. That means they can be used in numerous industrial situations, such as water treatment, dialysis, pharmaceutical purification, food processing, and gas separation [73].

The limitations of HF-LPME include the need for more research in automation and commercialization for everyday applications. Regardless of their high efficiency and environmental credentials, generic methods must be developed to ease method development. In addition, it is suggested that future research investigate the utilization of solvents that are less harmful to the environment. Another problem is that chemical composition, pH, and sample/acceptor phase conditions can all influence extraction efficacy. Finally, while HF-LPME is well-suited for complicated samples, more development is required for wider commercial use and application in a variety of disciplines [72].

1.4.3. Applications of HF-LPME

Since hollow fiber contactors are so effective at extracting and separating chemicals from complex matrices, they have a wide range of applications. In the food sector, they are utilized for the purpose of removing volatile fragrance compounds and dissolved oxygen from processing effluents. These effluents include distillery waste and seafood wastes, both of which contain considerable quantities of volatile organic compounds [74]. Those methods are used in pharmaceuticals to eliminate diclofenac and ibuprofen, as well as antibiotics, including penicillin G, and drug transporters, such as liposomes, from water samples [74], [75]. Particularly in fields like cell therapy, tissue engineering, and blood oxygenation, due to their delicate processing conditions, biotechnology depends much on them [74]. Using hollow fiber methods in environmental monitoring not only gives validity to sustainable analytical methods but also provides a more ecologically friendly way for removing herbicides and pesticides from water and soil [76].

These systems efficiently extract a wide range of compounds. Volatile organic compounds, such as dimethyltrisulfide and ethyl butyrate, are isolated using hollow fiber membrane

contactors [77]. Pesticides and herbicides, including organotin species and chlorophenoxyacetic acid herbicides, are extracted from food, soil, and water samples [76], [78]. The method is also widely used in pharmaceutical applications to isolate nonsteroidal anti-inflammatory drugs (NSAIDs), metoprolol, and anticancer drugs from biological and environmental samples [79], [80], [81]. Furthermore, it is effective in bioanalytical chemistry for extracting biological metabolites, such as trans,trans-muconic acid and hippuric acid, from urine samples through ion-pair-based hollow fiber microextraction [82].

1.5.Single Drop Sorptive Extraction

Single drop liquid microextraction (SDME) utilizes a single droplet to extract analytes from a sample, providing benefits in sensitivity and efficiency. Chemical analysis and environmental monitoring are just two of the many ways that this method has been used successfully.

1.5.1. Fundamentals of SDME

The diffusion rate of the analyte is the primary factor that determines how much of the analyte is transferred from the sample to the droplet (acceptor phase) [83]. The physicochemical characteristics of the extraction solvent have the greatest impact on the efficiency of the single-drop microextraction (SDME) method. Interactions between the solvent and the analyte are essential to successful extraction. These are influenced by factors such log Kow, volatility, and viscosity [83]. DME is divided into multiple categories based on how the droplet interacts with the aqueous sample: direct immersion (DI), drop-to-drop (DD), directly suspended droplet (DSD), continuous flow (CF), headspace (HS), and liquid-liquid-liquid (LLL) SDME (Figure 4) [84].

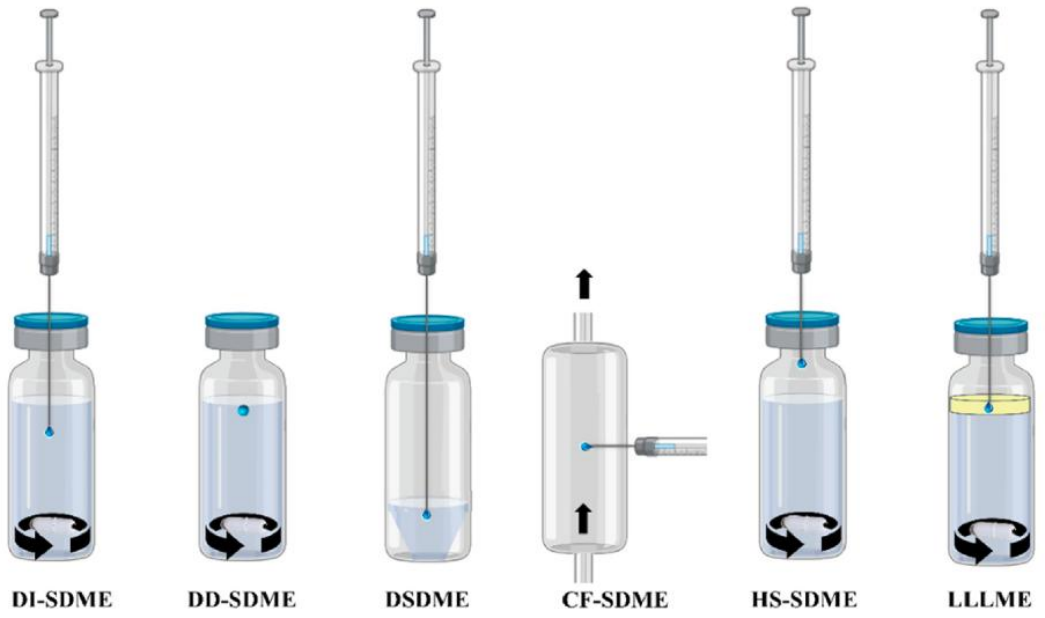

Figure 8: Various modes of single-drop microextraction (SDME) [84]

1.5.2. Advantages and limitations of SDME

Under optimal conditions, SDME boasts a high extraction efficiency—recorded rates of up to 97% [85]. By using tiny quantities of organic solvents, it also follows green chemistry principles [86]. Since SDME is so adaptable, it can be used in biological studies and environmental monitoring for antibiotic residues. Mass spectrometry and other modern

detection techniques help to increase the analytical capability of the procedure even further [87].

Single drop extraction (SDE) methods have significant drawbacks that can reduce their efficiency in a variety of applications. The stability and microdrop performance depend much on the composition of the sample matrix. Microdrop retention and extraction efficiency can be affected by pH, salt concentration, and organic content [88]. Complex matrices that contain proteins or alcohol can make the extraction process less reliable and lower the recovery rate. Additionally, the Poisson limit in droplet-based systems may lead to a high number of empty droplets, which reduces the efficiency of single-cell encapsulation and negatively impacts throughput [89]. Moreover, ensuring reproducibility in extraction results can be difficult because of the variability in microdrop formation and stability across different sample types, which can cause fluctuations in extraction efficiency [88].

1.5.3. Applications of SDME

Because it is so efficient in extracting trace compounds from complex matrices, SDME is useful in biological and environmental applications. It is widely used in environmental analysis to identify soil and water pollutants like antibiotics, pesticides, and volatile organic chemicals. In this way, it supports efficient environmental monitoring and pollution control [90], [91]. Its low solvent consumption and low waste production make it a sustainable alternative consistent with ideas of green analytical chemistry [91], [92]. In biological uses, SDME helps biomolecules from complicated biological materials to be preconcentrated, thereby improving their mass spectrometry detection [93] In clinical and pharmacological research, it is especially important since it helps to identify trace components and molecules, therefore enhancing the sensitivity and selectivity of analytical techniques [94].

1.6.Solid-phase microextraction (SPME)

Arthur and Pawliszyn came up with solid-phase microextraction (SPME) in 1990 as an alternative option to solid-phase extraction (SPE) [95]. This new method includes sampling, isolating, and enriching all in one fiber-based structure, which makes the process of sample preparation faster.

1.6.1. Fundamentals of SPME

The SPME method coats a thin sorbent layer on a silica, stainless steel, or plastic fiber. The fiber is either submerged in the sample solution or subjected to the headspace of the solution, based on the analytes and the sample matrix [96]. The optimum extraction method selected by scientists depends on the requirements of the investigation. The main Solid-Phase Microextraction (SPME) methods used for analyte extraction are shown in Figure 5. Headspace SPME (HS-SPME) and direct immersion SPME (DI-SPME) differ mostly in the manner pollutants are transferred to the sorbent [97]. DI-SPME allows one to extract analytes from the liquid phase by directly dipping the SPME fiber right into the sample matrix [98]. For polar chemicals in particular, this approach reduces coating saturation problems to a minimum. In contrast, HS-SPME uses the vapor phase above the sample to extract analytes. Increasing the sample's volatility by heating it makes it more amenable to less polar chemicals and decreases matrix interference [99]. Isolating target chemicals from highly polluted matrices is another prominent use of membrane-protected extraction [100].

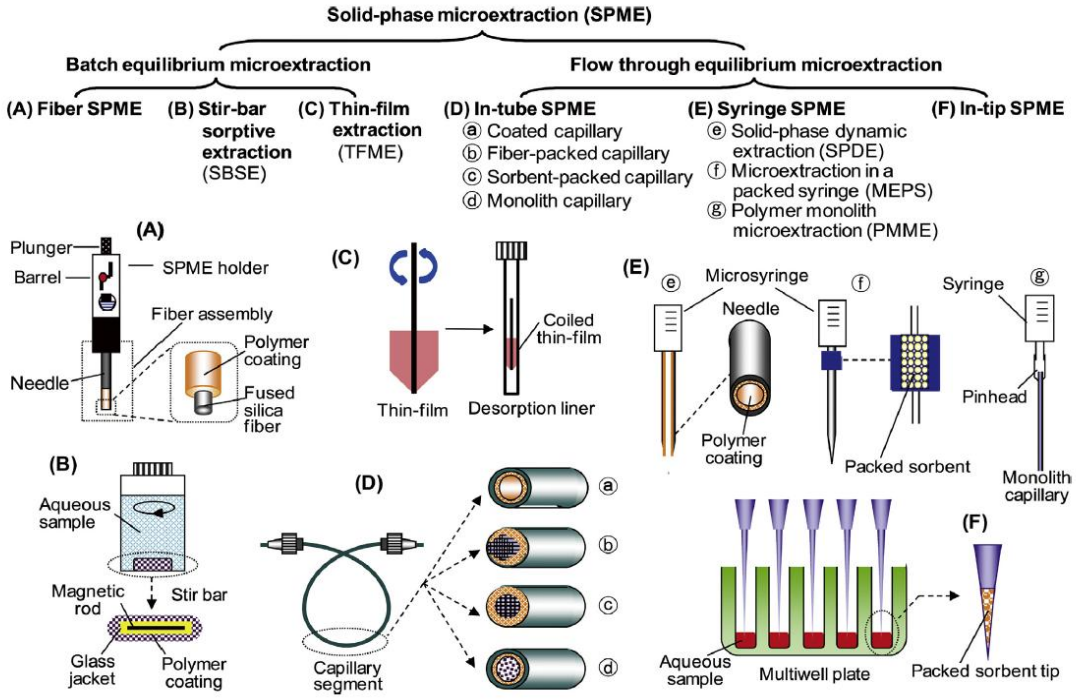

Figure 9: Different device configurations for SPME and other related microextraction methods [101].

Operating on the ideas of adsorption and absorption, the method lets analytes partition between the sample and the fiber covering until equilibrium is found [102]. One defining characteristic of SPME, a non-exhaustive method crucial for guaranteeing accurate and dependable analysis, is this equilibrium. The analytes can be extracted from the fiber in either one of two ways once the extraction procedure is complete: either by eluting them with a suitable solvent or by injecting them straight into the injection port via thermal desorption [96].

Mass transfer of organic molecules is influenced by variables including temperature and agitation, therefore enhancing the efficiency of extraction [103]. The stationary phase of the fiber greatly affects three factors: sensitivity, speed, and repeatability of the method [104].

1.6.2. Fiber coatings in SPME

New materials that mix several new technologies to make them operate better and be more flexible have helped coatings for SPME fibers evolve. Because of their vast surface area and significant adsorption ability, carbon and metal-organic frameworks (MOFs) are quite good at collecting analytes [105]. Polymers such as polydopamine (PDA) offer biocompatibility and environmental friendliness; the lightweight and porous structure of aerogels helps extraction to be more successful [105], [106]. Coatings such as ionic liquids and metal oxides provide still another degree of stability and selectivity to enable exact findings from complex mixtures [105]. One recent development that makes non-invasive extraction of small molecules in living entities possible is the development of biocompatible coatings for in vivo analysis [107]. Green coating methods using environmentally friendly materials as PDA, help to reduce the environmental impact of SPME activities by means of sustainable substitutes [106].

1.6.3. Advantages and disadvantages of SPME

SPME is a useful tool for many different types of analytical tasks. Two of its most important selling factors are its capacity to reduce the amount of solvents used and its compatibility with the principles of green chemistry [108]. This technology has many possible applications due to its versatility and the wide range of compounds it can extract, independent of their polarity. It might be used for environmental monitoring as well as biological analysis, among many others [108], [109]. Particularly in living biological systems, the ability to monitor analytes in space and time is crucial, and SPME makes this possible with little invasiveness [109]. Last but not least, it is fast and easy to use; simple methods allow for quick analysis with little to no sample preparation required [109].

Despite its many advantages, SPME has certain limitations that should be considered. One challenge is its sensitivity, which may not always be sufficient for detecting trace-level analytes in complex matrices [110], [111]. Another disadvantage is the possibility of matrix effects, which occur when there are interfering chemicals in the sample and affect the efficiency and accuracy of extraction [110]. To further complicate matters, SPME fibers must be stored and handled correctly to avoid analyte loss [103].

1.6.4. Applications of SPME

1.6.4.1.Environmental applications of SPME

In environmental studies, solid-phase microextraction (SPME) has been extensively used for the extraction and measurement of organic pollutants in many matrices. Firstly, SPME has been demonstrated to be useful in multi-residue analysis by detecting several pesticide types in water [112]. Offering a fast and solvent-free method of environmental monitoring, using SPME fibers enhances the pesticide detection in water samples even more [113]. Quantitative analysis of phosphoric acid esters in water samples is another example of SPME's versatility in identifying organic pollutants [114]. Methods based on SPME are also utilized for the detection of inorganic pollutants in water. For example, methods for the accurate determination of lead and cadmium concentrations in water samples include pseudo-stir bar hollow fiber solid/liquid phase microextraction [115]. Similarly, arsenic in water and wastewater may be analyzed using nanoparticle-assisted hollow fiber solid-phase microextraction [116].

Contaminant analysis in soil and sediments makes extensive use of SPME. Using cooling-assisted devices or porous carbon coatings has been employed to extract PAHs for solvent-free sampling [117], [118]. Combining ultrasonic extraction with SPME allows for the detection of fungicides like vinclozolin and dicloran, while SPME covered by a hollow fiber membrane can be used to extract triazine herbicides [119], [120]. Finally, SPME is useful for assessing air contaminants such as BTEX, volatile organic compounds (VOCs), and monoterpenes[121], [122], [123]. It provides quantitative analysis in a wide variety of contexts and uses special coatings to be selective.

1.6.4.2.Food and biomedical applications of SPME

Food analysis mostly uses SPME for safety and quality control. By separating volatile molecules causing aroma and taste, it helps with product development and quality control [124]. SPME combined with molecularly imprinted polymers (MIPs) increases selectivity for

pharmaceutical residues in food matrices, therefore addressing issues of uncontrolled chemicals [101], [125]. SPME also helps to identify toxins, including pesticides, guaranteeing food safety and regulatory compliance [124]. Not only does it ensure quality and safety, but it also helps nutritional research by assessing bioactive substances. Consequently, this is adding to what is already known about the positive effects on health and how to avoid diseases [124].

SPME is increasingly used in biomedical research since it has so many significant uses. Measurement of pharmaceutical concentrations in biological fluids helps one better manage treatments for diseases, including cancer and heart disease [126], [127]. Furthermore, the method enables untargeted metabolomics, which, by means of comprehensive metabolite profiling in tissues and biofluids, helps to grasp disease processes [126], [127]. Analyzing complex biological samples for pharmaceutical compounds using SPME makes sense and facilitates drug development and monitoring [15], [125]. SPME is a fundamental tool for the progress of biomedical research since it also allows single-cell analysis. This, of course, offers a vital understanding of cellular reactions and medication interactions [126], [127].

1.7.Dispersive Solid Phase Microextraction (DSPME)

Extracting and preconcentrating analytes can be accomplished through the use of a novel method known as dispersive solid phase microextraction. Because it provides a greater level of interaction between the sorbent and the sample matrix, this method is an advancement in comparison to the conventional SPE process.

1.7.1. Fundamentals of DSPME

The procedure starts by adding a small amount of solid sorbent to a liquid sample. The solid sorbent disperses and binds the analytes that are targeted analytes. After mixing, the absorption process is completed, and the sorbent is separated (usually by centrifugation or filtration). The analytes are then desorbed using an appropriate volume of solvent, and finally, a small quantity of this solution is injected into the detection system [128]. The procedure is shown in Figure 6.

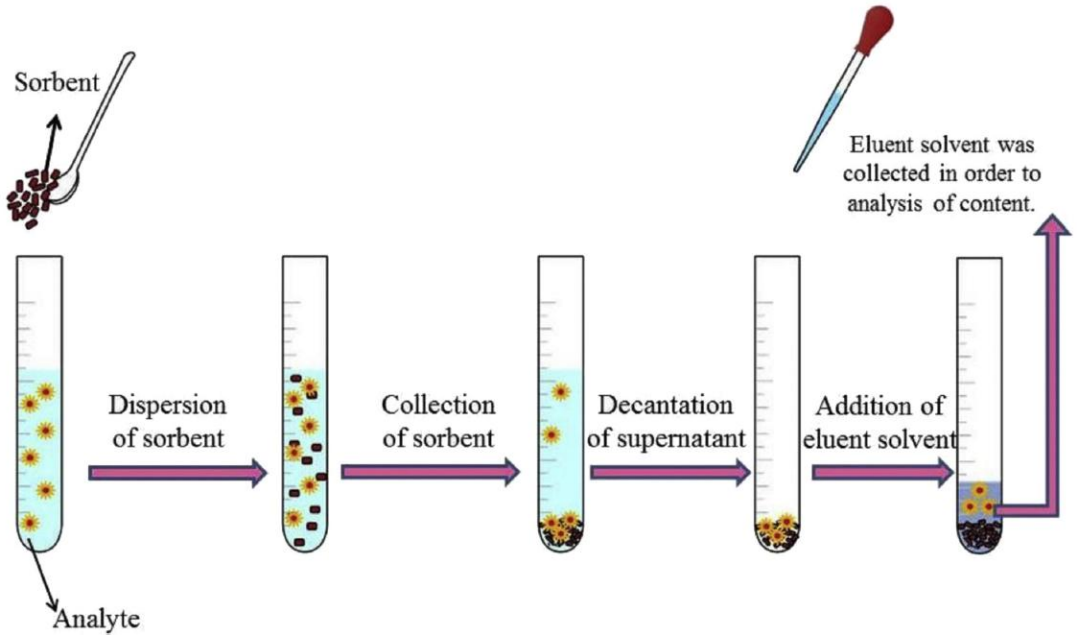

Figure 10: Diagrammatic representation of the D-m-SPE process [129]

Recent developments, such as ultrasound and vortex-assisted D-m-SPE, have been introduced to boost the mass-transfer kinetics of analytes. As shown in Equation 1, efficient stirring increases the mass-transfer coefficient (β) of analytes from the aqueous phase to the solid sorbent. This is valid because the thickness of the Nernst diffusion layer (δ) is reduced, thereby improving extraction efficiency within a short period. Surface-dependent D-m-SPE depends on the contact area between the analytes and the solid sorbent for its kinetics.

$$\beta = \frac{D}{\delta} \quad (1)$$

In D-m-SPE, the adsorption process takes place onto a solid sorbent. This allows for the target analytes to be isolated from the sample matrix. Some of the main mechanisms for adsorption include hydrogen bonds, dipole-dipole pairs, and π-π bonds. To achieve precise analyte detection, the total of the sorbent's characteristics should be considered. Ideally, the sorbent should have a large surface area and a high capacity, and it should be easily dispersed in liquid samples [129].

1.7.2. Sorbents in DSPME

Sorbents are essential to the success of D-mSPE. They are responsible for both capturing target analytes and enabling their subsequent release. The sorbent-analyte interaction must be reversible to allow for effective desorption. However, it may be skipped if analysis occurs directly on the sorbent. The available surface area for interaction determines the efficiency of sorption and desorption. For instance, nanostructured sorbents provide enhanced adsorption capacity due to their large surface area, compared to microscale materials. Recent advancements in these areas have increased D-mSPE's efficiency and selectivity.

1.7.3. Advantages and challenges of DSPME

DSPME offers several advantages over SPME. Firstly, it has a simplified setup that has replaced the necessity of a fiber. DSPME also increases process stability by lowering sorbent detachment and swelling in organic solvents [130]. Moreover, DSPME reduces the desorption and extraction times [130]. All the above make DSPME an appealing option for multiple uses.

DSPME has a few drawbacks in comparison to SPME. Firstly, it is difficult to separate the sorbent from the sample solution. Then, there is limited potential for automation, and it has limits in terms of in vivo analysis [130]. Furthermore, SPME has three modes: headspace, direct immersion, and membrane-protected. DSPME has only direct immersion. The SPME modes can be customized to accommodate a wide range of analytes, sample types, and conditions, which is something that DSPME can not provide [130].

Future advancements in D-m-SPE will probably involve the greater utilization of nanomaterials and the insertion of selectivity-enhancing molecules such as antibodies or proteins [131]. This will result in the method's application being expanded. For the method to be applied to routine laboratory use, it must be carried out in an automated manner [94]. Also, the commercial success of the method depends on the production of high-performance sorbents that are both economical and environmentally sustainable. Researchers must concentrate on developing effective, biodegradable sorbents that meet the environmental and financial criteria.

1.7.4. Applications of DSPME

DSPME is widely used in many fields because it is good at identifying and eliminating different pollutants. In food and beverage analysis, it is used to detect both organic and inorganic pollutants [132]. This method is additionally very useful for checking for traces of veterinary drugs in food samples [133]. Using sophisticated nanocomposites as sorbents, DSPME is used for the preconcentration of trace metals, including tellurium and thallium, in natural water systems [134]. Furthermore, proving its importance in environmental pollution analysis, it has been successful in extracting polycyclic aromatic hydrocarbons from aqueous samples [135]. DSPME also helps the biomedical and pharmaceutical sectors since it allows innovative sorbents, such as magnetic ionic liquids, to extract and quantify pharmaceutical compounds from difficult matrices, such as wastewater and human urine [136]. Furthermore, it has been demonstrated in the preconcentration of medications such as nortriptyline from biological specimens, therefore stressing its relevance in bioanalytical chemistry [137]. Development in sorbent technology has raised DSPME selectivity and efficiency [138]. Graphene-based materials and nanoparticles have been driving DSPME's increasing application over a broad spectrum of analytes [138], [139]. Furthermore, improved sorbent dispersion and extraction efficiency have been achieved using effervescent-assisted DSPME [140].

1.8.Effervescent-assisted microextraction

In analytical chemistry, simple, effective, and adaptable effervescent-assisted microextraction (EAME) has developed into a promising method. This method helps analytes to be extracted from various matrices and distribute by means of the generation of carbon dioxide bubbles from effervescent agents.

1.8.1. Fundamentals of EAME

The effervescent reaction combines a CO_2 donor (e.g., sodium carbonate) with a proton donor (e.g., sodium dihydrogen phosphate) to generate CO_2 bubbles. This is what defines EAM fundamentally. Acting as a dispersion agent, these bubbles enable the constant distribution of the extractant or adsorbent in the sample solution. By increasing the contact area between the analytes and the extractant, this dispersion improves mass transfer and extraction efficiency [141], [142]. Changing the concentration of the effervescent tablets or solutions will enable one to control the effervescent reaction. The ratio of CO_2 donors to proton donors and further component addition (such as carbon nanotubes or magnetic nanoparticles) might affect the pace and volume of bubble growth. The extraction procedure is being affected as a result of this [143], [144].

In the EAME context, the extraction process comprises the following actions:

1. Effervescence-Induced Dispersion: CO_2 bubbles cause the extractant or adsorbent to be dispersed throughout the sample matrix. This results in an increase in the contact area between the analytes and the extractant.

2. Mass Transfer: Occurs when analytes with a high affinity for the extractant move from the sample matrix to it

3. Phase Separation: The sample matrix is then removed from the extractant phase. Filtration, magnetic separation, or centrifugation are common tools for this [143], [144].

4. Elution and Detection: The analytes are desorbed from the extractant using an appropriate eluent and then studied using chromatography, spectroscopy, or another method [142], [145].

These steps are presented schematically in Figure 7.

1.8.2. Role of CO_2 Bubbles in EAME

The CO_2 bubbles, which are produced during the effervescence process, serve two purposes. Before anything else, they make sure that the adsorbent or extractant is spread uniformly across the sample matrix. Because of this, they can optimize the surface area that interacts with the

analytes [142], [146]. Continuous bubble release causes turbulence in the solution, which has the effect of accelerating the amount of analytes that are transferred from the sample matrix to the extractant phase. Because of this dynamic method, the amount of time needed for extraction is cut down significantly, and the efficiency of the process is significantly increased [147], [148].

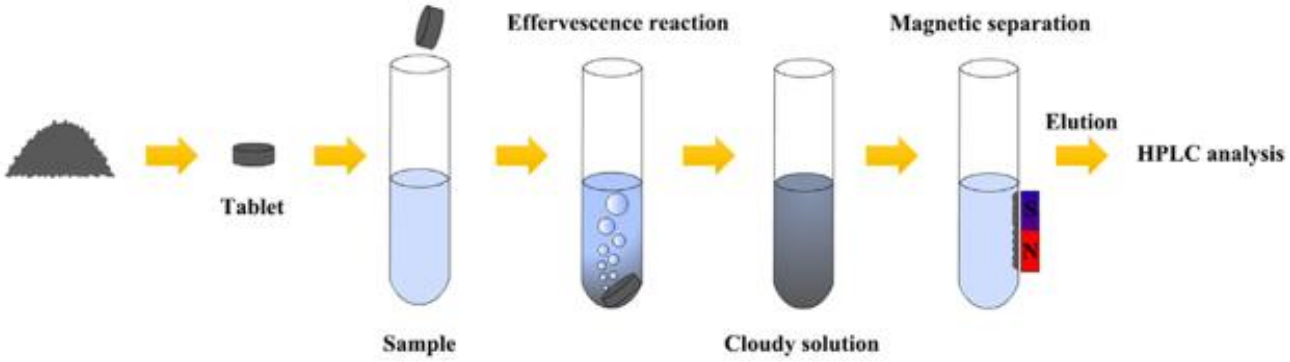

Figure 11: Schematic diagram of the effervescent microextraction process

1.8.3. Extraction Solvent/Adsorbent and Its Role in EAME

In the process of Effervescence-Assisted Microextraction (EAME), the selection of the extractant or adsorbent has an impact on both the selectivity and efficiency of the process. Both magnetic nanoparticles and ionic liquids have very high selectivity and extraction capacities [145], [149]. Magnetic nanoparticles make it possible to easily separate substances and extract them efficiently [143], [144]. High surface area carbon nanotubes rapidly adsorb several analytes [142], [150]. Physical and chemical forces control the interaction between analytes and the selected extractant or adsorbent. These forces include hydrogen bonding, electrostatic interactions, and hydrophobic interactions. It is therefore necessary to take into consideration the polarity, volatility, and functional groups of the analytes that are being targeted when selecting an extractant or adsorbent that is effective [151], [152].

1.8.4. Parameters Influencing Extraction Efficiency in EAME

Many factors can affect the extraction efficiency in EAME:

- **pH of the Sample Solution**: The pH affects how stable the extractant or absorbent is and how the analytes ionize [148].
- **Extraction Time and Temperature**: Longer extraction times and suitable temperatures can help mass transfer by themselves. They could, however, potentially lead to analyte deterioration [142], [152].

- **Type and Amount of Extractant/Adsorbent**: The extractant/adsorbent used and its quantity determine maximum analyte recovery [143], [145].
- **Effervescent Tablet Composition**: The ratio of CO_2 donors to proton donors, as well as the presence of additional components (e.g., magnetic nanoparticles), can significantly affect bubble production and extraction efficiency of the effervescent tablet composition [144].

1.8.5. Advantages and disadvantages of EAME

Effervescent-Assisted Microextraction (EAME) is popular in analytical chemistry for many reasons. Avoiding sophisticated instruments and dispersants simplifies and lowers costs. Effervescent tablets or powders simplify field or on-site analysis [143], [153]. EAME is economically friendly since it contains inexpensive effervescent ingredients and little solvent [154], [155]. Its effectiveness in extraction and preconcentration is still another advantage. From the effervescence reaction, CO_2 bubbles increase extractant dispersion in the aqueous phase and analyte-extraction solvent interaction. This precisely extracts certain compounds [156], [157]. EAME methods have shown low LODs for pesticides, heavy metals, and pharmaceuticals, as well as significant enrichment factors (up to 404%) [158], [159]. Reducing its environmental impact, the extraction process additionally makes use of biodegradable and non-toxic green solvents such as ionic liquids and deep eutectic solvents (DES). Lower organic solvent use increases its environmental friendliness [160]. Lastly, EAME takes a few minutes to less than an hour for extraction. Formation of in-situ CO_2 bubbles speeds sample preparation and analysis [154], [155].

The main limitations of Effervescent-Assisted Microextraction (EAME) need to be studied to make it a more practical option. How well EAME works depends on the type and concentration of effervescent agents, the extractant choice, and the samples' pH levels. Under less-than-ideal conditions, extraction recoveries or results could be inconsistent or poor [156], [161]. It is difficult to manage the generation of CO_2 bubbles since the rate and amount of bubbles vary with the effervescent agents used. Therefore, one experiences a lack of control in extractant dispersion homogeneity and extraction efficiency [162], [163]. Another drawback is matrix interference, which can be particularly problematic with complex products like food or biological fluids. High organic content or salts could reduce analyte extraction and preconcentration efficiency [151], [164]. EAME also emphasizes careful selection of some extractants, including magnetic adsorbents, ionic liquids, or deep eutectic solvents (DES).

Extractant compatibility with analytes and sample matrix is essential for good extraction recoveries [143], [165]. Finally, EAME is not suitable for volatile or unstable analytes under extraction circumstances. Sometimes additional steps like derivatization or complexation may be required to enhance analyte detection [166], [167].

1.8.6. Applications of EAME

Effervescent-assisted microextraction (EAME) is quite versatile and has numerous potential applications. Pesticides, including organochlorines and pyrethroids, as well as heavy metals like lead, cadmium, and zinc, have been detected in environmental water samples using EAME. It is ideal for on-site monitoring due to its mobility and ease of extraction [155], [158], [167]. For food safety research, EAME has been applied to identify synthetic colors, parabens, and fungicides in sophisticated food matrices. Low sample pretreatment requirements help to manage food quality [151], [154], [164]. The pharmaceutical and biological sectors apply this method to find calcium channel blockers and estrogens. Its great sensitivity and selectivity help it to be ideal for investigating traces [160], [162], [166]. EAME is used in both industrial and agricultural investigations since it allows one to detect nickel and cobalt in such samples. Other uses include looking for pesticides in grape juice to ensure it satisfies standards and is safe [151], [159], [165].

Table 4 provides a comparative analysis for EAME applications, key features and performance.

Table 4: Comparative Analysis of EAME Method

Application Area	Key Features	Performance Metrics
Environmental Monitoring	Analysis of heavy metals and pesticides in water samples	LOD: 0.045–1.88 µg/L, Enrichment factor: 42–404, Recovery: 85.8–103.6% [155], [158]
Food Safety Analysis	Determination of synthetic dyes and fungicides in food matrices	LOD: 0.002–0.19 µg/mL, Recovery: 76–111%, RSD: <10% [151], [154], [164]
Pharmaceutical Analysis	Preconcentration of estrogens and pharmaceuticals in biological fluids	LOD: 0.03–1.0 µg/L, Enrichment factor: 38–194, Recovery: 85.6–114.6% [162], [166]
Industrial and Agricultural	Analysis of industrial contaminants and pesticides in agricultural products	LOD: 0.9–4.1 µg/L, Recovery: 36–80%, Enrichment factor: 180–228 [159], [165]

1.9.Stir Bar Sorptive Extraction (SBSME)

Baltussen and colleagues invented stir bar sorptive extraction in 1999. Emerging from solid-phase microextraction (SPME), SBSME is a solventless, equilibrium-based method [168]. Its capacity to effectively extract analytes from a wide spectrum of matrices has won praise. This method makes advantage of a sorbent-covered stir bar. Target molecules are absorbed when the bar is swirled, and desorption for analysis follows.

1.9.1. Fundamentals of SBSME

Stir Bar Sorptive Extraction (SBSME) is a method that can be used to extract organic molecules from gas (headspace) or liquid (typically water-based) samples. This method is very similar to Solid Phase Microextraction (SPME), and consists of a PDMS stir bar which stirs the sample solution in a glass vial (Figure 8). Polydimethylsiloxane (PDMS) is a non-polar silicone-based polymer that primarily binds to analytes through the use of hydrophobic contacts and Van der Waals forces. However, occasionally it may create hydrogen bonds depending on the structure of the analytes [169].

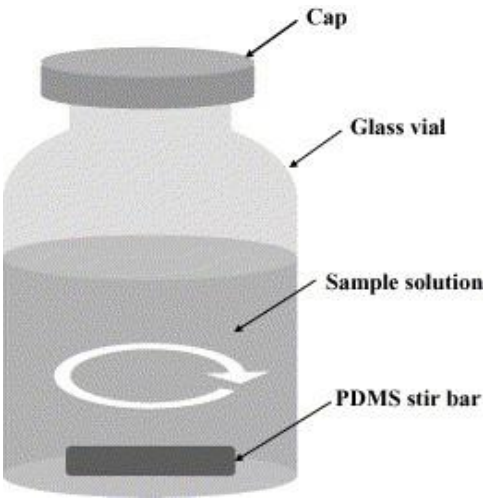

Figure 12: SBSME layout [170]

Usually between 24 and 126 µL in volume and 0.3 to 1.0 mm thick, the PDMS coating's great thermal stability and diffusion capacity help it to work over a broad temperature range [169]. SBSME behaves as a liquid-liquid extraction method in water-based materials. The extraction efficiency is affected by the phase ratio (β), the correlation between the sample volume (Vs) and the PDMS phase volume (V_{PDMS}), and the distribution coefficient ($K_{PDMS/w}$), which defines the inclination of the analytes towards PDMS instead of water [171]. Often reported as log Kow, or log P, this coefficient is comparable to the octanol-water partition coefficient (Kow). Combining the phase ratio with the distribution coefficient will help one determine the recovery. As the extraction process approaches equilibrium, it can reveal how well the analytes partition into the PDMS phase [171].

1.9.2. Coatings in SBSME

The extraction coating has a significant impact on the performance of the stir bar when subjected to SBSE. The dynamics, selectivity, and efficiency of the extraction process for the target analytes are all affected by the coating. The only three coatings that are now available for commercial sale are polydimethylsiloxane (PDMS), polyethylene glycol (PEG), and

polyether sulfone (PES). At the moment, absorption is the primary extraction method chosen for these coatings. Customized stir bars, on the other hand, often include adsorption and sometimes both absorption and adsorption. To improve extraction efficacy, these tailored coatings combine several solid-phase sorbents, including carbon compounds, metal-organic frameworks (MOFs), porous organic frameworks (POFs), imprinted materials, and monolithic macroporous polymers [172].

1.9.3. Advantages and challenges of SBSME

Stir Bar Sorptive Extraction (SBSME) is a reasonable choice for several reasons. SBSE streamlines the extraction process and lessens its negative environmental consequences by reducing the solvents need. Its great sensitivity and precision enable the exact identification of analytes at low concentrations, hence perfect for trace analysis [173]. Recent developments in miniature SBSME methods improve their mobility and fit for the limitedly available samples. Its convenience and application range have therefore been significantly expanded [173].

New stir bar coatings are desperately needed to permit the extraction of substances PDMS cannot, to maintain the material thermally stable, and to attain affordable manufacture. Even molecules incompatible with heat desorption could prove useful for polar solute analysis, provided they are compatible with liquid desorption and LC-MS. Making disposable stir bars functionally equivalent to SPE cartridges will help to satisfy some analytical requirements [171].

1.9.4. Applications of SBSME

Applications of this flexible analytical approach, stir bar sorptive extraction (SBSME), span environmental analysis, food safety, and method development. SBSME has been modified for trace metal detection in environmental monitoring so that, using appropriate coatings, heavy metals, including copper, cadmium, and mercury, may be extracted from water samples [174]. Moreover, the method has been applied for estrogen analysis in ambient water, displaying excellent extractive efficiency and repeatability [175]. SBSME is used in the realm of food safety for the selective extraction of allergenic proteins, such as concanavalin A, from food matrix, therefore stressing its prospects for ensuring food safety and regulatory compliance [176]. Moreover, ongoing research on method enhancement focuses on inventive coatings, like 3D-printed stir bars, which boost extraction performance and lower prices [175], [177].

1.10. Thin Film Micro Extraction (TFME)

Thin film microextraction (TFME) helps to separate and preconcentrate analytes from mixed materials more easily. Its sorption phase surface area is greater than that of conventional solid-phase microextraction (SPME). This generates improved surface capacity. Thanks to new materials and methods of sorption phase application, this strategy has undergone important changes.

1.10.1. Fundamentals of TFME

Thin film microextraction (TFME) is fundamentally based on analyte equilibrium-driven partitioning between the extractive phase and the sample matrix. The mass balance equation (equation 1) states that the amount of analyte extracted at equilibrium (n_e^{eq}) is directly related to its initial concentration in the sample (C_s^0), the distribution constant (K_{es}), and the volumes of both the sample (V_s) and the extractive phase (V_e) [178]. By optimizing analyte absorption and thereby raising V_e ,TFME uses a thin film with a higher surface area to improve analytical sensitivity. In this way, the method achieves better detection limits than standard microextraction methods.

$$n_e^{eq} = \frac{K_{es}V_sV_e}{K_{es}V_e+V_s} C_s^0 \quad \text{(Equation 1)}$$

Thin film microextraction (TFME) is used in different sampling formats to enhance extraction efficiency. The simplest approach involves directly placing the membrane on or in the sample or coating the thin film on the vial's surface [179]. Another format uses a stainless-steel rod or cotter pin as a support (Fig.9A), which is attached to the vial cap through the septa or a Teflon-made holder to prevent membrane folding [180], [181]. External holders, such as folded copper mesh (Fig. 9B), can be utilized to sustain the membrane and protect it against microbial development [182]. Lastly, the 96-blade TFME format substitutes rod-shaped substrates with blade-shaped ones (Fig. 9C). This improves stability, reproducibility, and coating diversity [183].

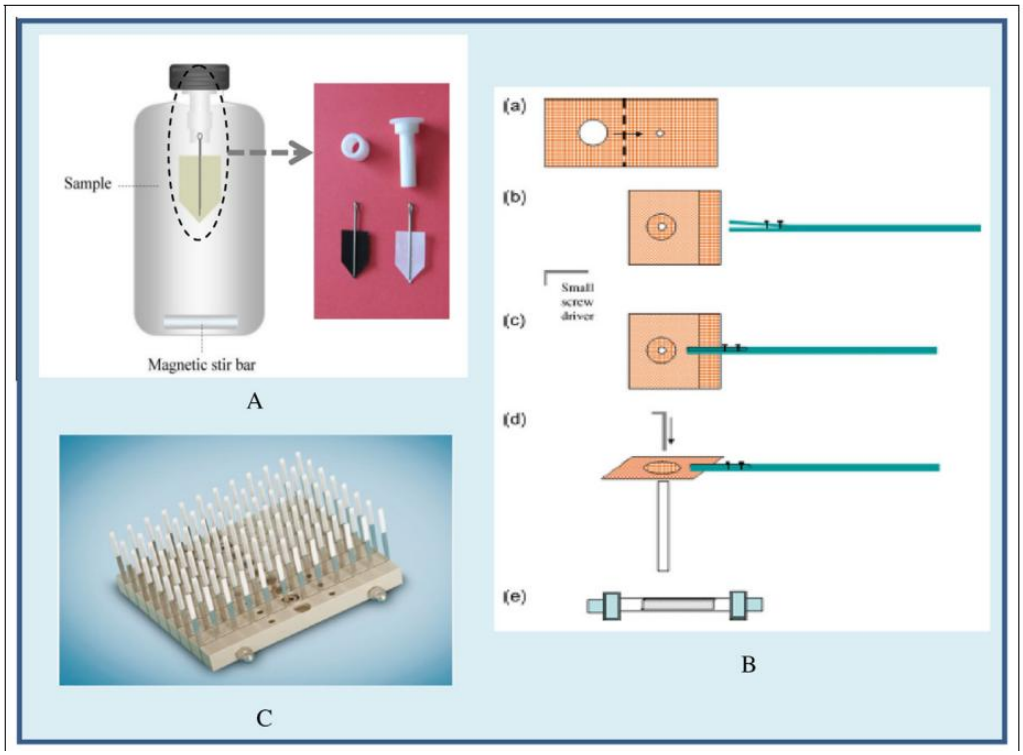

Figure 13: Various thin-film microextraction configurations: (A) Cotter pin-supported design [17], (B) Copper mesh-based holder], and (C) 96-blade thin-film format.[179]

1.10.2. Coatings in TFME

Several types of coatings are used in TFME to enhance extraction efficiency and selectivity. In comparison to more conventional materials, graphene-based coatings, which include graphene oxide (GO) embedded in polymers such as poly(styrene-co-divinylbenzene) (PS-DVB), have been shown to be more effective in extracting organic contaminants [184]. Molecularly imprinted polymers (MIPs) are specifically designed to selectively bind particular analytes, improving both sensitivity and selectivity in TFME applications [185]. Carbon nanotubes, particularly multi-walled carbon nanotubes (MWCNTs) incorporated into polymer matrices, have proven effective for monitoring organic pollutants, offering excellent repeatability and low detection limits [186]. Additionally, solid phase extraction (SPE) coatings, such as PS-DVB and C18, have been evaluated for their extraction capabilities across a wide range of polarities, with PS-DVB showing balanced extraction performance [187].

1.10.3. Advantages and disadvantages of TFME

The numerous advantages TFME presents help to increase its efficiency. One of the most important benefits is that the extraction process increases sensitivity since it makes use of a larger surface area. When compared to more traditional methods, this leads to an increase in

both mass transfer and sensitivity [185], [188]. Its solvent-free approach decreases solvent consumption, lowers the formation of secondary pollutants, and supports environmental sustainability [185]. Furthermore, TFME can be tailored for particular uses by allowing different extraction phases, including metal-organic frameworks and molecularly imprinted polymers [188], [189].

One should pay attention to the particular restrictions placed by TFME. Regarding optimization, one of the difficulties that can surface is the complexity. This results from the difficulty of choosing the suitable extraction phases and conditions [185]. Moreover, the existence of complicated matrices could disturb the extraction mechanism and influence the result correctness [188].

1.10.4. Applications of TFME

TFME has shown its adaptability and efficiency by being used in several domains. Particularly when using graphene oxide-based sorbents, it has been employed in environmental studies to effectively remove organic contaminants from water [190]. Achieving extraction efficiency above 80% the method has also been useful in identifying phthalate esters in biodegradable plastics [191]. Likewise, TFME has shown great sensitivity with low detection limits to recover organophosphorus pesticides from ambient materials [192]. TFME has been applied in the biological and clinical spheres for drug, metabolite, and other physiologically significant molecule analysis. For the apixaban extraction from plasma samples, for instance, a covalent organic framework (COF)-coated mesh was designed [193]. Integration of cutting-edge materials, such as covalent organic frameworks, improves their selectivity and efficiency even in challenging biological environments [193]. TFME has also been coupled with mass spectrometry for the quick polar metabolite identification in biological samples [194]. The food industry has benefited from TFME, particularly in the areas of additive, contaminant, and volatile component analysis. As an example, TFME has been used to identify sugars and preservatives in functional drinks and flavored waters [195]. Additionally, analysis of volatile compounds in red wine samples has shown remarkable extraction efficiency when using headspace thin-film solid-phase microextraction (HS-TF-SPME) [196].

1.11. In-tube SPME

In-tube solid-phase microextraction (SPME) is an advanced analytical method that uses a capillary column to extract analytes. This approach increases sample preparation efficiency by enabling extraction, concentration, and desorption to occur concurrently.

1.11.1. Principles of In-tube SPME

Under the conventional in-tube SPME method, a stationary phase covers a piece of an open-tubular fused-silica capillary column, therefore acting as the extraction device [197]. Fiber SPME is agitating the fibers in a predetermined volume of sample solution to extract compounds. In contrast, IT-SPME makes extraction easier as the sample solution passes through the apparatus [198]. In simpler terms, fiber SPME captures analytes on the outer surfaces of the fibers, while IT-SPME extracts them onto the inner surface of the capillaries [198]. A distribution coefficient, which governs the equilibrium process between the SPME and the sample solution phase, establishes the extraction efficiency. In fiber SPME, the analytes balance between the sample solution and the fiber coating. On the other hand, in IT-SPME, the analytes balance between the sample solution and the capillary's inner surface. There are four different kinds of capillary tubes used in IT-SPME, distinguished by the geometry of the extraction phase: (A) surface-coated capillaries, with the stationary phase coated on the inner wall; (B) fiber-packed capillaries, with fiber materials inside to capture analytes; (C) sorbent-packed capillaries, with sorbent particles inside to improve extraction; and (D) monolithic capillaries, with a continuous porous structure for effective extraction (Figure 10) [199].

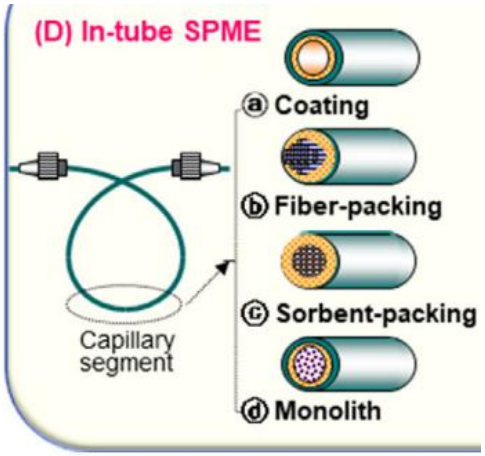

Figure 14: Configurations of In-Tube Solid Phase Microextraction (SPME)

1.11.2. Advantages and disadvantages of In-tube SPME

In analytical chemistry, several advantages make in-tube SPME a practical approach. First of all, capillary coatings raising sorption capacity enable the effective extraction of target analytes. Thus, this approach reveals great sensitivity and selectivity [197], [200]. In-tube SPME then also helps make analytical processes more ecologically friendly, thanks to the minimum amount of solvent utilized during the operation [201]. Still, several factors might

affect the outcomes, including low extractive efficiency and selectivity [201]. The mechanical stability of capillary columns has also come under question since their physical toughness may drop with time, influencing their performance and lifetime [201].

1.11.3. Applications of In-tube SPME

Because of its simplicity and adaptability, IT-SPME has been extensively used in many other disciplines. In-tube SPME with covalent organic frameworks (COFs) is used in environmental monitoring to identify contaminants, including phenolic chemicals and pesticides, in water samples [202]. In-tube SPME has also been tailored for PAH monitoring based on their toxicity and resilience in ecosystems [203]. Moreover, quite useful in drug monitoring, the method helps to detect trace amphetamine-type stimulants in sewage and urine [204]. In the food industry, IT-SPME is rather crucial in ensuring food safety and quality by means of collecting and analyzing volatile compounds [205]. This helps to analyze food freshness and contamination as well. It also helps to find pollutants in horticulture crops, therefore guaranteeing adherence to safety criteria [205]. Further improvements in IT-SPME's performance have been made possible by developments in extraction materials, particularly with the addition of molecularly imprinted polymers (MIPs) [206], [207]. Recent developments, notably the use of magnetic fields to help during extraction, have further enhanced MIPs-based IT-SPME, hence enhancing its usefulness in many other applications [207].

1.12. In-syringe SPME

Syringe solid-phase microextraction (SPME) is a novel technology that combines sample extraction and analysis in a single syringe, increasing efficiency and convenience of use. This method uses a syringe with a coated inner surface to extract analytes directly from a sample before desorption into a gas chromatograph (GC) for analysis.

1.12.1. Principles of in-syringe SPME

The syringe solid phase microextraction (SPME) method employs a syringe with a needle coated in a stationary phase. Analytes are extracted by contacting a sample fluid with the coated surface, and after desorption, the elutant is injected into a gas chromatograph for analysis [208]. This design allows for the effective extraction of both polar and non-polar molecules from aqueous solutions [209]. The plunger movement exposes the fiber for extraction and desorption while protecting it during storage and septum penetration, hence increasing sample efficiency [209].

1.12.2. Microextraction in a packed syringe (MEPS)

A new method called microextraction in a packed syringe (MEPS) simplifies sample preparation for analysis. MEPS drives a sample via a syringe filled with a packed solid-phase sorbent. Only the intended analytes can be absorbed. After eluting these analytes with a desorbing solvent, the analysis proceeds by techniques including HPLC or ICP-OES [210], [211]. The process is shown schematically in Figure 11. Among the several sorbents MEPS uses are covalent organic frameworks, molecularly imprinted polymers, and certain traditional materials, including C18 and C8 [210], [212], [213]. The selection of sorbent plays a crucial role in determining extraction efficiency, selectivity, and sensitivity. Any modification that takes place helps to achieve more efficient results [211], [212]. MEPS has been effectively utilized for extracting opiates from urine, quercetin from food samples, and rare earth elements from environmental water, highlighting the versatility of the method [210], [211], [212].

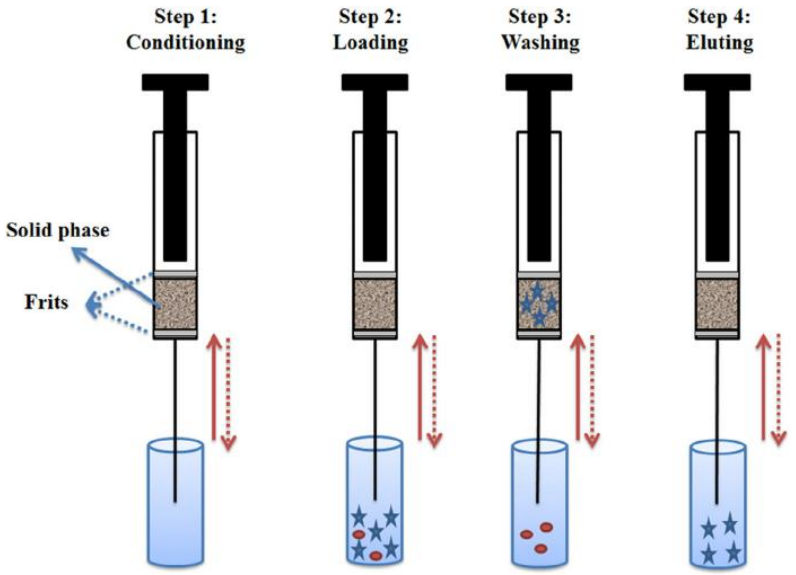

Figure 15: Microextraction by packed sorbent [214]

MEPS has several advantages, including efficiency and speed, since processes often take less than twenty minutes [215]. It reduces the need for large sample and solvent volumes, therefore supporting ecologically friendly methods [216], [217]. Moreover, fitting for automation, MEPS improves repeatability and lowers human error [218]. Its flexibility allows one to employ it on different matrices, including biological, environmental, and food ones [217], [218]. MEPS does, however, have several limitations, notably with complex sample matrices that may impact extraction accuracy [214]. The performance of the method depends considerably on the quality of the sorbent phase, so it may need optimization [216]. Moreover, MEPS could not be suitable without modifications for large sample sizes or high analyte concentrations [217].

1.12.3. Polymer monolith SPME

Polymer monolith microextraction is a new method that uses porous polymer frameworks to specifically capture target molecules. In this configuration, a syringe fitted with a pinhead directs the sample through a monolithic capillary tube that acts as the extraction medium (Figure 12). The bibliography notes several polymer monoliths for efficient extraction of different sample kinds. Poly(methacrylic acid-co-ethylene glycol dimethacrylate) is used for extracting psychoactive substances from urine, achieving recoveries between 80-118% and limits of quantification ranging from 0.2 to 2.7 µg/L [219]. Also, polydopamine-based monoliths are good for extracting triazine herbicides from water, with detection limits as low as 0.031 µg/L [220]. Graphene oxide reinforced monoliths can recover phenolic chemicals from groundwater with detection limits as low as 0.2 µg/L [221].

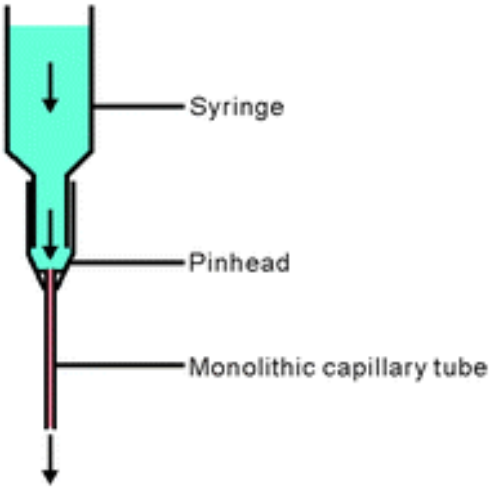

Figure 16:Polymer monolith SPME configuration

Polymer monoliths are widely used in a variety of fields. In environmental monitoring, they are used to analyze toxins in water, such as polycyclic aromatic hydrocarbons and herbicides, and provide accurate and sensitive detection methods [220], [222]. In biological sample analysis, the approach is used in clinical settings to extract medicines from biological fluids with minimal pretreatment [219]. These applications and many more highlight the versatility and the applicability of polymer monoliths in analytical contexts.

There are several advantages of polymer monolith microextraction (PMME). First of all, it has excellent extraction efficiency; for psychotropic medicines, reported recoveries vary from 80% to 118% [223]. Moreover, PMME reduces solvent use, in line with concepts of green chemistry [224]. Its flexibility allows it to be especially fit for numerous analytes, including pesticides and heavy metals [225]. Its portability is another main advantage since PMME-based devices are small and ideal for field use [225].

Still, the approach has rather limited possibilities as well. Matrix effects may limit extraction performance, and careful adjustment is required to provide accurate results [223]. Reusability can be challenging since time might cause the polymer monolith's performance to degrade [223]. Moreover, the synthesis of monoliths is sometimes complex and depends on particular conditions [226].

1.13. In tip SPME

The in-tip solid phase micro-extraction method (SPME-Tips) is an important method for achieving the extraction of different analytes. A microextraction step built into the tip of the pipette makes it possible to directly immerse in samples with this method. Because of this, the extraction process works better, and the ability to collect analytes gets enhanced.

1.13.1. Fundamentals of in-tip SPME

Solid phase microextraction in tips, or tip SPME, is a miniature form of solid phase microextraction. It is widely applied for therapeutic, forensic, and environmental uses, as well as for analytical purposes [227]. During the extraction, analytes are adsorbed onto the fiber when the pipette tip is submerged in the sample [228]. This approach facilitates direct immersion in biological fluids, which in turn speeds up the sample preparation process [228]. The steps of the method are also presented in Figure 13. In In-tip SPME, a variety of sorbents can be utilized. This includes commercially available choices, including activated carbon nanospheres or polymer-based monoliths, as well as home-made sorbents targeted for particular uses [229], [230]. The extraction process is heavily affected by the sorbent choice. SPME-Tips is quite successful in environmental analysis and hence beneficial for monitoring water, air, and soil quality. It is particularly effective for identifying persistent organic pollutants (POPs) and volatile organic compounds (VOCs) in the environment [231]. Additionally, the method has been successfully used to extract and quantify pesticides from agricultural water, achieving low limits of detection ranging from 0.3 to 2.5 ng mL^{-1} [232]. Because of its simplicity, cost-effectiveness, and efficiency in analyte extraction from complex matrices, this approach has become well-known [230], [233].

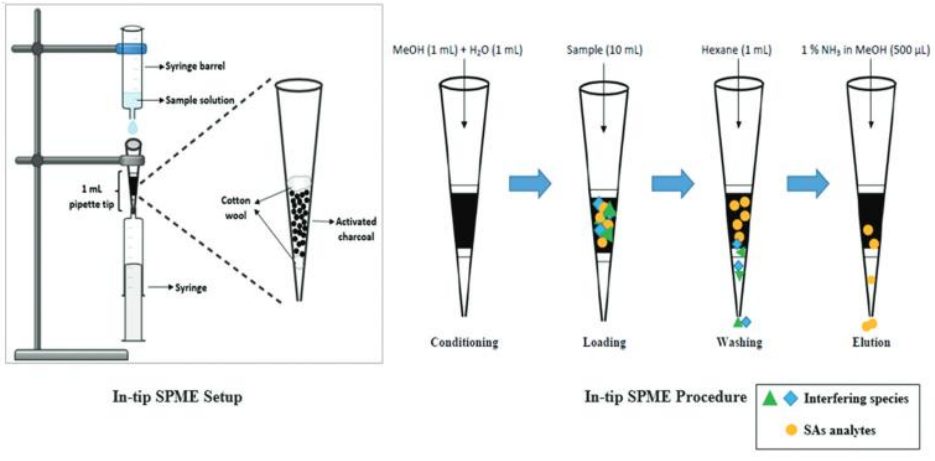

Figure 17: Schematic representation of the In-tip SPME procedure [233].

2. Sorbent materials

2.1. Introduction to sorbent materials

Sorbent materials play a crucial role in analytical chemistry, particularly in sample preparation and extraction processes. These materials enhance the efficiency and effectiveness of isolating and concentrating analytes from complex matrices, which is essential for accurate analytical measurements.

Research nowadays focuses on the evolution of miniaturized sorbent-based sample preparation, and this results in the development of various sorbent materials, each suitable for a different matrix or analyte. The choice of an appropriate method is obviously very important for the processes' successful results; however the extraction phase's affinity to the analyte plays the most crucial role. This means that vigorous attempts are made to obtain selective materials for different applications.

The integration of sol-gel processes, molecularly imprinted polymers (MIPs), magnetic nanoparticles, metal-organic frameworks (MOFs), covalent organic frameworks (COFs), ionic liquids, and carbon materials represents a significant advancement in material science, offering diverse applications across various fields (Figure 14). These materials are characterized by their unique properties, such as high selectivity, stability, and surface area, which make them suitable for applications in environmental, medical, and analytical fields.

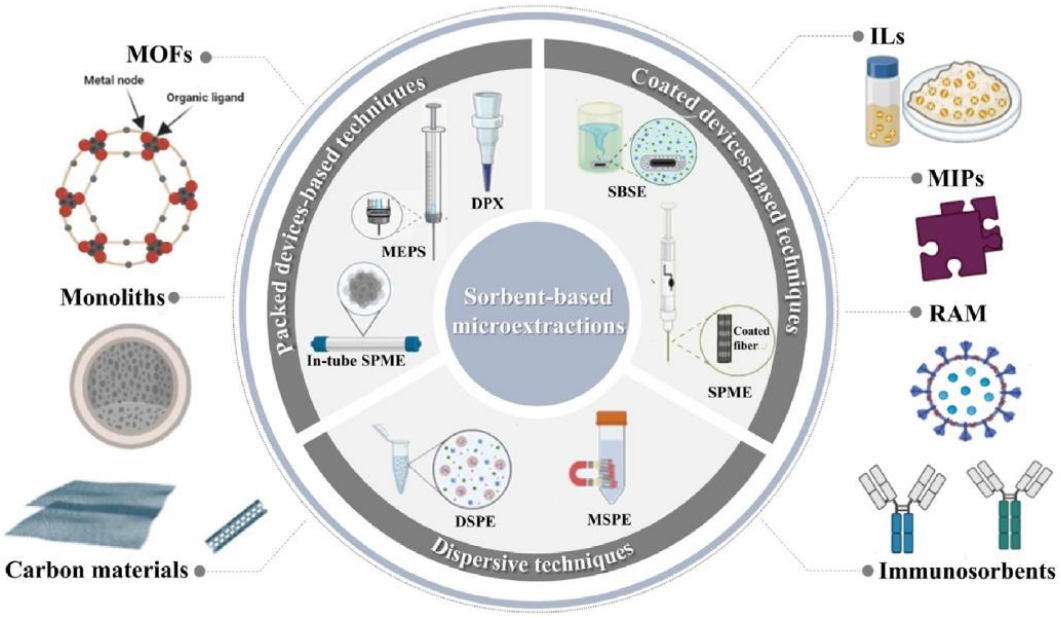

Figure 18: Diagram showing the primary sorbents currently employed in microextraction methods [234]

2.2.MOFs

Metal-organic frameworks (MOFs) are a class of highly porous crystalline materials composed of metal ions, coordinated to organic ligands that act as linkers [235]. The formation of well-defined three-dimensional network topologies is a result of the strong chemical bonding that occurs between these materials. In this way, periodic frameworks are produced that have a significant amount of surface area and a remarkable porosity [235]. Their tunable porosity, large surface area, and chemical flexibility make them ideal for gas storage, catalysis, and environmental remediation.

2.2.1. Fundamentals of MOFs

MOFs, also referred to as porous coordination polymers (PCPs), are hybrid materials formed through the coordination of metal ions or metal ion clusters (metal nodes) with organic ligands (Figure 15) [236]. Metal nodes in MOFs are essential since they provide readily available coordination sites that enhance the ability of the framework to generate coordinate bonds with other molecules, particularly Lewis base molecules [237]. Conversely, the ligands often employed in the manufacture of MOFs can be grouped into five primary categories: carboxylic acid ligands, imidazole ligands, N-heterocyclic organic ligands, phosphoric acid ligands, and crown ether ligands [238]. The length of the organic linker employed during the production process determines the number of adsorption sites in MOFs, hence [239].

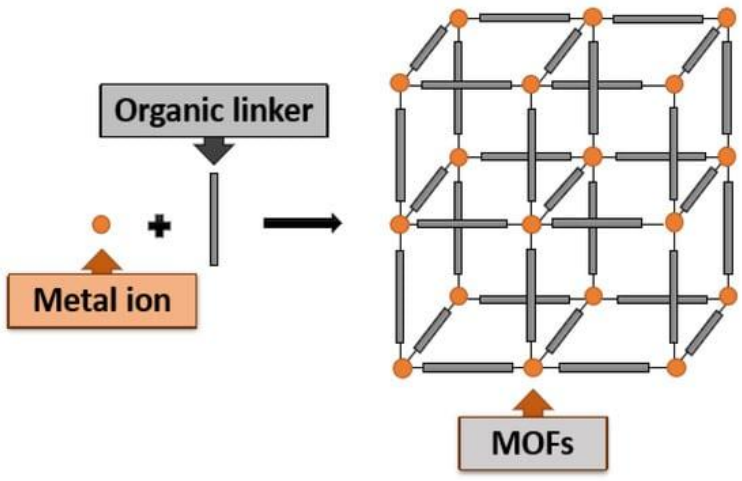

Figure 19: Composition and Structure of Metal-Organic Frameworks (MOFs) [240]

Structure flexibility is a key criterion in classifying metal-organic frameworks (MOFs). Like inorganic materials, rigid metal-organic frameworks (MOFs) have a constant structure and porosity, making them appropriate for long-term stability applications [241]. On the other hand,

flexible metal-organic frameworks (MOFs) are highly effective for applications such as controlled drug release and gas storage. They can dynamically modify their pore widths in response to guest molecules or environmental changes [241]. Metal-organic frameworks (MOFs) are structurally versatile and can be tailored for technological and industrial applications.

2.2.2. Synthesis of MOFs

The many methods that are utilized in the production of metal-organic frameworks (MOFs) each offer their own set of advantages. Hydrothermal and solvothermal methods require high temperatures in organic or water-based solvents to control MOF size and morphology [242], [243]. The yield could be increased using microwave synthesis, but the process would be sped up, and the synthesis time would be reduced [243]. One-pot synthesis is an example of an innovative method that simplifies the process by combining all of the reactants in a single stage, hence reducing the complexity of the process [243]. In a similar vein, fluid-fluid synthesis is a method that utilizes the interface between two immiscible liquids to improve the structural variation [243]. Ionothermal synthesis is yet another innovative concept that makes use of ionic liquids as solvents to improve the structural characteristics of the frame and make it possible to include ionic species into the framework [244]. Due to their many synthesis methods, MOFs can be tailored for separation technologies, gas storage, and catalysis.

2.2.3. Properties of MOFs

Metal-organic frameworks (MOFs) are flexible due to their unique structure. Their high porosity facilitates the manipulation of catalysts, and increases chemical process performance [245]. Changing MOF pore topologies allows precise pore size and shape variation, enabling selective adsorption and separation [246]. The different metal centers and organic linkers create a lot of different coordination modes. These modes help make complicated three-dimensional structures with their own unique properties [247].

MOFs are great for catalysis and have structural benefits. The multiple active sites of the material increase catalytic activity and selectivity. As a consequence of this, processes such as CO_2 reduction are getting less complicated [248]. Adding conductive components to MOFs boosts charge transfer. Consequently, they become much more efficient electrocatalysts [248]. Metal-organic frameworks (MOFs) offer a significant amount of potential in a wide variety of industries.

2.3.COFs

Covalent Organic Frameworks, more commonly referred to as COFs, are a class of crystalline materials that present a porous structure. Over the past few years, they have attracted a lot of interest due to the fact that they are versatile and possess special qualities.

2.3.1. Synthesis of COFs

The synthesis of COFs employs reticular chemistry, in which organic building blocks are joined by covalent bonds to form extensive networks. The building pieces are light elements like carbon, hydrogen, oxygen, nitrogen or boron and they are pre-connected to build 2-D or 3-D structures [249]. The synthesis method gives exact control of the chemical composition, pore size, and framework functionalization. By that way, adjustable materials are made out of COFs [250], [251].

Several synthetic strategies have been developed to fabricate COFs including:

1. Reticular Chemistry: This method creates crystalline frameworks with reversible covalent bonding. The topology and characteristics of the resulting COF are defined by the selection of building components and links [251], [252].
2. Bottom-Up and Post-synthetic Modification: These methods allow functional groups to be added to the structure of the COF. In bottom-up strategies functional groups are added during the synthesis. Post-synthetic changes make it possible to add more functional groups after the synthetic process [250], [251].
3. Solvent-Assisted Linkage (SAL) and Crystallization Methods: These methods improve the crystallinity and stability of COF. The quality of the finished product depends on the polarity of the solvent, the concentration of the substrate and the reaction conditions [253], [254].
4. Design of Building Blocks: Choosing appropriate building components helps to achieve desired structural and functional properties. For instance, the use of sp^2-carbon linkages in olefin-linked COFs has been shown to enhance chemical stability and π-conjugation. For catalytic and energy storage applications this is perfect [255].

The synthesis of COFs is a challenging process because it requires precise control over crystallization and stability. On the other hand, advancements in synthetic processes have led to the production of COFs of high quality with improved properties [256].

2.3.2. Structural Properties of COFs

Their structural qualities are influenced by the building components, the type of chemical bonds used, and the specific conditions under which covalent organic frameworks (COFs) are formed. Many important features are affected by these choices. For instance, COFs have very variable pore diameters, from tiny micropores to larger mesopores and exceptional surface area often exceeding 1000 m^2/g. These properties make them ideal for high-adsorption applications [250], [257]. Given their crystalline nature, stability is very crucial. Specific bonds, including sp^2-carbon, boost their heat and chemical resistance [258].Their potential to be functionalized allows researchers to tailor their properties to fit different purposes [249], [250]. COFs can also build two-dimensional layers or three-dimensional networks. Some examples of these 2D and 3D configurations are shown in Figure 16. The 3D versions with their interconnected pores are particularly useful in events requiring molecule separation or transport [259], [260]. Some COFs have fully conjugated structures that show promise for photonic performance, which could change fields like electronics and photocatalysis [259]. Their properties and applications are presented in Table 5.

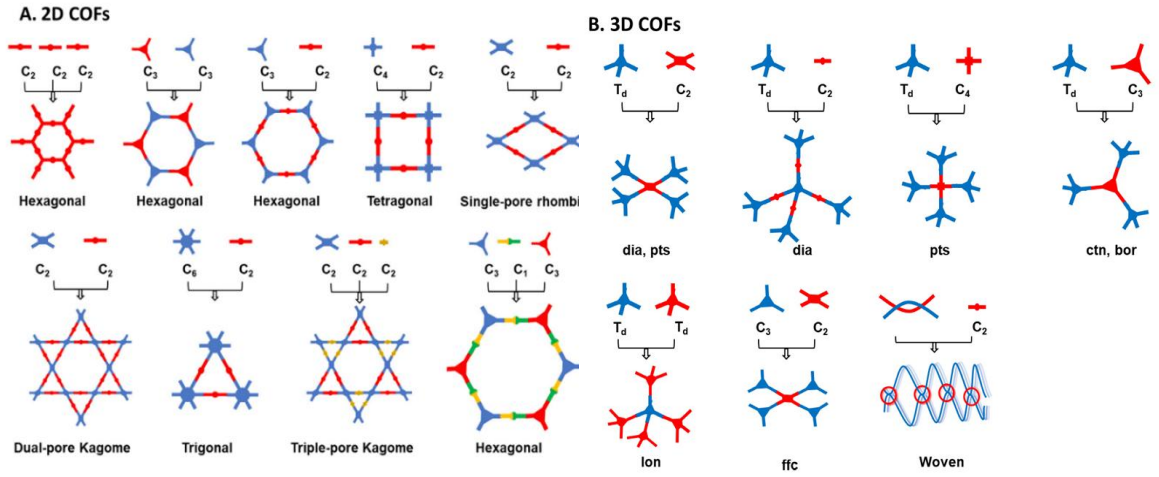

Figure 20: Examples of 2D and 3D COFs

2.3.3. Applications of COFs

Covalent Organic Frameworks (COFs) have drawn great interest in many different scientific disciplines due to heir high surface area, variable pore sizes and the ease with which they can be functionalized. These qualities make COFs very flexible. In environmental research their adsorption capacity and selectivity have shown great efficacy in removing various pollutants from water. This includes heavy metals, organic chemicals and even radioactive nuclides [261], [262], [263]. COFs have been utilized in the oil and gas industries to store gases like CO_2, CH_4, and H_2 and to effectively separate gas mixtures [249], [250]. Their catalytic potential is also

being investigated, especially in organic synthesis and electrocatalysis [264], [265]. Apart from that, COFs are developing in sensing and optoelectronics as their ability to integrate optoelectronic features qualifies them for sensors and complex electronic systems [249]. They're also being studied for energy storage applications like batteries and supercapacitors, as well as for enabling energy conversion processes like CO_2 reduction [264], [265]. Their porous, biocompatible nature helps controlled drug release in biomedicine, thus extending their application [249]. All these applications demonstrate how COFs are not merely materials of the future; they are today shaping solutions in numerous industries.

Table 5: Comparison of Key Properties and Applications of COFs

Property/Application	2D COFs	3D COFs	Fully Conjugated COFs
Pore Structure	Ordered, tunable pores	Interconnected pores	Large, uniform pores
Surface Area	High surface area	Higher surface area	Exceptional surface area
Applications	Gas storage, catalysis, sensing	Adsorption, separation, catalysis	Photocatalysis, energy storage
Stability	High stability	Enhanced stability	High chemical and thermal stability
Functionalization	Easily functionalizable	Functionalizable	Highly functionalizable

2.4.Ionic Liquids (ILs)

Ionic liquids (ILs) are popular solvents in environmental and sustainable chemistry due to their unique features and uses in various industries. They could replace conventional solvents due to their non-volatile nature and ability to dissolve many compounds. Naturally, this might promote environmentally friendly practices.

2.4.1. Fundamentals of ILs

Ionic liquids (ILs) are salts that remain in a liquid state at room temperature due to their low melting points (below 100°C) [266]. Because they are composed entirely of organic cations and inorganic anions, they are well-known for having a low vapor pressure and a minimal impact on the environment [266], [267]. They show great potential as environmentally friendly solvents in chemical processes and in the production of functional materials [267]. Due to the varying sizes of their constituent ions, they exhibit less dielectric forces than other types of liquids. This allows them to maintain their liquid state at room temperature [268].

Ionic liquids' (ILs) mix of cations and anions is quite important in deciding their thermal stability, viscosity, ionic conductivity, and environmental effect. Commonly, ILs include cations like imidazolium, phosphonium, and ammonium; well-studied cases are triethylammonium ([TEA]+) and trihexyl(tetradecyl)phosphonium ([P666,14]+) [269], [270]. As shown in phosphonium-based ILs, the shape of the cation greatly affects ionic conductivity and thermal stability [271]. Many of these features are summed up in Figure 17.

In a similar manner, ILs possess a wide variety of anions, such as bis(trifluoromethanesulfonyl)imide ([NTf2]−) and amino acid-based anions, both of which have been subjected to a substantial amount of research. The selection of the anion also plays a significant part in the thermal stability of the substance; for instance, trifluoromethanesulfonate anions exhibit considerably higher levels of stability in comparison to other anionic species [272].

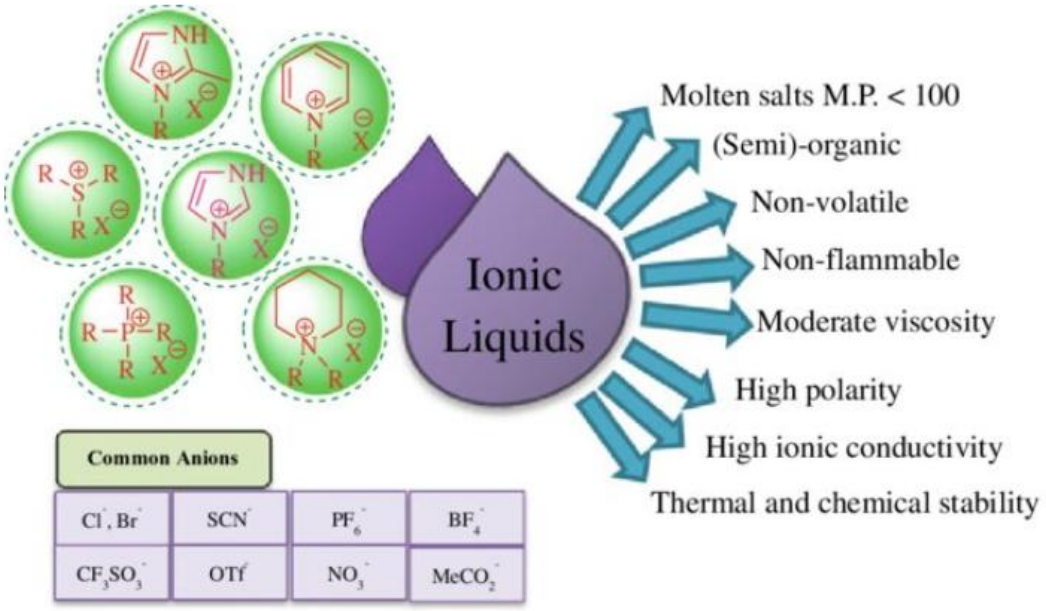

Figure 21: General profile of ILs [273]

2.4.2. Categorization of ILs

The three main groups we may name are (i) polymeric ionic liquids (PILs), (ii) magnetic ionic liquids (MILs), and (iii) task-specific ionic liquids (TSILs).

Polymeric ionic liquids are a type of polymer created by polymerizing ionic liquid (IL) monomers using a radical process, with a crosslinker helping to form a stable network [274]. PILs are useful for many different applications because they have a very special set of properties. Due to the great mechanical strength and thermal stability that they possess, they are suitable for application in situations that are difficult to work in (e.g., membranes, structural materials, etc.) [275], [276]. PILs have a high ionic conductivity because they have a natural ionic nature. This is important for energy storage and conversion devices like fuel cells, batteries, and supercapacitors [277], [278] Many PILs also include self-healing qualities and stimulus-responsiveness, in order to meet external factors as temperature or light [277], [279]. Moreover, their changing solvation properties allow for customized interactions. This makes them more useful in separation and catalytic processes [276], [277]. These features considered together make PILs a flexible class of materials with significant promise in modern technology.

MILs, which stand for magnetic ionic liquids, are materials that are flexible and possess remarkable paramagnetic properties. These materials allow magnetic response to take place without the presence of additional particles, which results in an improvement in separation processes because centrifugation is no longer necessary [280], [281]. In addition, they possess

thermochromic and luminous properties, which enhance their suitability for use in sensors and gas capture applications [282]. Drug delivery and sample pretreatment alteration are both made possible by their adaptable designs [283]. In industry, MILs are useful surfactants that reduce surface tension, facilitate self-assembly, and stabilize nanostructures. As a result, they provide support to industries such as the food, cosmetics, and pharmaceutical industries [284].

Task-specific ionic liquids, or TSILs, are useful because their features can be changed to suit different needs. And this is because their cations and anions can be changed, which impacts the solubility and reactivity in different ways [285], [286]. They are safer and better for the environment than regular solvents because of their low vapor pressure [285]. Their high thermal and electrochemical stability ensures their durability in industrial applications [286]. Consequently, TSILs are extremely effective in separation technologies. They are particularly applicable in the nuclear industry, where they enhance the process of extracting actinides such as uranium and molybdenum from acidic solutions [287]. In addition, they perform the role of catalysts in the process of converting carbon dioxide into useful molecules, with modifications that bring about an increase in the effectiveness of their catalytic activity [286].

2.4.3. Advantages and disadvantages of ILs

Ionic liquids (ILs) have multiple benefits that make them useful in many different fields. They are ideal for green chemistry applications because of their low toxic emissions and lack of volatility [288]. Their versatility has led to their use as catalysts, electrolytes, and solvents in diverse fields [289], [290], [291] Their great thermal and chemical resilience also enables several applications without major deterioration, hence improving recyclability [292]. On the other hand, ILs have drawbacks as well, including the high manufacturing expense, which limits their general application [289]. Furthermore, several ILs' toxicity issues require close consideration before use [292].

2.5.Carbon Materials

2.5.1. Categories of Carbon Materials

Carbon materials' unusual qualities make them very beneficial in chemistry. These materials could be classified into three primary groups: carbon dots, graphene derivatives and carbon nanotubes. First, carbon nanotubes are cylindrical nanostructures which are made of sp^2-hybridized carbon atoms. These atoms are organized in a hexagonal lattice. They can be classified as multi-walled carbon nanotubes (MWCNTs) or single-walled carbon nanotubes (SWCNTs). The number of graphene sheets rolled to create the tube is what makes the categorization [293].

Then, graphene derivatives are created from graphene, via chemical or physical changes. There are several types of graphene derivatives, including graphene oxide (GO), reduced graphene oxide (rGO), graphene quantum dots (GQDs), and few-layer graphene (f-LG). Their structure and functionalization influence their qualities [294], [295].

At last, carbon dots are quasi-spherical nanoparticles usually under 10 nm in size. There are three types of quantum dots: graphene quantum dots (GQDs), carbon quantum dots (CQDs), and biogenic carbon dots (BCDs). These quantum dots are classified according to the production methods that they use. These materials are known for their great optical qualities and biocompatibility [296], [297]. The evolution of carbon-based nanomaterials is shown in Figure 18.

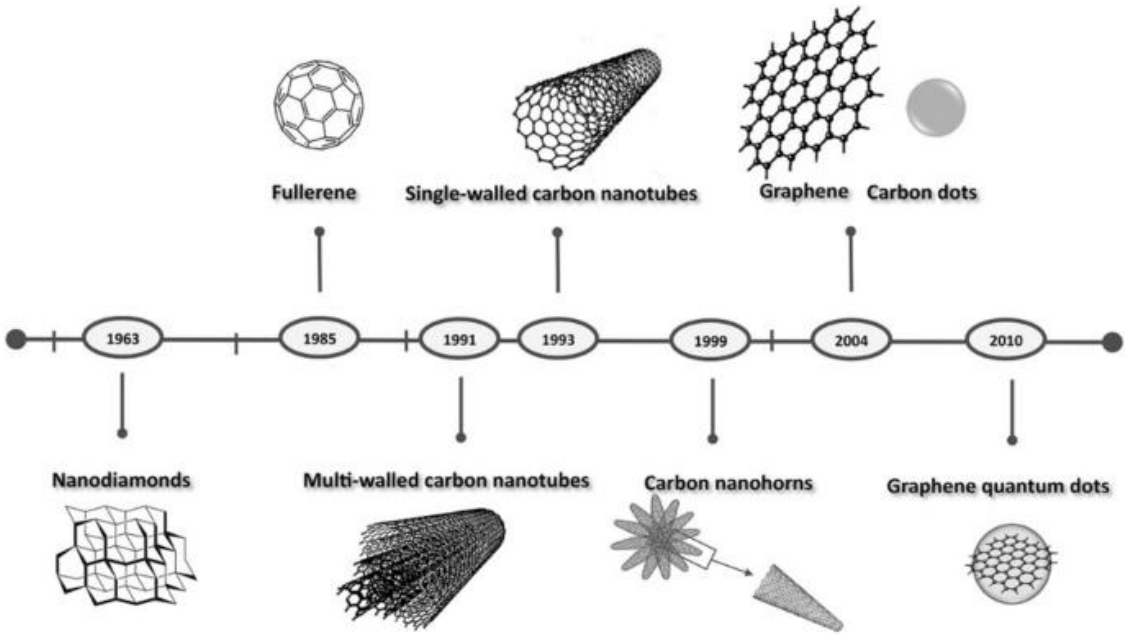

Figure 22: Significant milestones in the creation of carbon-based nanomaterials [298]

2.5.2. Synthesis Methods of Carbon Materials

Synthesis of carbon-based nanomaterials, including carbon nanotubes (CNTs), graphene derivatives, and carbon dots, can be accomplished by a wide range of methods. Arc discharge, laser ablation, and chemical vapor deposition (CVD) are the most common methods for producing carbon nanotubes (CNTs). These methods include the vaporization or decomposition of carbon atoms to create tubular structures [299].

The preparation of graphene derivatives can be accomplished using either a top-down or bottom-up strategy. In top-down methods, such as mechanical and chemical exfoliation, bigger carbon structures are separated into smaller nanoparticles by breaking them down. Bottom-up approaches, such as chemical vapor deposition (CVD), require the construction of carbon dots from smaller molecules [294].

Meanwhile, carbon dots are manufactured through the use of top-down methods such as hydrothermal oxidation cleavage or laser ablation, as well as bottom-up methods such as hydrothermal or microwave-assisted synthesis (Figure 19) [296], [298]. Finally, there is also green synthesis methods that utilize renewable biomass sources [300].

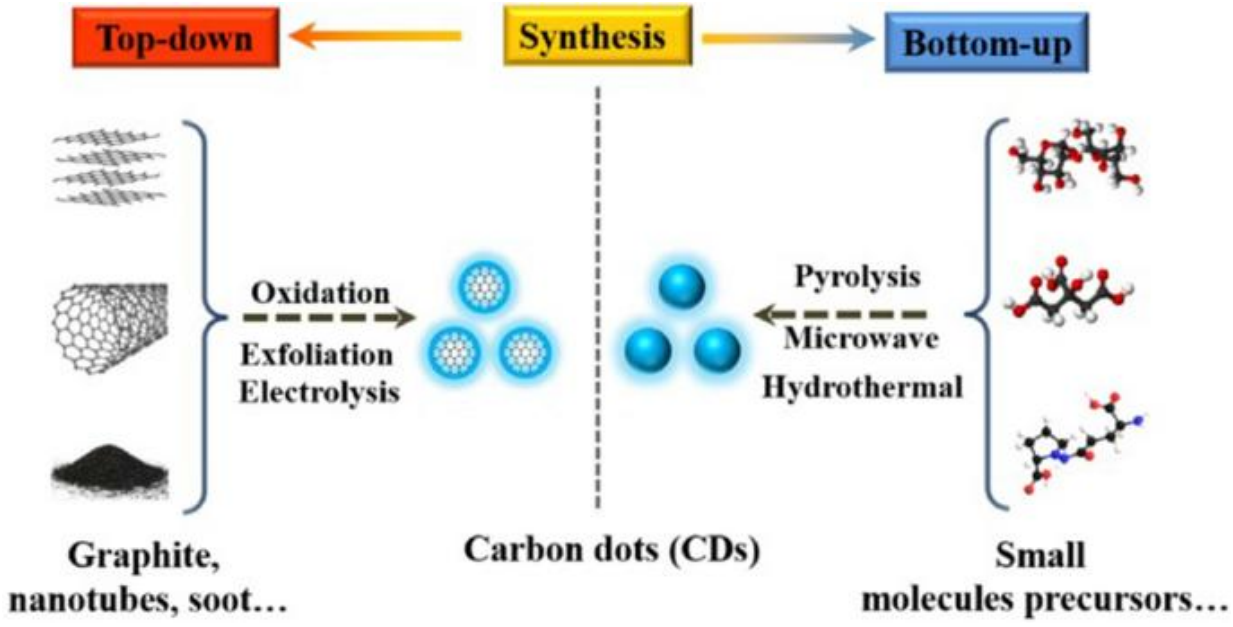

Figure 23: An illustration of common synthesis methods for carbon quantum dots [298]

2.5.3. Applications of Carbon Materials

In the biomedical sector, energy storage and electronics, carbon nanotubes offer a great range of uses. Carbon nanotubes (CNTs) are utilized in the field of electronics for the purpose of producing nanoscale electronic devices, such as transistors and interconnects [299], [301]. CNTs are utilized as electrodes in supercapacitors and batteries within the energy storage industry. This is due to the fact that they possess a high surface area and a high electrical conductivity [301]. Then they are also used in biomedicine and specifically in drug delivery, biosensing, and tissue engineering due to their biocompatibility and ability to penetrate biological barriers [299].

Graphene derivatives are used mainly as gas, chemical, and biological sensors due to their high sensitivity and selectivity [295]. They are also used in the energy storage sector, in supercapacitors, batteries, and fuel cells [301]. Finally, graphene derivatives are further used to enhance the mechanical and thermal properties of polymer composites [301].

The use of carbon dots has expanded into many other industries. Fluorescent CQDs are useful for both in vitro and in vivo imaging due to their photostability and biocompatibility [296]. Carbon dots are also used for ion and heavy metal detection due to their fluorescent properties [296]. Wastewater treatment, pollutant adsorption, and photocatalytic degradation are three areas where their adsorption capabilities are useful in environmental remediation [296].

2.5.4. Advantages and disadvantages of Carbon Materials

Carbon-based nanomaterials like carbon nanotubes (CNTs), graphene derivatives, and carbon dots have gained a lot of interest. For instance, CNTs are very strong and flexible, have high electrical and thermal conductivity, and are biocompatible [299], [301]. These features give them prospects for electronic applications and medical uses. But they also have several disadvantages, including questions regarding toxicity, environmental effects, and the high expense and complexity of manufacturing [299], [301]

Especially given their great surface area, high conductivity, and mechanical strength, graphene derivatives show likewise much potential. They're quite flexible and are being looked at in all from composite materials to energy storage [294], [295]. Producing high-quality graphene is still costly, and getting it to be uniformly dispersed can be challenging [294].

Then there are carbon dots—small, flexible particles with tunable optical qualities that make them excellent for imaging and sensing, simple to manufacture, safe for biological usage, and

so on [296], [297]. They can be unstable under some circumstances, though, and they don't conduct electricity as well as CNTs or graphene [296], [297]. Every one of these substances has advantages and disadvantages, and selecting the appropriate one actually relies on what one requires it to perform.

Table 6 gathers the key aspects of the main carbon materials.

Table 6: Comparison of Carbon Materials

Material	**Key Properties**	**Applications**
Carbon Nanotubes (CNTs)	High electrical conductivity, mechanical strength, and thermal conductivity	Electronics, energy storage, biomedical applications
Graphene Derivatives	High surface area, electrical conductivity, and chemical tunability	Sensors, energy storage, composites
Carbon Dots (CDs)	Tunable optical properties, biocompatibility, and photostability	Biomedical imaging, sensing, environmental remediation

2.6.Sol-gel materials

2.6.1. Synthesis Methods of Sol-Gel Materials

In the realm of synthesizing advanced materials, particularly those with mesoporous and nanostructured properties, the sol-gel process is a flexible and often employed technology. In the field of sol-gel chemistry, there are a number of different synthesis methods available, and each of these has its own set of advantages and applications.

The colloidal sol-gel method produces nanoparticles that present great repeatability and homogeneity. Specifically, this is accomplished by hydrolyzing metal precursors such as alkoxides, which results in the formation of a colloidal suspension or sol [302]. An additional method of synthesis is known as electrochemically assisted self-assembly (EASA). This involves the utilization of an applied potential in order to vertically align pore channels. In light of this, the production of well-ordered mesoporous thin films is made possible. This design is ideal for enhancing the efficiency of mass transfer. Changing variables such as temperature, precursor-water ratio, and precursor-catalyst ratio control the particle size. Coatings can be made straight from the sol, or they can be dried to create powders [303].

The non-hydrolytic sol-gel (NHSG) method is an alternative to traditional aqueous methods. This approach allows for better control over the distribution of organic and inorganic components in hybrid materials. It is appropriate for creating hybrid heterogeneous catalysts with improved stability and catalytic activity [304]. Finally, low-temperature sol-gel synthesis enables the production of ceramic and hybrid materials at near-room temperature. It's ideal for thermally sensitive structures with large surface areas and small pore size distributions [305].

All these different sol-gel synthesis methods make it easier to create and use a wider range of materials in fields like coatings and catalysis.

2.6.2. Fundamental Chemistry of Sol-Gel Processes

The sol-gel process involves chemical reactions that transform a sol (a colloidal solution) into a gel (a three-dimensional network). This process includes three steps:

1)Hydrolysis and Condensation Reactions

2)Precursors and Solvents

3)Gelation and Aging (Figure 20)

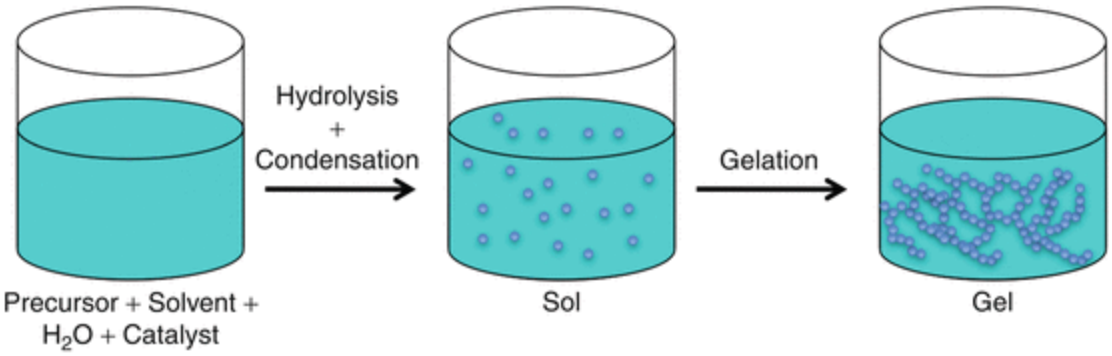

Figure 24: Sol-gel method [306]

The sol-gel method begins with the hydrolysis of metal alkoxide precursors, which, by means of condensation, create a three-dimensional network. Hydrolysis produces hydroxyl groups that interact by polycondensation to create a gel. These reactions are sensitive to pH, temperature, and precursor type among other variables. All these parameters have to be closely managed to customize the final material characteristics [307], [308]. It is very important to choose the right precursor and solvent because metal alkoxides provide reactivity, and solvents like alcohols or water can change the rate of hydrolysis and the structure that is formed. Furthermore, using chelating agents could help to adjust material properties [307]. Gelation is the process by which a sol transforms into a rigid network. The aging phase allows the gel to relax and rearrange, influencing porosity and texture [307]. Understanding these steps is essential for optimizing the material's properties.

2.6.3. Basic Categories of Sol-Gel Materials

Generally speaking, sol-gel materials can be classified depending on their chemical composition and structural characteristics. Among the most popular sol-gel materials are silica-based ones. They are chemically stable, having a great surface area and tunable pore size. Their adjustable design makes mesoporous silica especially popular in drug delivery systems, catalysis, and energy storage [303], [307]. Primarily made of titanium dioxide (TiO_2), titania-based materials are valued for their photocatalytic properties. The sol-gel method may produce different types of TiO_2, such as anatase, rutile, and brookite. Anatase is the most efficient for applications such as solar energy conversion and environmental remediation [309].

The mechanical strength of inorganic networks is combined with the flexibility of organic molecules in hybrid organic-inorganic materials called hybrid organic-inorganic materials. As a result of their greater thermal stability, these hybrids are finding use in a variety of sectors, including biology, optics, and sensing [310].

With the use of sol-gel processes, it is possible to synthesize not only silica and titania, but also other metal oxides such as alumina, zirconia, and ceria. Considering the fact that these materials are prized for their extended life and wide surface area, they are excellent for use in a variety of applications [307].

2.6.4. Applications of Sol-Gel Materials

Sol-gel materials present various applications in many fields, thanks to their high surface area, tunable porosity, and chemical stability. Mesoporous silica materials are widely used in drug delivery and biomedical applications due to their high surface area and tunable pore size. Sol-gel materials are also employed in biomedical applications, including implants and biosensors [303], [307]. These materials have importance in energy conversion for uses including solar cells, supercapacitors, and fuel cells. Dye-sensitized solar cells, for example, employ TiO_2 and TiO_2/SiO_2 nanoparticles made using the sol-gel method [311]. Sol-gel materials are also used as catalysts, and they are employed in both epoxidation reactions and heterogeneous catalysis with great results. The sol-gel process allows for the synthesis of catalysts that have tailored properties and textures [312]. Finally, sol-gel materials are used in environmental applications such as water purification and gas sensing. Their high surface area and chemical stability make them effective in adsorption and filtration processes. Additionally, photocatalytic TiO_2 materials are used for the degradation of pollutants [307], [309].

2.6.5. Advantages and Disadvantages of Sol-Gel Processes

Compared to conventional methods of material synthesis, the sol-gel process has significant benefits. One extremely important aspect of the sol-gel method is its ability to enable the production of ceramic and glass materials at rather low temperatures. This reduces the energy costs and facilitates the production of thermally sensitive materials [305]. Sol-gel materials often exhibit high surface areas and tunable porosity, which broadens their applications to many sectors [303], [307]. With this process, one can achieve better homogeneity and control over the chemical composition of the product, and it is also very inexpensive to employ. Thus, a large-scale production can be achieved economically [302], [308].

There are also some disadvantages to this method. Firstly, the sol-gel process is sensitive to parameters such as pH, temperature, and precursor concentration [303], [307]. Careful control is then required in order to have the desired properties. During drying, gels frequently shrink and break, which compromises the end quality of the product [307]. Often amorphous, sol-gel

materials can not be used in applications needing crystalline structures. High-temperature treatments can induce crystallization but may alter the material's properties [305].

Table 7 provides a comparative assessment of sol-gel materials.

Table 7: Comparison of Sol-Gel Materials, Synthesis Methods, and Applications

Material Category	**Synthesis Method**	**Applications**	**Citation**
Silica-Based Materials	Colloidal Sol-Gel, EASA	Drug Delivery, Catalysis, Energy Storage	[303], [307]
Titania-Based Materials	Alcohol-Based Sol-Gel, Aqueous Sol-Gel	Photocatalysis, Solar Cells, Environmental Remediation	[309], [311]
Hybrid Organic-Inorganic	Non-Hydrolytic Sol-Gel, Colloidal Sol-Gel	Sensors, Optics, Biomedical Devices	[310]

2.7.Molecularly Imprinted Polymers

Molecularly imprinted polymers (MIPs) are created in order to mimic the molecular recognition that takes place in biological systems. They are produced with a process called molecular imprinting, where a template molecule generates specific binding sites in the polymer matrix.

2.7.1. Synthesis of Molecularly Imprinted Polymers

Several important processes make up MIP synthesis: template molecule, functional monomers, cross-linkers, and initiators are chosen first; then polymerization and template removal follow. The characteristics of the produced MIPs are greatly affected by the choice of polymerization method.

2.7.1.1.Traditional Synthesis Methods

Bulk polymerization is one of the most common methods for synthesizing MIPs. It involves mixing the template molecule, functional monomers, cross-linkers and initiators in a solvent. Then the polymerization process takes place. The resultant polymer is ground into tiny particles for application (Figure 21) [313]. Surface imprinting is another method; it involves placing molecules on the surface of a substrate (fex, in fibers or nanoparticles). It is good for imprinting large molecules, such as proteins, and has faster binding kinetics [314]. Then there is precipitation polymerization, which is polymerization in a solvent in which the resulting polymer is insoluble. Consistent particle size microspherical MIPs are made using it [315].

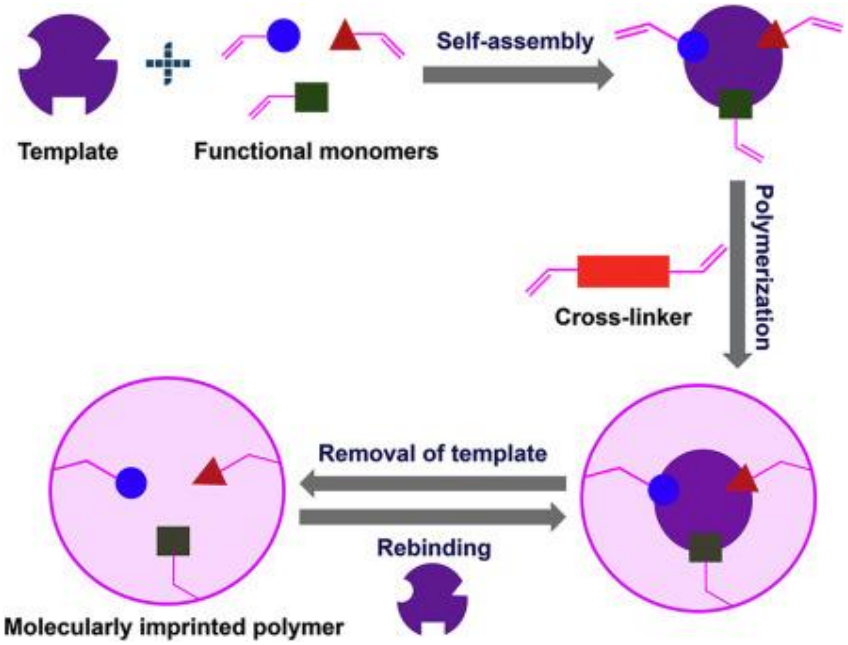

Figure 25: Schematic depiction of the creation of molecularly imprinted polymers [316]

2.7.1.2.Green Synthesis Approaches

Researchers are working to find more sustainable ways to synthesize MIPs, with the goal of reducing the use of potentially harmful compounds and solvents. One well-known green synthesis method is microwave-assisted synthesis. This method utilizes microwave radiation to speed up the polymerization process. This reduces energy use and reaction times [317]. Ionic liquids and deep eutectic solvents are eco-friendly alternatives to regular organic solvents. They help the imprinting process be more stable and selective [317]. Finally, supercritical fluid technology is also used as a green synthesis method. In this method, carbon dioxide and other supercritical fluids are used as agents. It is especially useful for creating MIPs with great surface area and porosity [318].

2.7.2. Applications of Molecularly Imprinted Polymers

MIPs have been used in the biomedical, environmental cleanup, food, and pharmaceutical industry. Their great selectivity, stability, and adaptability explain this. MIPs are first and foremost commonly employed to remove contaminants from wastewater, including phenolic compounds and dyes. They provide great adsorption capacity and selectivity [319]. Gas sensors for the identification of dangerous gases, such as volatile organic compounds (VOCs), also make use of MIPs. Ideal for environmental monitoring, they offer great sensitivity and stability [315].

MIPs are employed in drug delivery systems in the biomedical industry to provide regulated and targeted release of medications [320]. MIPs are used in biosensors to find infections and biomarkers. High selectivity and sensitivity let them help to identify disorders early [321]. At last, pharmacological and food uses are somewhat prevalent as well. MIPs serve to identify food impurities including heavy metals and pesticides. Food packaging also makes use of them to guarantee quality and safety [322]. MIPs are also employed to isolate and purify active pharmaceutical ingredients (APIs) from contaminants. They provide great adsorption capability and target molecule selectivity [323].

2.7.3. Pros and Cons of Molecularly Imprinted Polymers

MIPs are very selective and sensitive for target molecules since they show outstanding molecular recognition characteristics [313]. Chemically and thermally stable, MIPs allow one to utilize them several times without notable performance loss [321]. MIPs are also affordable when compared to natural antibodies and enzymes; therefore, they could be used in many different contexts [321]. From simple organic chemicals to big macromolecules, MIPs can be created for a wide spectrum of substances [314].

MIPs have many drawbacks, one of which is the diversity in their binding sites, which has an impact on the binding affinity and selectivity characteristics [324]. It is possible for the polymer matrix to occasionally hold residual template molecules, which may be an obstacle to applications [324]. Optimizing the circumstances under which the reaction takes place is essential to the successful synthesis of MIPs [322]. Therefore, it can be a lengthy and difficult process. Also, the binding ability of MIPs for target molecules may be limited, particularly in complex matrices [324].

Table 8 demonstrates the key aspects of molecular imprinted polymers.

Table 8: Key aspects of MIPs

Aspect	Description	Citation
Synthesis Methods	Bulk polymerization, surface imprinting, precipitation polymerization, and green methods	[313], [324]
Applications	Environmental remediation, biomedical diagnostics, food safety, and drug delivery	[320], [322]
Advantages	High selectivity, stability, reusability, and cost-effectiveness	[321]
Limitations	Heterogeneous binding sites, template leakage, and limited binding capacity	[324]

2.8.Magnetic Nanoparticles

2.8.1. Synthesis of MNPs

The synthesis of magnetic nanoparticles dramatically affects their physicochemical properties and potential usage. Researchers have altered the size, shape, and composition of magnetic nanoparticles (MNPs) to improve their effectiveness in biomedicine, environmental remediation, and electronics. These researchers have developed a number of different methods to conduct these modifications.

2.8.1.1.Chemical Synthesis Methods

One of the methods that is utilized the most frequently is called coprecipitation, and it is particularly useful for the production of iron oxide nanoparticles. The formation of nanoparticles is accomplished through the simultaneous precipitation of metal ions in an aqueous solution. Its simplicity and scalability make it preferred [325], [326]. The thermal breakdown method is another method that is used a lot. In this method, metal precursors are broken down using an organic solvent at high temperatures. Significant control over the crystallinity and shape of the particles is possible [327].

Hydrothermal and solvothermal synthesis are also efficient. These methods involve the interaction of metal salts in aqueous or organic solvents under increased pressure and temperature. These methods are used to produce consistent nanoparticles with well-defined shapes [326], [328]. Microwave-assisted synthesis also rapidly heats the reaction mixture using microwave radiation. By this means, reaction durations are significantly decreasing, and nanoparticles are produced with consistent size and form [329].

2.8.1.2.Physical and Biological Methods

The production of MNPs can be accomplished in a variety of ways, including chemical pathways, physical approaches, and biological applications. Laser pyrolysis is a physical method that utilizes laser radiation to break down precursor molecules. Consequently, this enables precise control of the nanoparticles' characteristics [330]. Green synthesis is a method that works by using biological agents such as plant extracts or bacteria to synthesize magnetic nanoparticles. These eco-friendly methods are common in bioanalysis because they are biocompatible and eliminate toxic chemicals [331].

2.8.1.3. Surface Functionalization

Magnetic nanoparticles are surface functionalized after synthesis to improve stability, solubility, and application. One common method is to coat the particles with surfactants or polymers since this helps to prevent agglomeration and enhances dispersion in various solvents

[325], [326]. Silica coating deposits a thin silica layer on the nanoparticle surface to improve stability and provide a basis for more functionalization [326], [330]. Eventually, ligand exchange replaces hydrophobic surface ligands with hydrophilic ones. This makes the nanoparticles water-soluble, and they are suitable for biomedical applications [331].

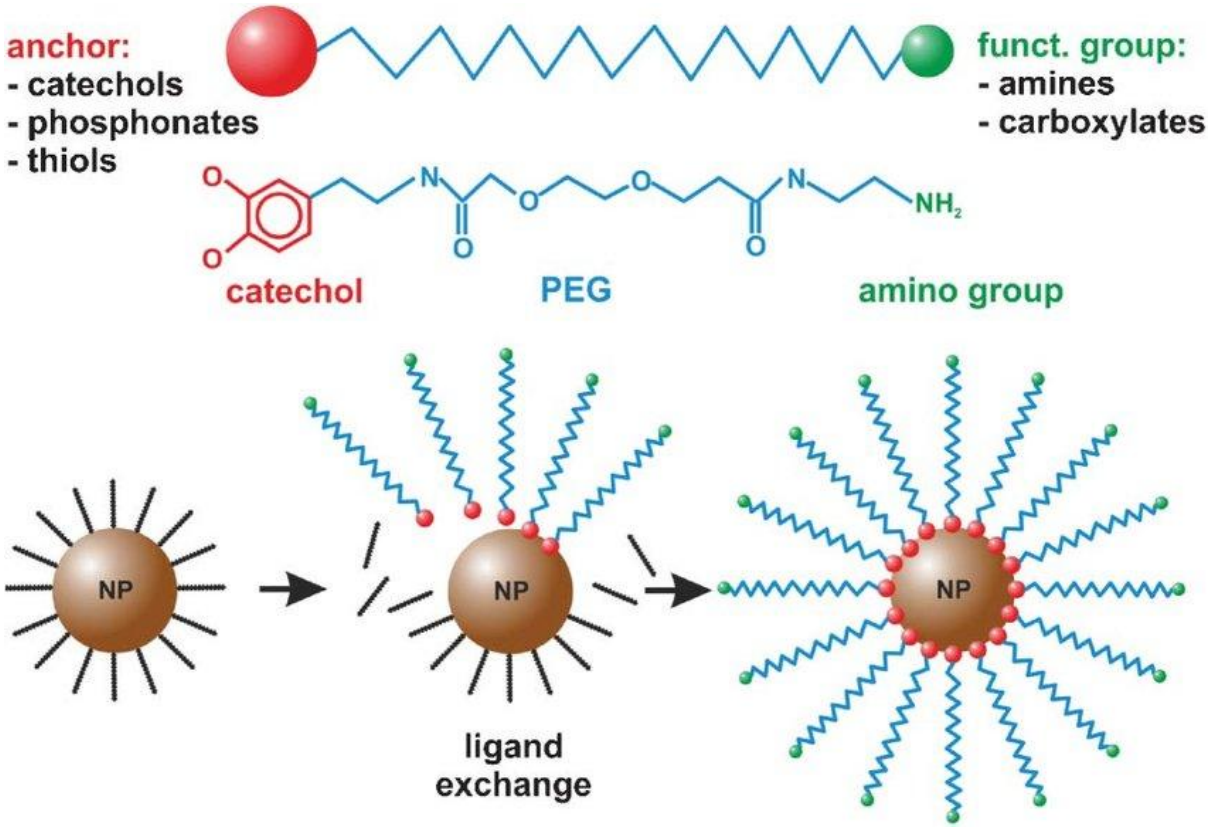

Figure 26: Surface modification of magnetic NPs using bi-functional ligands [332]

The image above (Figure 22) illustrates the ligand exchange process. In this process, the original hydrophobic ligands on the nanoparticle (NP) surface are replaced with hydrophilic ligands, such as polyethylene glycol (PEG) molecules. These ligands typically contain anchor groups (e.g., catechols, phosphonates, or thiols) that bind to the nanoparticle surface, and functional groups (e.g., amines or carboxylates) that remain exposed to interact with the surrounding medium.

2.8.2. Properties of MNPs

Due to their unique features, magnetic nanoparticles are useful in many science and industrial fields. They are useful in environmental science, technology and health care because of their nanoscale size and special magnetic properties.

2.8.2.1.Magnetic properties

The magnetic properties of these materials are amazing, and one of the most surprising is their superparamagnetism. In contrast to bulk magnetic materials, superparamagnetic nanoparticles only get magnetized when they are in the presence of an external magnetic field. When the field is removed, the nanoparticles lose their magnetization. This property is very useful in biological applications such as magnetic separation and personalized medicine administration [333]. In addition, magnetic nanoparticles typically have high saturation magnetization, which indicates that they are capable of achieving a high level of magnetization. This makes them ideal for applications like magnetic resonance imaging (MRI) and magnetic hyperthermia [334].

2.8.2.2.Physical and Chemical Properties

Magnetic nanoparticles also show adjustable physical and chemical characteristics that can be modified during synthesis. The key is size and shape control, as changing these factors would directly affect magnetic strength, surface area, and biological interactions [330]. In addition, the surface chemistry of these nanoparticles can be customized by the process of functionalization. This makes it possible for them to be utilized in biosensing, drug delivery, and catalysis [325], [326].

2.8.2.3.Biocompatibility

In biological and medical applications, biocompatibility is extremely crucial. Uncoated magnetic nanoparticles could be hazardous. They could get safer by altering the surface and coating it with biocompatible materials, including silica or polymers. Due to the fact that these modifications not only enhance biocompatibility but also reduce cytotoxicity, the nanoparticles are now suitable for usage in vivo [335].

2.8.3. Applications of MNPs

Magnetic nanoparticles, with their unusual magnetic qualities and nanoscale size, have drawn much interest in several sectors including healthcare, environmental cleanup, energy, and data storage.

2.8.3.1.Biomedical Applications

Magnetic nanoparticles have several interesting uses in the biological field. They have a role as carriers for drugs that can be guided to certain organs or tissues using an external magnetic field [336], [337]. Magnetic resonance imaging (MRI) makes use of superparamagnetic iron oxide nanoparticles as contrast agents. They significantly improve image resolution and make a more exact diagnosis [338], [339]. Moreover, in hyperthermia therapy, magnetic

nanoparticles can generate localized heat under alternating magnetic fields, hence providing an effective approach for cancer treatment [340], [341]. By enabling the sensitive and selective detection of pathogens and biomarkers, functionalized magnetic nanoparticles can support biosensing applications [342].

2.8.3.2.Environmental Applications

Magnetic nanoparticles help to the protection of the environment. MNPs in water treatment help to remove organic contaminants and heavy metals from wastewater. This is due to their great surface area and simplicity of magnetic separation [343], [344]. Moreover, especially in the breakdown of persistent organic pollutants, they serve as effective catalysts in environmental cleanup activities [329], [330].

2.8.3.3.Energy Applications

Magnetic nanoparticles in the energy industry improve the performance of thermoelectric materials. In this way, there is an increasing energy conversion efficiency in several applications [336], [342]. Their high magnetic moments and exceptional stability make them also rather important for magnetic energy storage technologies, especially for magnetic data storage systems [331].

2.8.3.4.Other Applications

Magnetic nanoparticles are beneficial in a variety of other applications. As a result of their high sensitivity and rapid reaction times [6, 20], they are crucial components of sensors that are designed to identify gases, biomolecules, and other types of analytes, respectively [330], [345]. Studies that are just beginning to emerge in the field of agriculture are looking into their potential applications for crop improvement and regulated pesticide delivery [329]

Table 9 outlines a comparison of key aspects of magnetic nanoparticles.

Table 9: Comparison of Key Aspects of Magnetic Nanomaterials

Synthesis Method	Key Properties	Applications
Coprecipitation	High yield, uniform size	Drug delivery, MRI contrast agents
Thermal Decomposition	Controlled size and shape	Catalysis, hyperthermia therapy
Green Synthesis	Biocompatible, eco-friendly	Biomedical applications, water treatment
Hydrothermal Synthesis	Uniform nanoparticles	Environmental remediation, biosensing

Synthesis Method	Key Properties	Applications
Laser Pyrolysis	High purity, controlled composition	Data storage, energy applications

2.8.4. Challenges and Future Directions of MNPs

Researchers are currently attempting to find solutions to the issues that magnetic nanoparticles present. Safety is one of the primary issues, particularly when these materials are utilized in biomedicine. Concerns regarding their compatibility with the human body continue to be challenging [331], [344]. Producing on a larger scale presents further difficulty. Producing high-quality nanoparticles on a large scale is neither cheap nor easy [325], [326]. There are also environmental issues to take into account—how these particles act in nature and whether they create any hazards once set free into the ecosystem [344].

Research should be conducted with the goals of enhancing the stability of these nanoparticles. The synthesis process should be more environmentally friendly, and the investigation should focus on novel applications in intriguing fields such as agriculture and energy storage.

3. UV filters

3.1.Introduction on UV-filters

Ultraviolet (UV) filters, often called UV absorbers or UV filters, are chemicals that are made to absorb or reflect UV rays. In this way, they are keeping us safe from the damaging effects of sunlight [346]. They are important parts of sunscreens and other personal care products, as well as of many industrial uses such food packaging and plastics [347], [348].

3.1.1. Types of UV Filters and Their Functions

There are two basic types of UV filters: organic (chemical) filters and inorganic (mineral or physical) filters [349], [350].

1. **Organic UV Filters**: These filters work by collecting UV light and turning it into heat, which the skin then releases [351]. Avobenzone, octinoxate (also known as octylmethoxycinnamate or OMC), octocrylene, and benzophenones are some common examples [352], [353].
    - *Avobenzone*: This chemical mostly absorbs UVA light. However, it is noted for being photolabile, which means it needs to be stabilized with other filters [352].
    - *Octinoxate (OMC)*: It is a popular UVB filter; however there are concerns about its ability to affect the endocrine system [353].
    - *Octocrylene*: It works as a screen for both UVB and UVA rays and can help keep avobenzone stable [352].
    - *Benzophenones (e.g., oxybenzone)*: They are broad-spectrum UV filters that can absorb both UVA and UVB radiation. However, they have raised concerns since they may be harmful to people and the environment [354].
2. **Inorganic UV Filters**: These filters function by reflecting, scattering, and absorbing UV radiation [350], [354]. The most commonly used are zinc oxide (ZnO) and titanium dioxide (TiO_2). People frequently choose them because of the protection they offer and their lower irritation possibility [354].
    - *Zinc Oxide (ZnO)*: Protects against both UVA and UVB radiation and is thought to be safe for people to use [354].

- *Titanium Dioxide (TiO_2)*: Good in blocking UVB and short-wave UVA radiation; sometimes used in nanoparticle form to reduce white cast on the skin [354].

3.1.2. Mechanism of Action

UV filters operate because they can absorb UV rays at certain wavelengths [351]. UV radiation is divided into three main categories:

- **UVA (315-400 nm)**: Contributes to skin aging [355].
- **UVB (280-315 nm)**: This is the main cause of sunburn and a big reason why skin cancer develops [353], [355].
- **UVC (100-280 nm)**: The Earth's atmosphere mostly absorbs it, so it doesn't reach the surface (Figure 23) [355].

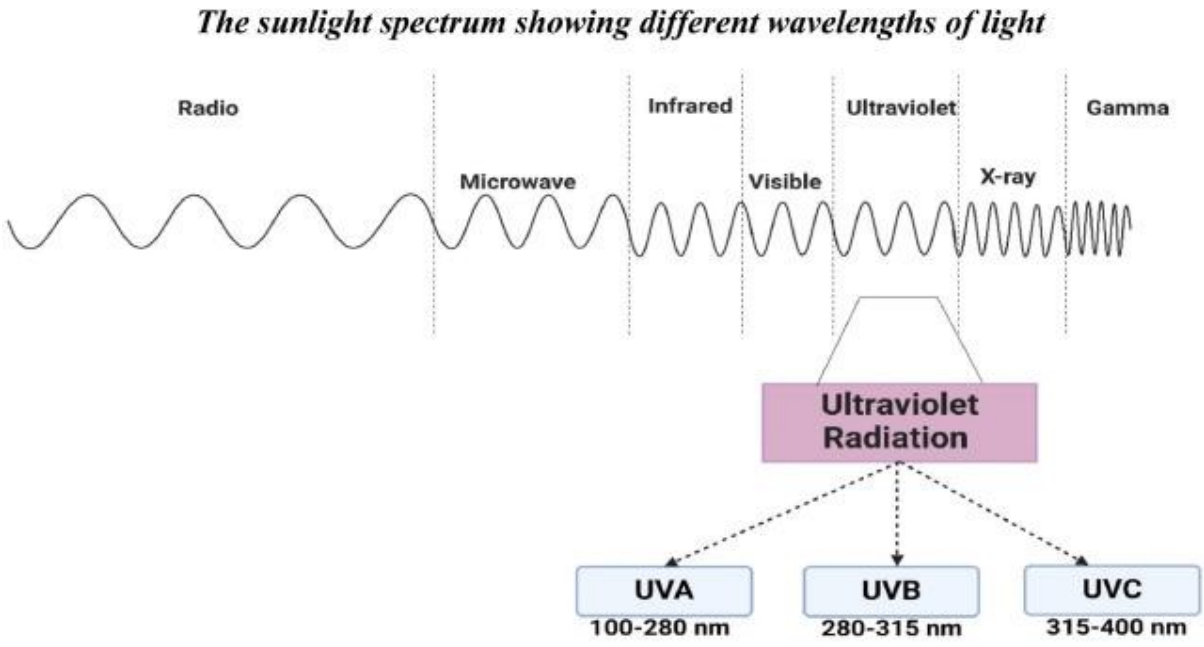

Figure 27: The sunlight spectrum showing different wavelengths of light [355]

UV filters are designed to absorb or reflect UVA and UVB radiation in order to prevent it from penetrating the skin [351]. Organic filters absorb the radiation and release it as heat, while inorganic filters reflect and scatter the radiation [351].

3.2.Sources and Environmental Pathways of UV filters

UV filters are utilized in a wide range of personal care products, as well as in industrial applications. Therefore, they are increasingly recognised as environmental pollutants due to their extensive use and persistence [356]. These compounds find their way into the environment through multiple anthropogenic pathways [357].

3.2.1. Sources of UV Filters

There are many different sources of UV filters in the environment, but most of them come from human activities and products. These filters, both organic and inorganic, exist in personal care products, industrial applications, and recreational activities. This subsequently leads to their release into various environmental matrices (Figure 24). Understanding these sources is crucial for assessing their ecological and health impacts.

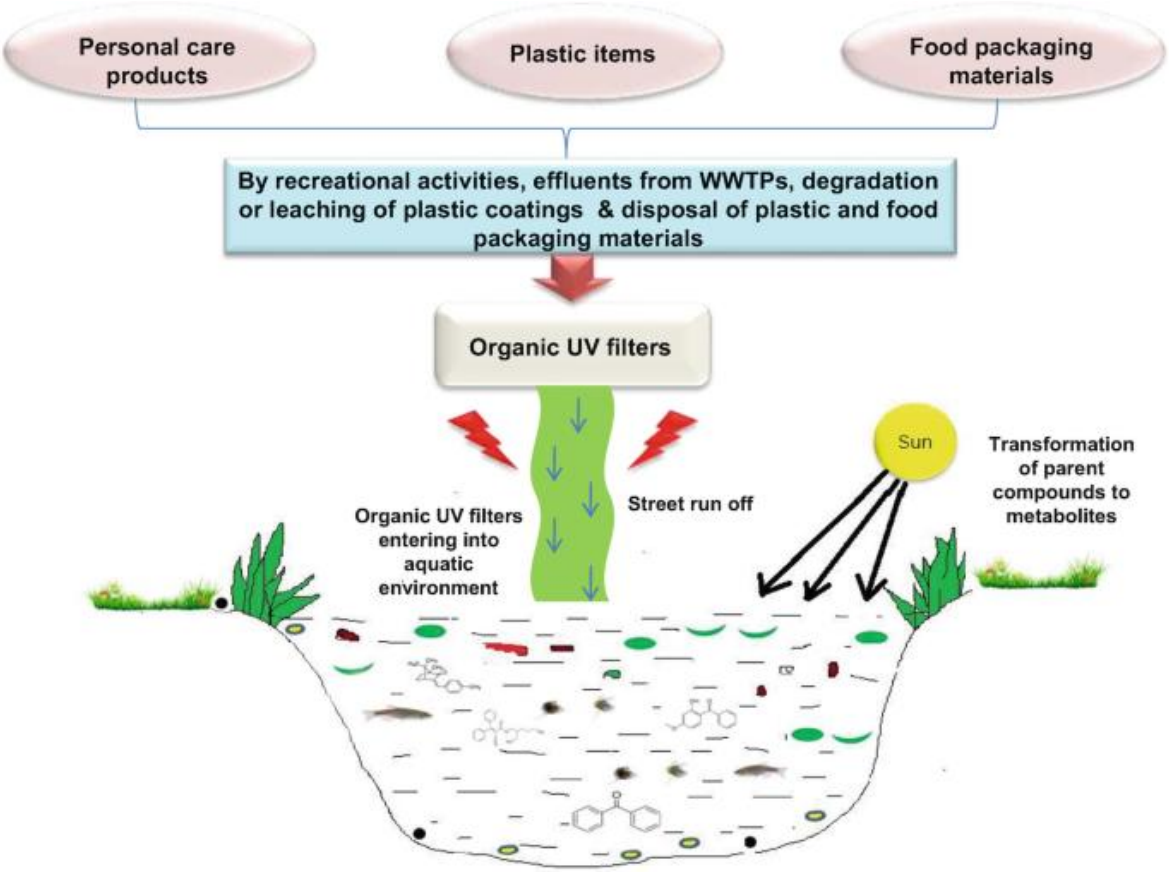

Figure 28: Fate of UV-filters in the environment [358]

Sunscreens are a primary source of UV filters in aquatic environments. When people at the beach and in the water put on sunscreen, the UV filters can wash off right into the water [359]. Similarly, the use of cosmetics and lotions that include UV filters results in their release during washing and bathing. [360].

UV filters are also incorporated into plastics, coatings, and textiles to protect these materials from UV degradation [361]. UV filters can be released into the environment by leaching from these goods while they are being used or discarded. Furthermore, the insufficient removal that occurs during the treatment of wastewater makes it possible for ultraviolet filters to infiltrate aquatic ecosystems [362]. Finally, household wastewater contains UV filters from personal care products [363].

3.2.2. Environmental pathways

An estimation of the lipophilicity of compounds may be obtained by calculating the octanol-water partition coefficient (log kow) value. After it has been released into the ecosystem, this is what decides how it will be distributed between water and sediment. Compounds that are poorly soluble in water tend to build up in sludge and sediments [359].

3.2.2.1.Accumulation Mechanisms

Sediment Accumulation: A lot of UV filters are hydrophobic, which means they don't dissolve easily in water and tend to stick to particulate matter, which eventually settles into sediments [364]. Researchers have found different UV filters in sediment samples, including benzophenone-3 (BP-3), octocrylene (OCR), and 4-methylbenzylidene camphor (4-MBC), among others [365], [366]. For example, a study in Hong Kong and Japan revealed that all sediment samples included seven of the eleven target UV filters [367]. Researchers in Nigeria have also found UV filters in sediments in freshwater [365].

Bioaccumulation: It has been shown that some ultraviolet (UV) filters, such as benzophenone-3, may accumulate in organisms, which suggests that trophic transfer might take place [364]. It has been shown that bioaccumulation occurs in a variety of aquatic organisms, such as mussels, fish, and corals [368], [369], [370]. For example, the tissue concentrations of 4-MBC, BP-4, and OC reached 418, 263, and 327 μg/kg d.w. after just 24 hours of exposure to 1 μg/L, as demonstrated by research conducted on Mytilus galloprovincialis mussels [368]. Fish are also regarded to be important creatures for detecting sources of pollution in aquatic ecosystems. There have been studies that have reported the existence of ultraviolet (UV) filters in fish from river basins in Iberian countries [369].

UV filters can undergo trophic transfer, moving through the marine food web. A study in South Korea investigated the occurrence and distribution of benzotriazole UV stabilizers (BUVs) and UV filters in seawater, sediment, and various biota species [371]. The diagram in Figure 25

highlights how plankton and filter feeders accumulate substances, transferring them to higher trophic levels and potentially leading to biomagnification.

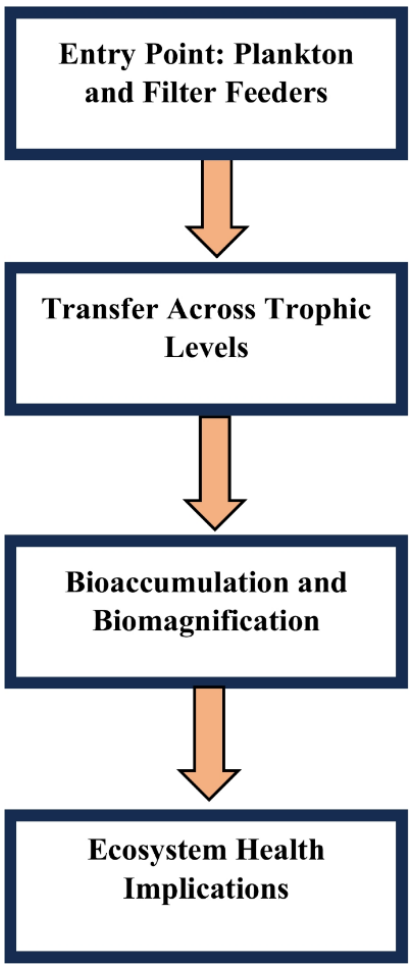

Figure 29: UV filters trophic transfer [371]

3.2.2.2.Photodegradation

While being in the aquatic environment, UV filters may undergo photochemical degradation. This could, of course, alter both the toxicity and the permanence of these filters [372]. The photodegradation isn't just a single process, but instead, a number of different chemical processes. These are influenced by many factors, like the chemical structure of the UV filter, the presence of other compounds in the environment (such as dissolved organic matter-DOM), or the intensity of the UV light to which they are exposed [373].

- **Direct Photolysis:** In the direct photolysis of UV filters, the compound breaks down directly after exposure to UV light. This can lead to the formation of many different degradation products. Firstly, the molecule absorbs the UV radiation and ultimately it is being excited and then broken down [374]. What determines the efficiency of this process is the ability of each UV filter to absorb specific wavelengths of light [375].

Octyl methoxycinnamate (OMC), for example, is a UV filter that presents rapid degradation through the process of direct photolysis. As a consequence of this, cyclodimers and several other photoproducts are being produced [376].

- **Indirect Photolysis (Photosensitization):** When other substances are present in the environment (fex, DOM), they can potentially absorb and transfer energy to UV molecules, which in turn initiates their degradation [373]. DOM can act as a photosensitizer, accelerating the degradation of UV filters [373]. Also, the presence of persulfate is important in this process. For example, it boosts the photodegradation of benzotriazole under sunlight, with up to 90% degradation in two hours [377].

- **Reactive Oxygen Species (ROS):** Reactive oxygen species (ROS) such as singlet oxygen, hydroxyl radical, and superoxide radicals are often used in the process of photodegradation [378]. ROS are produced by photochemical reactions with ultraviolet light and other elements of the environment. Then, they may attack UV filters [379]. The reaction kinetics of UV filters with ROS are usually second-order kinetics. This classification shows that the concentration of both the UV filter and ROS affects the rate of degradation [380]. The presence of chromophoric dissolved organic matter (CDOM) also has the potential to boost the production of reactive oxygen species (ROS), leading to a sped-up indirect photolysis [381].

- **Photocatalytic Degradation:** There are many mechanisms in the photocatalysis of ultraviolet filters in aquatic environments. The use of materials such as titanium dioxide (TiO_2) and other new composites is important to break down UV filters. Several factors can affect the efficiency of photocatalysis. Two important factors are the type of catalyst that is utilized (for example, TiO_2 or $AgI/Bi_2Fe_4O_9$) and the light source. Under UV radiation, TiO_2 can achieve virtually full degradation of some UV filters in a couple of minutes [381]. Additionally, photocatalysis is responsible for the production of reactive species, including superoxide radicals (·O2–) and holes (h+). These species play an important role in the breakdown of ultraviolet filters like Benzophenone-1 (BP1) [382].

Factors Influencing Photodegradation

The rate and mechanisms of UV filters are influenced by many variables.

- **Matrix Effects:** The degradation of UV filters is influenced by the matrix effects that exist due to the environmental conditions around them. The surrounding matrix, such as water or sediment, plays a great role in their degradation. For instance, organic UV filters showed slower degradation rates in sediment compared to aqueous environments, where biodegradation is of great importance [383]. The degradation of UV filters is affected by environmental conditions such as salinity and dissolved organic matter, which can inhibit photolytic processes [381].
- **Concentration Effects:** Higher concentrations of ultraviolet (UV) filters have been shown to increase the production of chlorinated by-products in chlorinated water. This has been observed experimentally using 2-ethylhexyl-4-methoxycinnamate (EHMC) and 4-tert-butyl-4'-methoxydibenzoylmethane (BDM) [384].
- **Wavelength and Intensity of UV Radiation:** Different wavelengths of UV light can result in different photodegradation processes [375]. Both the intensity and the wavelength of the UV radiation are important. In general, increasing the UV intensity causes degradation rates to increase more quickly [375].
- **pH:** The pH is one of the most important elements that determines how quickly the UV filters disintegrate. Different UV filters present different degradation behaviour in different pH ranges. Among the factors contributing to this phenomenon is the presence of reactive species, such as radicals. In the case of acidic circumstances, the breakdown of benzotriazole (BT) in a system involving sunlight and persulfate is accelerated. The most reactive species in this system are sulfate radicals ($SO_4 \cdot -$) and hydroxyl radicals ($\cdot OH$). As a consequence, the rate of deterioration is accelerated in comparison to settings that are neutral or alkaline [377]. On the other hand, alkaline conditions, in general, have the effect of reducing the rates of degradation. Because of the lower activation rates of persulfate and the deprotonated form of BT, which is less reactive, the breakdown rate of benzotriazole is significantly reduced [377]. Here are, however, a few isolated instances in which ultraviolet (UV) filters demonstrate accelerated degradation in alkaline environments. One such instance is the photodegradation of polyaminobenzoic acid (PABA) [385]. During UV-only processes, the most effective conditions for the breakdown of atrazine are those with a neutral pH. This means that the equilibrium of reactive species is favorable for degradation, and therefore, there is no need for further oxidants [386].

- **Temperature**: For instance, 3-methylbutyl-(2E)-3-(4-methoxyphenyl)-acrylate (IMC) displays a reduced degradation in the absence of DOM when it is subjected to higher temperatures [384]. The fact that this is the case suggests that higher temperatures could make the breakdown of IMC more gradual under these circumstances.
- **Presence of other substances**: Humic acids have a great influence on the degradation of UV filters. They are presenting both enhancing and inhibiting effects, which depend on their concentration and molecular characteristics [387], [388]. At lower concentrations, HAs can enhance the photodegradation of UV filters by facilitating the formation of ROS. At high concentrations, they tend to inhibit this process due to the presence of larger colloidal organic matter that absorbs UV light and scavenges reactive oxygen species (ROS) [388].

Environmental Implications

The photodegradation of UV filters leads to the formation of several degradation products [384]. The majority of these products may be hazardous to the environment [389]. For example, the degradation products from the UV filters 2-ethylhexyl-4-methoxycinnamate (EHMC) and 4-tert-butyl-40-methoxydibenzoylmethane (BDM) seem to have more toxicity than the parent UV filters (Figure 26) [384]. Because of this, it is essential to research the level of toxicity of these degradation products [390]. However, it is worth mentioning that the breakdown of UV filters could also lead to the production of less toxic intermediates. For instance, researchers have discovered several degradation routes for the UV filters para-aminobenzoic acid (PABA) and octyl methoxycinnamate (OMC). There is hope that these many routes and intermediates can have a positive impact on the treated water [391].

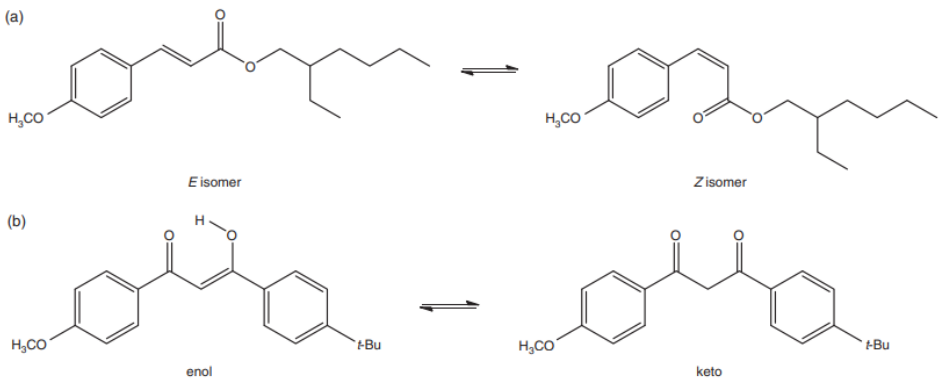

Figure 30: (a) Photoisomerisation of the UV filter 2-ethylhexyl-4-methoxycinnamate (EHMC) – E and Z isomers. (b) The keto–enol tautomerism of the UV [29]

3.3. Occurrence and Environmental Toxicity of UV Filters in Biotic and Abiotic Compartments

3.3.1. Toxicity in Abiotic Compartments

UV filters have been found in both surface waters and sediments, and the fact that they are persistent, lipophilic, and have the capacity to form reactive intermediates is causing scientists to be concerned about the influence they have on the environment. Water samples help determine solubility and concentration, while sediments and the SML are particularly relevant for tracking lipophilic compounds [392], [393]. Titanium dioxide (TiO2) and zinc oxide (ZnO) are two of the most widely used inorganic ultraviolet (UV) filters. The behavior of these filters varies depending on whether they are in micrometric or nanometric forms. The micrometric form of titanium dioxide may be washed away up to 49%, whereas the nanometric form can be released at rates ranging from 8% to 72%, depending on the composition of the cosmetic [394]. Following that, they are either dispersed or aggregated according to characteristics such as the pH, salinity, and the presence of organic matter, such as humic acids [395], [396]. TiO_2 nanoparticles exhibit photocatalytic activity, which results in the production of reactive oxygen species (ROS) such as hydrogen peroxide (H_2O_2) and hydroxyl radicals (HO•). These have the potential to place aquatic creatures under oxidative stress. This activity is also strongly impacted by the particle size. Nanoparticles are considerably more reactive, and they need protective coatings in order to restrict the generation of reactive oxygen species (ROS) [397], [398].

There is a tendency for organic UV filters to accumulate at the air–water interface in the SML. This prevents sunlight from penetrating, which in turn causes issues for the photosynthetic processes of marine primary producers [393]. When exposed to sunlight, several organic filters, including EHMC, OCR, PABA, and OD-PABA, generate reactive oxygen species (ROS). Some other organic filters, such as BP-3, BP-8, and OCS, are less photoreactive [399]. While photodegradation may, in some instances, lessen toxicity, the potential for genotoxicity continues to be a cause for concern at levels that are often reported in coastal waters [400]. As an additional point of interest, the presence of sunscreens is a contributor to the release of heavy metals and nutrients such as nitrates, phosphates, and ammonium. This can occur either as a result of the decomposition of organic compounds or as a result of manufacturing wastes. The result is eutrophication, which in turn causes algal blooms [401]. Simulations conducted on beaches in the Mediterranean region have revealed a notable increase in the concentrations of

some metals, including a twenty percent increase in titanium and a five percent increase in aluminum [401].

The potential for synergistic toxicity is often neglected. This happens when ultraviolet (UV) filters interact with other pollutants sediments, like heavy metals or pharmaceuticals. This has the potential to increase both their bioavailability and their overall toxicity [402]. It is important to note that UV filters have extended half-lives in sediment matrices, which can range from a few weeks to several months. This highlights the possibility of low-dose, chronic exposure to aquatic species, particularly in poorly flushed systems, such as lagoons or harbors [403].

3.3.2. Toxicity in Biotic Compartments

3.3.2.1.Primary Producers and Lower Trophic Levels

Phytoplankton and zooplankton are crucial to aquatic food webs. There are exposure studies that show that UV filters such as BP-3 and homosalate are quite toxic, especially to green algae like Tetraselmis sp.. This causes inhibited growth, lysis and metabolic dysfunction in them , even at very low concentrations at 10 µg/L [404].

Zooplankton species such as Artemia salina also show some toxicity to UV filters like OC and DHHB, with LC_{50} values in the hundreds of µg/L range. Although this is higher than the typical environmental levels, it indicates the potential risk when there is concentrated exposure [404].

3.3.2.2.Invertebrates and Fish

Bivalves, such as Mytilus galloprovincialis and sea urchins (Paracentrotus lividus), show cellular damage and oxidative stress when they are exposed to nano-TiO2 and ZnO. Fish generally exhibit toxicological symptoms, which include endocrine disturbance, reduced reproduction, developmental abnormalities, and mortality [405]. OC and 4-MBC are two examples of UV filters that can be found in the liver, muscle, and gills of zebrafish (Danio rerio) and brown trout (Salmo trutta). Their hormonal signaling is disrupted as a result of the exposure [406].

3.3.2.3.Coral Reefs and Symbionts

Coral reefs are especially sensitive to the damage that can be caused by UV filters. It has been proven that organic filters like BP-3 and 4-MBC can cause bleaching in corals. This is due to the initiation of the lytic cycle of dormant viruses in Symbiodinium spp., which are the algae that live in corals. The exposure of Stylophora pistillata to ZnO at a concentration of 90 µg/L led to a decrease of 38% in the efficiency of photosynthetic processes. This underlines the potential phototoxicity of metal oxide filters [407]. Within a few hours, even the smallest

concentrations of sunscreen, which can be as low as 10 µL/L, have the potential to induce stress reactions and mucus secretion in corals [405].

Table 10 compiles representative examples of UV filter toxicity.

Table 10: UV Filter Toxicity Examples

UV Filter	**Exposure Conditions**	**Organism**	**Effects**	**Reference**
BP-3	10–312 µg/L for 14	Zebrafish (Danio rerio)	Bioaccumulation in tissues, antiandrogenic gene expression changes	[405]
EHMC	Up to 4.1 mg/L in water	Mytilus galloprovincialis (Mediterranean mussel)	Cellular damage, glutathione S-transferase stimulation	[405]
n-TiO_2	0.5–250 mg/L for 24 h to 6 days	Cyanobacteria (Anabaena variabilis)	Reduced nitrogen fixation, growth rate, and induced toxicity	[405]
n-ZnO	10–80 mg/L for 72 h	Diatoms (Phaeodactylum tricornutum)	Growth inhibition, Zn bioaccumulation, and toxicity	[405]
OC (Octocrylene)	0.1–2 mg/L	Tetraselmis sp. (Green algae)	Reduced growth and metabolic activity	[404]
4-MBC	1–10 µg/L for 7 days	Japanese clam (Ruditapes philippinarum)	100% mortality at 100 µg/L, LC50 = 7.71 µg/L	[405]
ZnO	90 µg/L	Stylophora pistillata (coral)	38% reduction in photosynthetic efficiency	[405]
BP-3	Various, up to 2700 ng/L in surface water	Common carp (Cyprinus carpio)	Bioaccumulation in liver and muscle; no anti-progestogenic activity in tissue	[406]

3.3.2.4.Bioaccumulation and Biomagnification

As it is mentioned before, UV filters are lipophilic, which means that they tend to accumulate in fatty tissues. According to fish studies, the fish liver is a major site of bioaccumulation, followed by gills and muscle tissues. Filters such as EHMC and HMS display high bioaccumulation factors in crustaceans like swamp crayfish (*Procambarus clarkii*).

Also, there is evidence for biomagnification. UV filters have been detected in birds such as Eurasian sparrowhawks and French owls, which is a result of trophic tranfer from aquatic to terrestrial food chains. These findings raise concerns not only for the ecosystem but also for the possible human exposure via seafood consumption.

3.3.2.5.Endocrine Disrupting Potential of UV Filters in Humans

There are a number of common UV filters that have been shown to cause damage to the endocrine system in humans. Because of this, concerns have been raised about their safety in the long run. Benzophenone-3 has been the subject of the greatest research among them. There is a great deal of cause for concern because it has been found in human urine, blood plasma, breast milk, amniotic fluid, and even placental tissues. Not only does this demonstrate system absorption, but it could also potentially lead to fetal exposure [408], [409].

Studies suggest that BP-3 can mimic estrogen, and it can act as an anti-androgen, while also interfering with thyroid hormonal regulation. For instance, it altered hormone levels in healthy volunteers after whole-body application of sunscreen containing BP-3 [410]. Additionally, other UV filters like 4-methylbenzylidene camphor (4-MBC) and ethylhexyl methoxycinnamate (EHMC) have shown similar estrogenic and anti-androgenic activity in both in vitro assays and in vivo animal studies [411], [412].

Studies show that persistent exposure to UV filters through cosmetics and personal care items could contribute to hormone imbalances. They could be specifically dangerous during sensitive life periods such as pregnancy, infancy, and puberty. With this in mind, ultraviolet filters are becoming more widely known as developing endocrine-disrupting chemicals (EDCs) that pose a threat to human health.

3.4. Current Regulations in the EU, USA, and Other Regions

3.4.1. European Union (EU)

The European Union (EU) regulates ultraviolet (UV) filters in accordance with the Cosmetics law (EC) No 1223/2009. This law mandates that every UV filter that is being used in cosmetics must be subjected to the scientific safety evaluations that the Scientific Committee on Consumer Safety (SCCS) requires. Then these UV filters may be included in Annex VI of the regulation [413]. At the moment, around thirty ultraviolet (UV) filters are permitted for use in sunscreens inside the European Union [413]. The rule also mandates that the labelling of sun protection (SPF) and the efficacy tests must be executed according to ISO methods (ISO 24442/24443). Even though sunscreens are considered to be consumer goods that do not require a prescription, the European Union takes various measures. This precautionary approach involves reviewing safety data in case there are new facts about the environment or toxicology [414]. REACH is responsible for categorizing the dangers of ultraviolet (UV) filters when they are used in industrial applications, whereas the cosmetic law legislation controls UV filters in cosmetic applications [415].

3.4.2. United States (US)

In the United States, UV filters are controlled by the Food and Drug Administration (FDA) because they are considered to be over-the-counter (OTC) medications. Zinc oxide and titanium dioxide are the only two filters that have been approved as GRASE (Generally Recognized as Safe and Effective) in 2022. Other filters, such as BP-3 and avobenzone, are still under evaluation due to their health implications [416]. Notably, the United States has not approved any new UV filter since 1999. This is a great obstacle to the modernization of the regulatory system. To avoid this obstacle, the Sunscreen Innovation Act of 2014 was enacted, but it only succeeded in speeding up the review process.

3.4.3. Other Regions

- In Australia, the Therapeutic Goods Administration (TGA) is responsible for the regulation that is implemented for UV filters. It demands, of course, comprehensive safety and various efficacy data. The TGA has approved more UV filters than the United States, such as tinosorb S and M.

- In Canada, sunscreens are considered either natural health products or pharmaceuticals. 27 UV filters have permission for use in sunscreens. Additionally, there are restrictions on UV filters that may cause endocrine disruption [417].

- The ASEAN Cosmetic Directive, which was derived from EU laws, is followed by the countries that make up ASEAN. However, individual member states can apply national limits [417].
- Japan and South Korea have their own regulatory systems, which emphasize the efficacy of each cosmetic product and its effects on the skin. When compared to the standards of the EU or the United States, Japan allows for larger concentrations of some UVA filters.

The following comparison bar chart (Figure 27) shows the maximum allowed levels of common organic UV filters (OUVFs) like BP-3, EHMC, and avobenzone. As one can observe, they vary greatly from one place to another in the United States, the European Union, the Association of Southeast Asian Nations (ASEAN), Canada, and Australia. These variances might make things harder as the world works to harmonize sunscreen formulas internationally.

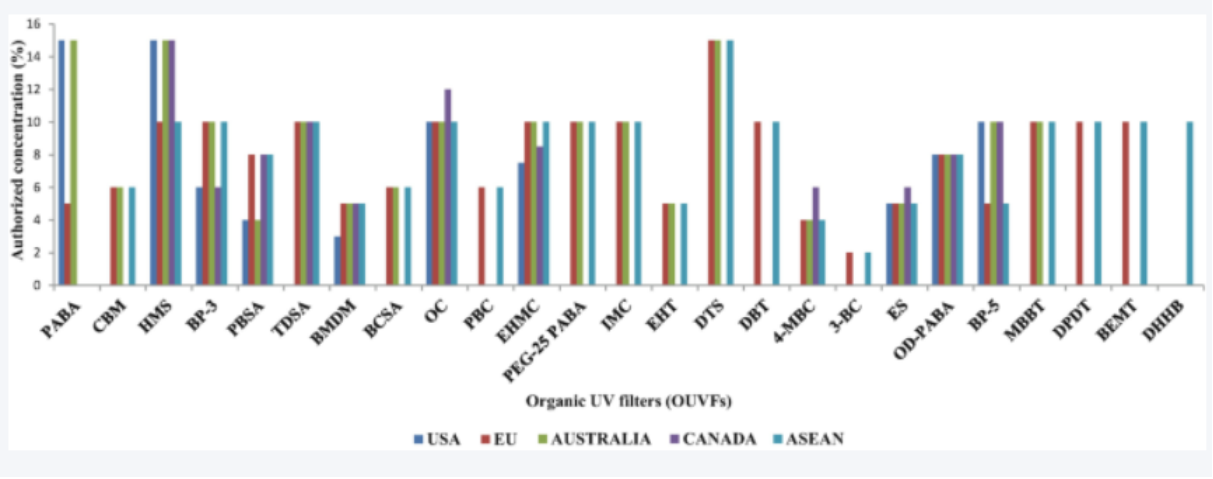

Figure 31: Comparative bar chart showing significant regional variation in the maximum allowable concentrations of common organic UV filters [417]

3.4.4. Bans or Restrictions on Specific UV Filters Benzophenone-3 (BP-3 / Oxybenzone):

BP-3 has been restricted or prohibited in several different jurisdictions. This is valid because of research suggesting its negative effects on corals and the possible endocrine disruption. Hawaii, Palau, the United States Virgin Islands, Aruba, and Bonaire are some of the countries that prohibit the use of BP-3 in sunscreens [418], [419]. Also, SCCS has put restrictions on the maximum safe use concentration of UV filters in the EU, to protect consumers from possible hormonal effects [420].

Octinoxate(EHMC):

Octinoxate also raises concerns regarding human and environmental health. Therefore, it is banned along with BP-3 in Hawaii. EHMC has also been linked to systemic absorption in humans, just like BP-3 is linked to estrogenic effects and bioaccumulation in aquatic organisms [419].

Octocrylene, Homosalate, and 4-MBC:

- **Octocrylene:** Octocrylene has the potential to form benzophenone, which is a carcinogenic substance, as a degradation product. This is why it has been prohibited in certain reef-sensitive locations.
- **Homosalate**: Homosalate has been judged safe by the SCCS only at concentrations below 0.5%. This is a decrease from the levels that were previously known [420].
- **4-Methylbenzylidene camphor (4-MBC)**: Even though it has been demonstrated to have endocrine-disrupting effects, 4-MBC is nonetheless allowed in some nations that are not members of the European Union, as well as in other countries [421].

3.5.Extraction methods used in UV filter detection

Current extraction methods for UV filters range from classic techniques like SPE and LLE to innovative, eco-friendly ones such as SPME and DLLME. In this chapter, the different extraction methods are presented and discussed specifically for their use in UV filter detection.

3.5.1. Liquid phase microextraction

Liquid-liquid microextraction (LLME) and its variants are efficient techniques for UV filter extraction. In particular, dispersive liquid–liquid microextraction (DLLME) and vortex-assisted DLLME (VA-DLLME) are widely utilized. Yücel et al. (2022) developed a VA-DLLME with solidification of floating organic droplets (SFOD) for river water analysis. The technique produced detection limits of 1.1–5.5 ng L^{-1} and recoveries of up to 107% [422]. Similarly, Liao et al. (2020) coupled vortex-assisted and ultrasound-assisted DLLME for UV filters. The method achieved good precision detection limits < 0.05 µg mL^{-1} [423].

Green extraction solvents, like natural deep eutectic solvents (NADES), have also been introduced the recent years. Wen et al. (2024) extracted benzotriazole UV filters from soil samples using a choline chloride:lactic acid NADES, with low detection limits (0.010–0.083 µg mL^{-1}) and good recoveries [424]. Ionic liquid-based single-drop microextraction has been applied to determine typical UV filters in surface water samples, with recoveries up to 115% [425]. For benzophenone-type filters, ionic liquid-based DLLME can also be used. It can provide recoveries above 90% and linearity up to 1000 ng mL^{-1}[426]. Hollow-fiber liquid-phase microextraction (HF-LPME) is another intriguing strategy used. Yang et al. (2011) used dynamic HF-LPME linked to HPLC to report enrichment factors of 24–57 and detection limits as low as 1 µg L^{-1} for a number of UV filters in cosmetics [427]. All these examples are summarized in Table 11.

Table 11: Overview of Liquid Phase Microextraction (LPME) Methods for UV Filter Analysis

Technique	Variant / Modification	Sample Type	Analytical Coupling	Reference
Liquid–Liquid Microextraction (LLME)	Dispersive (DLLME), Vortex-assisted (VA-DLLME), Ultrasound-assisted (UA-DLLME)	River water, general aqueous	GC-MS HPLC-DAD	[422], [423]

Green Solvent-based LPME	NADES-based (Natural Deep Eutectic Solvent)	Soil	GC-MS	[424]
Single Drop Microextraction	Single-drop, DLLME	Surface water	LC-UV	[425]
Hollow-Fiber LPME (HF-LPME)	Dynamic HF-LPME	Cosmetics	HPLC	[427]

3.5.2. Solid phase microextraction

As mentioned before, solid-phase microextraction is one of the most well-known methods for the extraction in general, but also for UV filters in environmental matrices. Recent innovations have expanded the use and analytical performance of SPME. For example, gold nanoparticle–modified fibers (HO–C_{11}–S–AuNPs/ESSW) have achieved detection limits as low as 0.024–0.081 μg L^{-1} for four UV filters in environmental waters [428]. Similarly, mixed-sorbent SPME blades incorporating hydrophilic–lipophilic balanced (HLB), weak cation exchange (WCX), and weak anion exchange (WAX) particles embedded in a polymeric binder provide broad extraction coverage [429].

It is also known that SPME can be performed in different operational modes. This depends on the analyte's volatility and the matrix type. Because the fiber in headspace SPME (HS-SPME) is exposed to the gas phase above the sample, it is especially well-suited for GC-MS/MS analysis of semi-volatile UV filters. For instance, Yücel et al. (2024) optimized an HS/SPME–GC–MS/MS procedure for nine UV filters in wastewater using a polyacrylate fiber. The achieving recoveries were up to 115% and detection limits between 4.21 and 12.0 ng L^{-1} [430].

Thin film SPME (TF-SPME) is also used widely as an extraction method. Devices coated with hydrophilic–lipophilic balanced (HLB) or C_{18} sorbents allow simultaneous monitoring of polar and nonpolar UV filters under time-weighted average (TWA) conditions for up to 70 [431]. In-tube solid phase microextraction is also mentioned in the bibliography as an effective method for online analysis of UV filters, with Mei et al. achieving recoveries in the range of 44.0–100% [432]. Polymer monolith devices are well known due to their practical use, and they are applied successfully in the enrichment of UV filters in water samples [433], [434].

Table 12 compiles representative SPME methods and their respective variants.

Table 12: Overview of Solid Phase Microextraction (SPME) Methods and Variants

Technique / Variant	Sorbent or Coating	Sample Type	Analytical Coupling	Reference
HS/DI-SPME (including AuNP-modified and mixed-sorbent variants)	Polyacrylate, PDMS, HO–C_{11}–S–AuNPs/ESSW, HLB/WCX/WAX blends	Environmental waters, wastewater	GC–MS/MS, LC–MS/MS	[430]
Thin Film SPME (TF-SPME)	HLB or C_{18} sorbents	Field monitoring (TWA, up to 70 days)	LC-MS/MS	[431]
In-tube SPME	Capillary/polymer monolith	Water samples	LC–MS	[432]
In-tip microextraction (dispersive pipette)	Styrene-divinylbenzene	Seawater	HPLC-DAD	[435]
Stir Bar Sorptive Extraction (SBSE)	PDMS-coated stir bar	River, sewage water	UHPLC–ESI–MS/MS	[436]

In-tip microextraction or dispersive pipette extraction is a novel method for extraction and is successfully applied in UV filter detection for eleven sunscreen molecules in seawater samples with recoveries ranging from 80 % to 116% [435]. Stir bar sorptive extraction (SBSE) is similar to SPME but uses a stir bar coated with a sorptive material, usually polydimethylsiloxane (PDMS). As mentioned in a previous chapter, extraction can be performed in direct immersion (SBSE) or headspace (HSSE) modes. Pedrouzo et al. (2010) demonstrated the use of SBSE combined with UHPLC–ESI–MS/MS for the determination of UV filters such as benzophenone-3 and octocrylene in river and sewage water. Detection limits reached 2.5 ng

L^{-1} in river water and 5–10 ng L^{-1} in wastewater, with reported environmental concentrations for BP-3 between 6 and 28 ng L^{-1} [436]. However, SBSE performance depends strongly on coating selectivity. Traditional PDMS coatings are most effective for nonpolar analytes, whereas more polar UV filters may require derivatization or modified coatings.

Finally, there is no reported application in the reviewed bibliography concerning the detection of UV filters using effervescent-assisted microextraction.

The choice of extraction technique should align with both the chemical nature of the target UV filters and the complexity of the sample matrix. The following table (Table 13) summarizes the extraction methods with their analytical goals.

Table 13: Selection of extraction techniques based on matrix, analyte polarity, and analytical goals

Extraction Technique	**Suitable Matrix Type**	**Suitable Analyte Polarity**	**Recommended Analytical Method**	**Main Advantages**	**Sustainability / Innovation Aspect**
HS/DI-SPME	Clean to moderately complex aqueous samples	Nonpolar to semi-volatile UV filters	**GC–MS/MS**	Solventless, easy automation, compatible with volatile analytes	Magnetic or nanomaterial-modified fibers enhance performance
SBSE	River, sewage, or surface waters	Nonpolar, semi-volatile	**GC–MS/MS**	High enrichment factors, solvent-free	Reusable PDMS stir bars; limited for polar analytes

DLLME	Complex aqueous or biological matrices	Polar to moderately polar	**LC–MS/MS**	Rapid extraction, high recovery	**NADES-based DLLME** offers greener, biodegradable solvents
HF-LPME	Highly complex or viscous samples (cosmetics, wastewater)	Polar compounds	**LC–MS/MS**	High selectivity and enrichment	Minimal solvent use, reusability of fibers
Magnetic nanoparticle-assisted SPME	Environmental or biological matrices	Broad polarity range	**GC–MS/MS or LC–MS/MS**	Fast separation, easy retrieval with a magnet	Improved sustainability and reusability

3.6.Sorbent materials used in UV filter detection

In this chapter, different sorbent materials are presented and discussed with a focus on their use in the detection of UV filters. Emphasis is given to their composition, selectivity, and performance in different extraction techniques.

3.6.1. Metal-organic frameworks (MOFs) and Covalent organic frameworks (COFs)

MOFs and COFs provide tunable pore sizes and high surface areas. MOFs provide tailored pore diameters and functional groups to reach ultra-low detection limits in aqueous matrices, specifically for the detection of UV filters. In contrast, COFs prefer hydrogen bonding and π-π interactions with aromatic UV filters. Table 14 displays a short comparison of COFs and MOFs.

Table 14: Comparative table for COFs and MOFs for UV filter detection

Sorbent class	**Structural features**	**Adsorption mechanisms**	**Example targets and matrices**	**Representative metrics**
COFs (magnetic COFs/COF-MSPE)	crystalline, tunable pores, π-conjugated frameworks, can be magnetized (Fe_3O_4@COF)	π-π stacking, hydrogen bonding, hydrophobic interactions; functional groups (thiophene, cyan) enhance binding	UV filters, estrogens, organophosphate esters, PAHs; surface/wastewater, beverages, food matrices [437], [438]	COF-MSPE for UV filters: LODs 0.001–0.15 µg/L, recoveries ~ 76.9–95.6 %, adsorption capacities 80.8-120.1 mg g^{-1} [439]
MOFs (UiO-66-NH2 and derivatives)	highly porous, adjustable pore size, modifiable functional groups (–NH_2)	size/shape selectivity, H-bonding, and coordinative interactions with polar analytes	organic UV filters in water, phenols in tap/bottled water [438], [440]	Fe_3O_4@UiO-66-NH2 MSPE for nine UV filters: LODs 0.01–0.07 ng·L^{-1}, LOQs 0.03–0.4 ng·L^{-1}, recoveries 86.5–104.2% [5]; UiO-66-NH_2 frits for phenols: LODs 0.04–0.67 µg·L^{-1} [438]

It is possible to develop MOFs and COFs to extract UV filters selectively. When combined with magnetic recovery, functionalized MOFs, such as UiO-66-NH_2, can approach extremely low detection limits in water and target polar UV filters [441]. Through π–π and hydrophobic interactions, COFs with extended π systems or thiophene groups enhance binding to aromatic UV filters. They have also shown efficacy for similar endocrine chemicals in water and beverages [437], [442].

3.6.2. Carbon materials

Magnetic carbonaceous sorbents and graphenic aerogels have been applied to extract UV filters from environmental waters. They show good enrichment, but they have differing desorption and sensitivity challenges. Representative studies report low-ng-L^{-1} detection with graphitized carbon composites and high recoveries with reduced graphene oxide aerogels.

Because of their hydrophobic surfaces and wide π-electron domains, graphenic materials have a great affinity for nonpolar UV filters. As a result, molecules like benzophenones and p-aminobenzoates have good enrichment and recovery [443], [444]. These strong interactions can, however, make desorption difficult. That is why stronger organic solvents or heat may be needed to release the analytes from the surface.

Table 15: Comparison table for three carbonaceous sorbents used to detect UV filters

Material	**Advantages**	**Limitations**	**UV filters/matrices**	**Representative performance**
Fe3O4-graphitized carbon black (mGCB)	magnetic recovery, moderate surface area, broad affinity to nonpolar analytes	Some analytes are difficult to desorb	benzophenones and p-aminobenzoates in surface water	recoveries 85–114%, RSD 5–15%, LODs ≈1–5 ng·L^{-1} [443]
Reduced graphene oxide (rGO) aerogel	high graphenic domains → strong affinity for nonpolar UV-benzotriazoles,	Organic elution solvents are often required	UV-benzotriazoles in river water	recoveries 80–100%, enrichment factors 12.5–50, LOD 1

	high enrichment factors			ng·mL^{-1} (1000 ng·L^{-1}) [444]
MOF-derived magnetic hierarchical carbon (CoZn-MHC)	high surface area after carbonization, magnetic MSPE friendly	Synthesis involves carbonization and templating	benzophenones and bisphenols (EDCs) in water	high specific surface area; reported high extraction efficiency for typical EDCs [445]

3.6.3. Sol-gel

Sol-gel-derived approaches are used both to fabricate porous sorbent matrices and to immobilize graphenic domains for SPE and SPME coatings. This enables tailored porosity and surface chemistry for UV-filter extraction. Reviews and application studies highlight sol-gel, in-situ growth, and physical adhesion as common fabrication routes for porous extraction coatings.

Sol–gel methods are widely used to prepare advanced sorbent materials for UV filter analysis. For example, adding graphene oxide during resorcinol–formaldehyde gel synthesis creates reduced graphene oxide (rGO) aerogels that work well as SPE cartridges, giving high recoveries of UV benzotriazoles in river water [2]. Sol–gel processes are also used to make COF-based SPME coatings, together with other methods like physical adhesion or in situ growth, allowing control over pore size and good mechanical strength [4]. The main benefits of sol–gel synthesis are the easy control of pore structure and the ability to include materials like graphene, MOFs, or COFs that improve the adsorption of UV filters [2,4]. However, some sol–gel composites need strong solvents or high temperatures for elution [2].

3.6.4. MIPs and ionic liquids

Molecularly imprinted polymers (MIPs) are highly selective because they form template-shaped cavities that match the target molecule. For example, a polyaniline molecularly imprinted polymer (PANI@MIP) was used for the detection of benzophenone-4 (BP4) from aqueous matrices [446]. Also, electrochemical sensors based on molecularly imprinted

polymers (MIPs) can selectively detect Benzophenone-3 (BP-3) and Octocrylene (OC) with recovery rates of 77 % and 101 % respectively [447].

Ionic liquids (ILs) are also used in the detection of UV filters in environmental samples, because their characteristics may be adjusted to match the polarity and functional groups of various UV filters. They can form strong interactions such as hydrogen bonding and π–π stacking with aromatic and polar groups. ILs are also thermally and chemically stable, and when used in molecularly imprinted polymers, they improve the quality of binding sites and target recognition. A double-confined polymeric ionic liquid (PIL) sorbent coating was used in a SPME setting coupled to HPLC for the detection of 9 UV filters [448]. Ionic liquids-based nanoemulsion could achieve recoveries of 82–119 % of benzophenone-3, octocrylene, octisalate, and octinoxate [449]. Additionally ionic liquids (ILs) were used as extraction solvents for the determination of four ultraviolet filters with a dispersive liquid–liquid microextraction method, achieving LODs in the range of 0.06–0.16 ng mL^{-1} [450].

3.6.5. Magnetic nanoparticles

Fe_3O_4-based magnetic cores are widely used in magnetic solid-phase extraction (MSPE) because they are easy to separate with a magnet and can be modified for better performance [440]. MOF-based Fe_3O_4@UiO-66-NH_2 effectively preconcentrates nine UV filters with very low detection limits (0.01–0.07 ng L^{-1}) and high recoveries (86.5–104.2%) using GC–MS [440]. Stearic-acid-coated Fe_3O_4 nanoparticles were used for octocrylene, ethylhexyl methoxycinnamate, and avobenzone, achieving LODs of 0.05 µg mL^{-1} and recoveries of 81.2–112% in water and sunscreen samples [451]. Oleic acid-coated cobalt ferrite ($CoFe_2O_4$@oleic acid) nanoparticles successfully concentrated commonly used UV filters at trace levels in water [452]. FeO_4–graphitized carbon black composites (mGCB) were used to treat benzophenones and p-aminobenzoates, yielding recoveries of 85–114% and LODs of 1–5 ng L^{-1} [453].

Table 16 summarizes the main magnetic materials reported for UV filter analysis.

Table 16: Comparison table of magnetic materials used to detect UV filters

Magnetic Material / Composite	**Target UV Filters**	**Analytical Method**	**Detection / Quantification Limits**	**Recoveries (%)**	**Notes / Advantages**	**Reference**

Fe_3O_4@UiO-66-NH_2 (MOF-based)	Nine organic UV filters	GC–MS	LOD: 0.01–0.07 ng L^{-1} LOQ: 0.03–0.4 ng L^{-1}	86.5–104.2	High selectivity, very low detection limits, suitable for real water samples	[440]
Stearic-acid-coated Fe_3O_4 MNPs	Octocrylene, ethylhexyl methoxycinnamate, avobenzone	UV–Vis / GC–MS	LOD: 0.05 µg mL^{-1}	81.2–112	Simple, reusable sorbent; applied to both water and sunscreen samples	[451]
$CoFe_2O_4$@oleic acid (cobalt ferrite MNPs)	Common UV filters in cosmetics	GC–MS	Trace to ultratrace levels	Not specified	Effective for hydrophobic UV filters; good stability in water	[452]
Fe_3O_4–graphitized carbon black (mGCB)	Benzophenones, p-aminobenzoates (10 UV filters)	GC–MS	LOD: 1–5 ng L^{-1}	85–114	High enrichment and reproducibility; some analytes are hard to desorb	[453]

PART II

EXPERIMENTAL

1. Introduction

Effervescence-assisted microextraction, developed over a decade ago, is a method that simplifies and streamlines sample preparation processes employing dispersed sorbent materials [454]. The method is based on a simple reaction that produces carbon dioxide bubbles in situ in an aqueous sample solution, effectively promoting the dispersion and mixing of the sorbent (receiving phase) into the solution (donor phase). This approach was developed to minimize the effort associated with the manual and time-consuming steps (e.g., vortex, end-over-end or orbital agitation, ultrasounds) required to bring a small amount of sorbent in contact with the sample solution to achieve the extraction of the analytes [455], [456]. Moreover, the method could facilitate on-site sample treatment thus minimizing the problems associated with sample transportation and storage [455], [457]. In the course of this time, effervescence-assisted microextraction has evolved to include magnetic sorbents and liquid solvent media (ionic liquids, organic solvents, etc.), further simplifying its use and expanding its analytical application and scope to the extraction of a wide range of organic and inorganic analytes in multiple sample matrices (water, food, biofluids, etc.) [454], [455], [458], [459].

2. Aim of study

In this thesis, we elaborate on the experimental conditions affecting the efficiency of effervescence-assisted microextraction by testing a wide range of acid/base combinations, aiming to identify the influence of the process of effervescence on extraction efficiency. Using stearic acid-coated magnetic nanoparticles as extraction sorbent, we tested 12 acid/base combinations at two mass ratios. We used these data to develop a sample preparation method for the extraction of organic UV filters from water samples as model hydrophobic organic compounds. The parameters affecting the extraction efficiency, namely the concentration of ionic strength, effervescence time, and the solution pH, were evaluated and discussed in relation to their effect on the extraction efficiency of UV filters. To our knowledge, a quantitative analysis of the experimental parameters affecting the efficiency of effervescence-assisted microextraction has not been reported before. The extraction and determination of UV filters using effervescence-assisted microextraction by magnetic nanoparticles is also presented for the first time.

3. Materials and Methods

3.1. Reagents

Sodium bicarbonate, sodium carbonate anhydrous, sodium di-hydrogen phosphate monohydrate, and L(+)-tartaric acid were obtained by Merck (Darmstadt, Germany). Cobalt(II)

nitrate hexahydrate and oxalic acid were procured from Fluka. 2-hydroxy-4-methoxybenzophenone (benzophenone-3 (BZ3)) >98%, 22-Ethylhexyl 4-(olimethylamino)benzoate (EDP) >98% and L-ascorbic acid was purchased from Sigma-Aldrich (Steinheim, Germany). Fumaric acid was obtained from BLD PHARMATECH (Reinben, Germany). Citric acid from Mallinckrodt (St.Louis, USA) and potassium bicarbonate from Carlo Erba (Milan, Italy). Iron(III) chloride hexahydrate was purchased from VWR Chemicals (Darmstadt, Germany). 2-Ethylhexyl 4-Methoxycinnamate (EMC) >97.0%, 2-Ethylhexyl 2-Cyano-3,3-diphenylacrylate (OCR) >98% and Iso-amyl 4-Methoxycinnamate (IMC) >95% were purchased from TCI (Zwijndrecht, Belgium) while 3-(-4-methyl benzylidene)camphor (MBC) >99,7% was from Guinama S.L (Valencia, Spain).

3.2. Instrumentation

ATR-IR spectra were recorded in a Perkin Elmer Spectrum Two IR. PXRD diffraction patterns were recorded on a Bruker D2 Phaser X-ray diffractometer (CuKα radiation, wavelength = 1.54184 A). Scanning electron microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) studies were performed in samples, sputter-coated with a 5–10 nm Au film on FEG-SEM Zeiss SUPRA 35VP (resolution 1.7 nm at 15 kV) equipped with an EDS detector (QUANTA 200, Bruker AXS, Billerica, MA, USA). Water contact angles were determined using the drop shape analysis utility of the ImageJ software (v. 1.52a, National Institutes of Health, U.S.A.), and specifically the Low-Bond Axisymmetric Drop Shape Analysis (LBADSA) method. Zeta potential measurements were conducted with a Malvern Zetasizer Nano ZS (Malvern Analytical,Worcestershire, UK) in a two-electrode capillary cell.

The chromatographic separation of the examined UV filters was performed in a Shimadzu HPLC system (Shimadzu, Kyoto, Japan) (LC-20AD high-pressure solvent delivery pump, DGU-20A3 degasser, CTO-10A column oven) equipped with a Hypersil ODS C18 column (250 mm length, 4.6 mm I.D., 5 μm particle size) obtained from MZ Analysentechnick (Mainz, Germany), thermostated at 40 ◦C. The elution of UV filters was performed isocratically (1.0 mL min−1) with MeOH and water at a mixing ratio of 80:20 (v/v). The chromato-graphic peaks corresponding to each UV filter were recorded at 313 nm for all analytes in an SPD-10AV UV/Vis detector controlled by LC Solution software (v.1.25-SP4, Shimadzu, Kyoto, Japan). The magnetic properties of the samples were studied using a conventional Vibrating Sample Magnetometer (VSM) (LakeShore 7300, Westerville, OH, USA). M versus (vs.) external magnetic field (H) isothermal loops were recorded at constant temperature of 300 K in fields up to +/− 20 kOe.

3.3. Synthesis of Stearic Acid-Coated Cobalt Ferrite Magnetic Nanoparticles

$CoFe_2O_4$@stearic acid magnetic nanoparticles (MNPs) were synthesized by mixing 100 mL of a 0.4M$FeCl_3 \cdot 6H_2O$ and 100 mL of a 0.2M$CoNO_3 \cdot 6H_2O$ solutions. Then, 100 mL of a 3M sodium hydroxide solution was added dropwise under continuous stirring. To this solution, 0.5 mL of stearic acid was introduced, and the mixture was heated to 80 ◦C for 1 h. The black suspension produced from the above procedure was cooled to room temperature. The magnetic nanoparticles were retained with a strong Nd magnet and washed several times with deionized water until the pH of the washing solution was neutral. Finally, the excess stearic acid was removed by washing the magnetic precipitate with ethanol. The magnetic nanoparticles were dried overnight at 80 ◦C and manually pulverized into fine (black) powder.

3.4. Preparation of Effervescent Tablets

To prepare effervescent tablets, 50 mg of MNPs, 150 mg of base, and 150 mg of acid (or 200 mg of acid and 100 mg of base for 2:1 acid: base mixtures) were mixed and manually blended in a mortar. The solid mixture was transferred to a 12 mm diameter mold and pressed for 30 min. The tablets were carefully removed and stored in a desiccator until use.

3.5. Experimental Procedure

An effervescent tablet was added to a 10 mL aqueous solution to extract UV filters. A large quantity of CO2 bubbles was immediately produced, lasting 40–240 s depending on the composition of the tablet, causing the vigorous dispersion of the MNPs. All tablets were allowed to complete effervescence up to 300 s. After extraction, a Nd magnet was placed alongside the tube to rapidly collect the MNPs, and the aqueous phase was discarded. The residual water was poured under a gentle stream of nitrogen, and 1 mL of HPLC-grade methanol was added to elute the analytes. Elution was carried out for 5 min, aided by vortex agitation. Finally, the methanolic extract was collected in a new vial (using a Nd magnet to isolate the MNPs), and a 50 μL aliquot was injected into the HPLC for analysis.

3.6.Real Samples

Real water samples (river, lake, and tap water) were collected in amber glass containers from the Louros River and Lake Pamvotis, (Epirus, NW Greece), while the tap water was obtained from the local water supply network. All samples were filtered through 0.45 μm membrane filters and stored in the dark for no more than one week at 4 ◦C before analysis. Refrigeration during storage was performed to inhibit microbial activity that could lead to changes in the physicochemical properties of the sample (e.g., pH, organic matter, etc.) which may influence the solubility and stability of the target contaminants. Filtration of the samples was employed

to remove suspended solids [19]. In clean samples used for spiking experiments, the removal of suspended solids is necessary to avoid sorption of the spiked contaminants. In polluted samples filtration is required to to avoid the re-distribution of the analytes between the solids and the water phase that may lead to an under- or over-estimation of the soluble concentration of the target analytes.

4. Results

4.1. Characterization of CoFe2O4@Stearic Acid Magnetic Nanoparticles

Powder XRD verified the successful synthesis of $CoFe_2O_4$@stearic acid MNPs. The XRD pattern shown in Figure 28 shows the characteristic index peaks at 2θ = 18.53, 30.3, 35.74, 37.26, 43.25, 57.35, 62.94, corresponding to (111) (220) (222) (311) (400) (511) and (440). Bragg reflection, in agreement with JCPDS 22-1086 [460], [461]

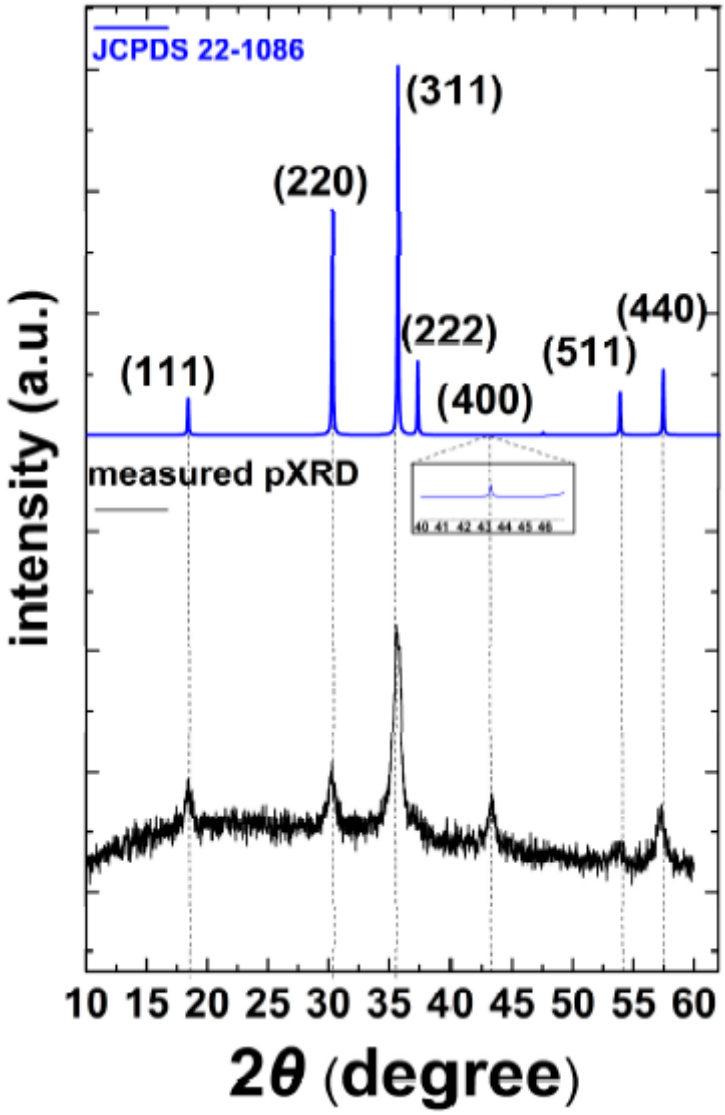

Figure 32: XRD pattern of CoFe2O4@stearic acid MNPs (black line) and comparison with Joint Committee

SEM images (Figure 29a,b) show that the morphology of several MNPs exhibits a cubic spinel structure. Still, due to their high surface energy, they tend to form agglomerates in an order of several hundreds of nanometers. However, agglomeration is not as intense as that usually reported for bare MNPs due to the presence of the fatty acid coating [460]. At higher resolution, the particles appear like snowflakes. These observations agree well with previous studies reporting on the synthesis of $CoFe_2O_4$@stearic acid MNPs by coprecipitation [461], [462].

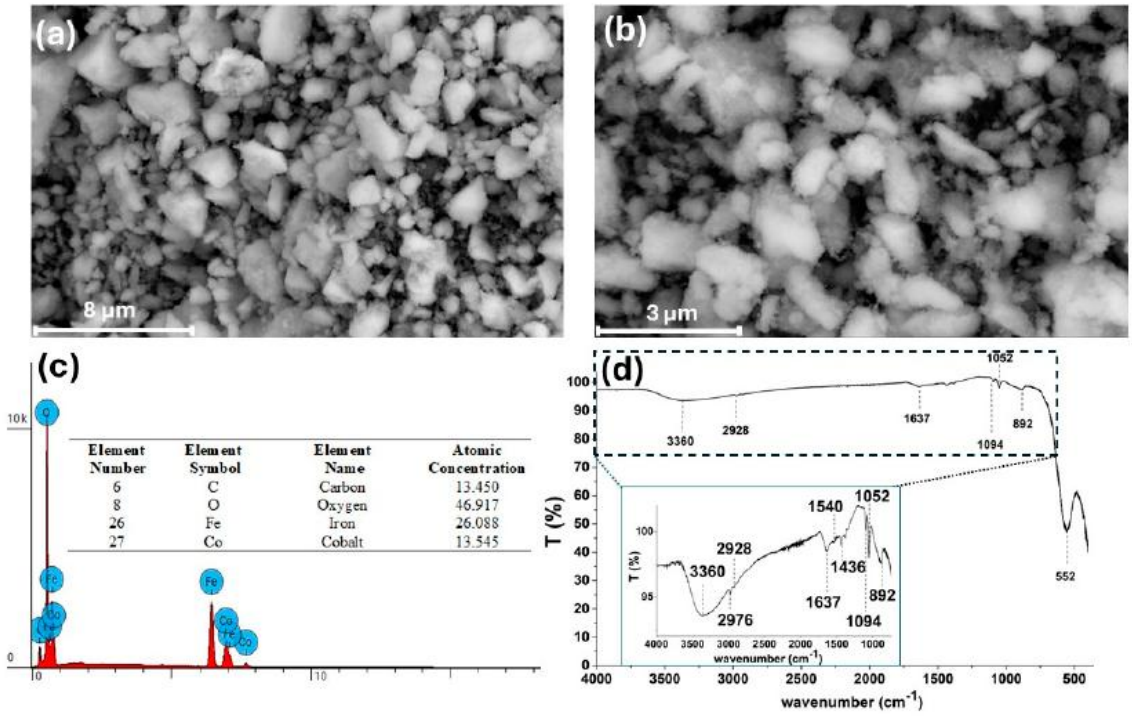

Figure 33: SEM images (a,b), EDS spectra (c), and ATR-IR spectra (d) of $CoFe_2O_4$@stearic acid MNPs

The composition of $CoFe_2O_4$@stearic acid MNPs was firstly corroborated by EDS measurements (Figure 29c), showing a stoichiometric Fe: Co ratio (2:1) and the presence of carbon at an almost equal percentage to Co, which verifies the presence of stearic acid. Evidence of the formation of the stearic acid coating was also obtained with ATR-IR analysis (Figure 29d). Although the ATR-IR bands of $CoFe_2O_4$@stearic acid MNPs were very weak due to the minimal amount of stearic acid used during synthesis [463] (0.23 g/L in this work), several characteristic bands can be detected. The bands at 3360 cm^{-1} and 1637 cm^{-1} bands can be assigned to–OH symmetric stretching and H–O–H bending, respectively, of water vapor adsorbed on the nanoparticles [464], [465]. Stearic acid has a long aliphatic chain, and the methylene modes appear at 2920 and 2850 cm^{-1}, respectively [466], [467]. However, in the ATR-IR spectra shown in Figure 2d only the asymmetric CH2 stretch at 2928 cm^{-1} appears clearly. An additional band at 2976 cm^{-1} is also evident that may be assigned to C-H stretching

[468], [469]. This band may appear shifted towards higher wavenumbers in the presence of metal ions, especially with the decreasing size of divalent metal cations, due to the smaller size of the unit cell for smaller divalent cations [468]. The 1094 and 1052 cm^{-1} peaks are related to the C–C and C–O stretching vibrations, respectively [467], [470]. The ATR-IR spectra also shows two bands at 1540 and 1436 cm^{-1} which correspond to the asymmetric (v_{as}) and symmetric (v_s) stretching vibrations of COO-, indicating the interaction between the MNPs and the fatty acid. The Δ (v_{as} - v_s) is 104 cm^{-1} which corresponds to chelating bidentate interaction and indicates that two O atoms of carboxylate group were equivalently bonded to Fe [467]. However, the lack of a stretching vibration of the C=O bond around 1700 cm^{-1} indicates the nonexistence of physically absorbed stearic acid and the formation of a monolayer coating on the surface of the MNPs [467]. Finally, the peak at 552 cm^{-1} could be assigned to the Fe-O lattice vibration.

The coating of stearic acid on the $CoFe_2O_4$ MNPs induced several changes in their properties. The water contact angle of bare MNPs (<20◦) increased to 76◦ in $CoFe_2O_4$@stearic acid MNPs, indicating that the stearic acid coating decreased the wettability of the MNPs, but they remained hydrophilic, which is favorable for facilitating their dispersion into water. In the same line, the z-potential of the MNPs changed from negative (−23 mV) in bare ($CoFe_2O_4$) MNPs, to neutral (+2.3 mV) in stearic acid-coated MNPs. As a result, the zero point of charge (ZPC) of the $CoFe_2O_4$@stearic acid MNPS was neutral (6.90) (Figure 30a), which facilitates its interaction with non-polar analytes. Finally, the magnetization of the MNPs, examined by VSM (Figure 30b), shows that the saturation magnetization of $CoFe_2O_4$@stearic acid MNPs is reduced to 52 Am^2/kg (from 58.5 Am^2/kg in bare MNPS). They also exhibit smaller coercivity due to the formation of particle agglomerates, as also evidenced in the SEM images [471].

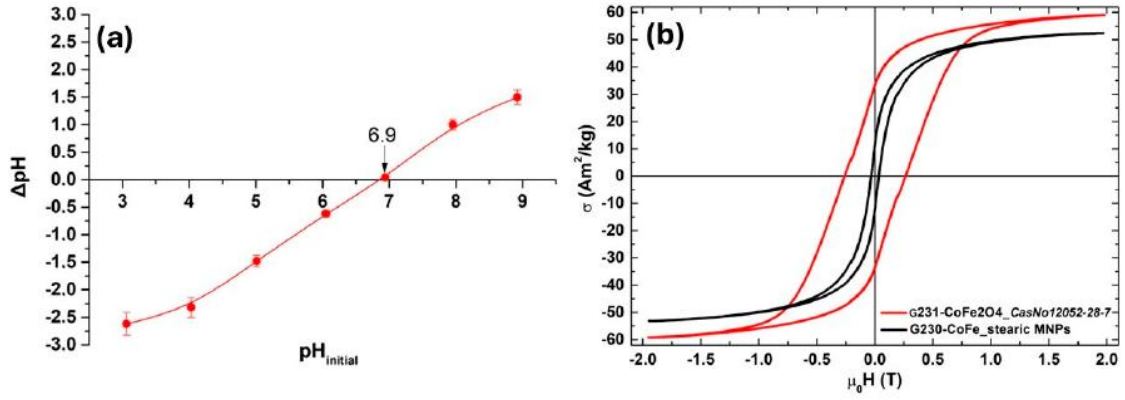

Figure 34: (a) Zero point of charge and (b) magnetization curves of $CoFe_2O_4$@stearic acid MNPs.

4.2. Effect of Effervescence on the Extraction Efficiency

After adding the tablet to water, the effervescence starts rapidly and is completed in two steps: the first involves the violent formation of CO_2 bubbles, and the second is a milder effervescence stage until all reagents have been consumed. During this process, beyond the dispersion of the sorbent, ionic strength gradually increases, and the pH changes until all reagents have been completely dissolved and an equilibrium is established. All these factors, however, are not independent of each other. For example, adding more effervescent precursors generates more bubbles and causes more intense effervescence but it also increases the solution's ionic strength and substantially affects sample pH. Moreover, on some occasions, intense effervescence may rapidly dissolve the reagents and decrease the overall extraction time. Therefore, the composition of effervescence precursors brings about different effects on all these factors.

To shed light on the factors that affect the efficiency of effervescecent-assisted microextraction, we investigated 12 combinations of acid/base mixtures (six weak acids with two bases) in two acid/base (1:1 and 2:1) ratios (a total of 24 combinations) in the extraction efficiency of four UV filters as model non-polar organic compounds (log K_{ow} = 3.8–6.1). The variability in the pH, effervescence time, and ionic strength of the solution obtained by each combination and gathered in Table 17. The total extraction time for all combinations was set at 300 s to ensure that all effervescence reactions have been completed and that the sorbent remains in contact with the donor solution for the same time, thus avoiding variations in the extraction efficiency attributed to different extraction times for each acid/base combination.

The first observation from the data of Table 17 is that mixtures composed of a 1:1 acid/base ratio exhibit approximately 30% longer effervescent times compared to mixtures consisting of a 2:1 acid/base ratio at the same total mass of effervescent reagents. This can be attributed to the lower amount of acid employed in a 1:1 mixture that causes a less violent reaction. The Pearson correlation matrices of Tables 18 and 19 show that effervescent time exhibits a positive correlation with extraction efficiency, indicating that increased effervescent time (i.e., slower dissolution of the tablet) has a positive influence on the extraction efficiency because it increases the contact time of the sorbent with the aqueous phase.

Table 17: Composition of effervescent reagents and their influence on the experimental conditions.

Acid:Base Ratio	Acid	Base	Solution pH	Duration of Effervescence (s)	Ionic Strength (M)
1:1	Citric Acid	Na_2CO_3	5.6	40	0.54
		$NaHCO_3$	5.3	120	0.57
	Tartaric acid	Na_2CO_3	5.8	40	0.42
		$NaHCO_3$	4.6	60	0.18
	Oxalic acid	Na_2CO_3	5.3	50	0.34
		$NaHCO_3$	5.3	240	0.35
	Ascorbic acid	Na_2CO_3	8.0	60	0.25
		$NaHCO_3$	6.5	50	0.18
	NaH_2PO_4	Na_2CO_3	7.4	60	0.80
		$NaHCO_3$	6.7	30	0.43
	Fumaric acid	Na_2CO_3	4.8	180	0.42
		$NaHCO_3$	4.2	180	0.24
2:1	Citric acid	Na_2CO_3	4.5	60	0.38
		$NaHCO_3$	3.9	210	0.64
	Tartaric acid	Na_2CO_3	4.6	60	0.36
		$NaHCO_3$	3.3	60	0.12
	Oxalic acid	Na_2CO_3	2.6	40	0.22
		$NaHCO_3$	2.4	60	0.34
	Ascorbic acid	Na_2CO_3	6.9	90	0.10
		$NaHCO_3$	5.6	40	0.12
	NaH_2PO_4	Na_2CO_3	6.8	60	0.62
		$NaHCO_3$	6.4	180	0.41
	Fumaric acid	Na_2CO_3	3.9	60	0.24
		$NaHCO_3$	3.2	60	0.24

Table 18: Pearson correlation analysis among the extraction efficiencies of UV filters and experimental

1:1 Acid:Base Ratio	pH	Effervescence Time	Ionic Strength	BZ3	MBC	EDP	EMC
pH	1.00						
Effervescence time	*−0.54* *	1.00					
Ionic strength	0.12	0.11	1.00				
BZ3	−0.38	0.28	−0.25	1.00			
MBC	−0.39	0.25	−0.34	*0.82* *	1.00		
EDP	−0.15	0.15	−0.31	0.11	0.42	1.00	
EMC	*−0.57* *	*0.48* *	−0.21	0.31	*0.56* *	0.28	1.00
2:1 Acid:Base Ratio	**pH**	**Effervescence Time**	**Ionic Strength**	**BZ3**	**MBC**	**EDP**	**EMC**
pH	1.00						
Effervescence time	0.20	1.00					
Ionic strength	0.05	*0.54* *	1.00				
BZ3	−0.21	0.17	0.08	1.00			
MBC	−0.20	0.32	0.23	*0.85* *	1.00		
EDP	0.18	0.09	−0.09	*0.66* *	*0.77* *	1.00	
EMC	−0.44	−0.08	−0.16	0.46	*0.60* *	0.44	1.00

* Statistically significant at the $p = 0.05$ probability level.

The ionic strength of the solutions produced from the tested combinations ranged from 0.15 to 0.8 M in 1:1 acid/base mixtures (average 0.37 M) to 0.1–0.62 M (average 0.286 M) in 2:1 acid/base mixtures. The higher ionic strength of a 1:1 mixture is because weak acids are employed for effervescence. Hence, an increase in the mass of the acid over the mass of the base does not contribute significantly to the ionic strength of the solution because weak acids do not dissociate significantly. From these values, it can also be inferred that effervescence-

based extraction is performed under high ionic strength conditions (>0.1 M). The correlation matrices (Tables 18 and 19) show a negative effect of ionic strength in the extraction efficiencies. This is more evident in mixtures of a 1:1 ratio, which exhibit higher ionic strength, possibly due to the higher viscosity of the solutions. However, the extraction time is positively correlated to the ionic strength of the solution, especially at a 2:1 ratio, which exhibits a statistically significant positive correlation coefficient at a $p = 0.05$ confidence level. This means that at lower ionic strength, longer extraction times are accomplished. Therefore, lower ionic strength increases the salting-out effect and increases the effervescence (extraction) time; both conditions are favorable to extraction. In contrast, as ionic strength increases, the viscous resistance effect becomes important while effervescence time only increases slightly.

Table 19: Main analytical parameters of the proposed method.

UV Filter	Slope ± s_b $\times 10^3$ (μg mL^{-1}) [a]	Regression Coefficient R^2 [a]	Linearity (μg mL^{-1})	LOD [b] (μg mL^{-1})	(%RSD) [c]	
					Repeatability	Reproducibility
BZ3	105 ± 4.4	0.995	0.5–10	0.5	9.2	10.4
MBC	323 ± 4.0	0.999	0.1–10	0.1	1.8	11.1
EDP	394 ± 9.0	0.998	0.1–10	0.1	8.6	4.2
EMC	101 ± 4.9	0.998	0.1–10	0.1	3.4	10.1

[a] Number of calibration points: 6 (s_b = standard deviation). [b] LOD: Limit of detection, calculated as $3S_{y/x}/a$ criteria, where Sy/x is the residual standard deviation and a is the slope of the calibration curve. [c] RSD: Relative standard deviation, calculated by analyzing an aqueous standard solution containing 0.5 μg mL^{-1} of the target analytes at five replicates.

The pH of the solution after the effervescence reactions shows that it is feasible to adjust the pH over a wide range from 2 to 8 by appropriately selecting the acid/base mixture and their ratio. As expected, tablets composed of 2:1 acid-base mixtures produce lower pH (2–7, average ~4.35) than those prepared from 1:1 mixtures (4–8, average 5.53). As revealed in Tables 17 and 18, improved extraction efficiencies were obtained with decreasing pH, which agrees with our previous studies reporting on the optimum extraction of UV filters at acidic pH values (pH < 4) [472], [473].

Although the above data provides some evidence of the effect of experimental parameters in the extraction efficiencies of non-polar organic compounds, on most occasions, they did not exhibit statistically significant correlations (at the $p = 0.05$ confidence level), which means that no general guidelines on how to select the experimental parameter can be derived. In a broader context, the optimum pH should be investigated first since it is determined mainly by the properties of the target analytes and their interactions with the sorbent. The positive correlation between ionic strength and extraction time at lower ionic strength conditions suggests that effervescence reagents that induce an ionic strength of <0.35 M may be used as a basis to find

a compromise between ionic strength and effervescence time, provided the pH does not deviate significantly from the optimum range.

In this study, the composition that compromises these factors and affords the highest extraction efficiency is a mixture of fumaric acid as a proton donor and sodium carbonate or bicarbonate as a CO_2 donor. According to the results depicted in Figure 31, the extraction efficiencies of UV filters are comparable for all acid-base combinations except for EDP, which is optimally extracted at 2:1 fumaric acid/Na_2CO_3. Therefore, the tablets were formulated by mixing 0.2 g of fumaric acid and 0.1 g of Na_2CO_3 for further experiments.

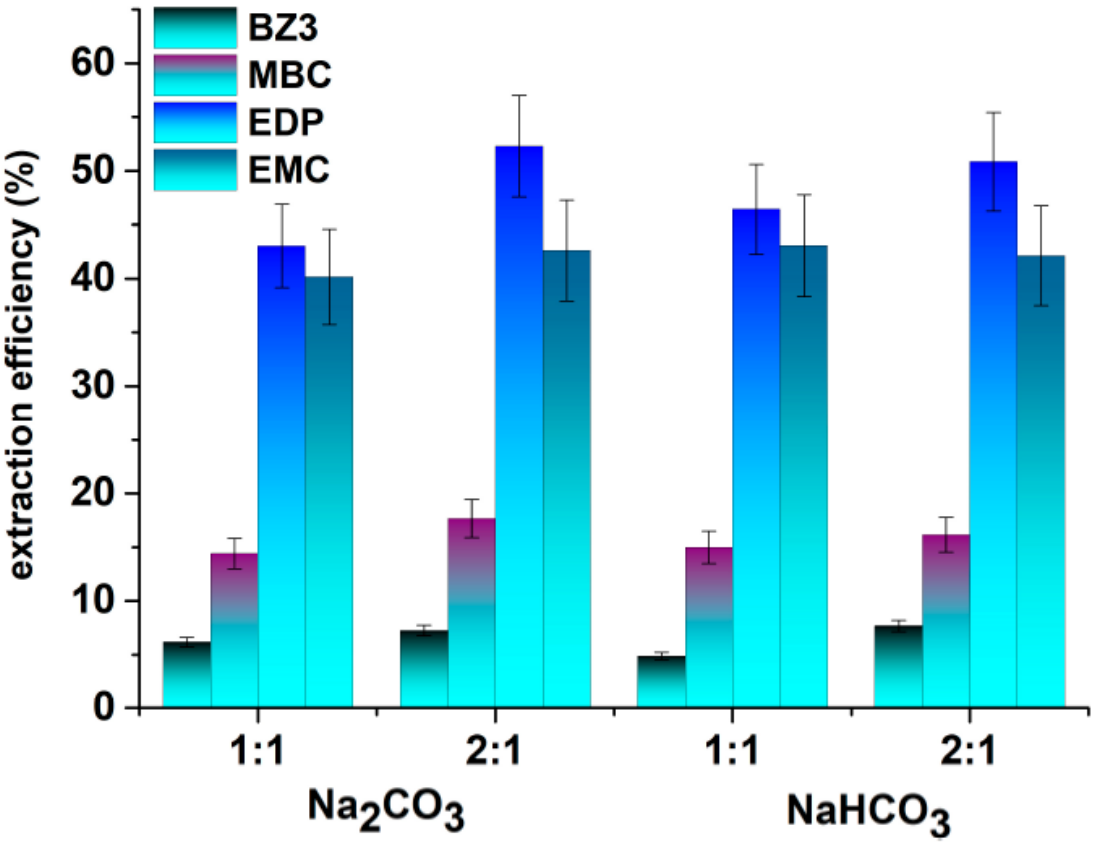

Figure 35: Extraction efficiency of UV filters using fumaric acid and carbonate/bicarbonate mixtures

4.3. Effect of Sorbent Mass

The amount of sorbent is an essential parameter in microextraction methods because they are performed under diffusion-controlled conditions since the mass of sorbent is significantly lower than the mass of the aqueous sample [455]. Therefore, the amount of sorbent used per volume of aqueous solution affects the mass transfer rate and the equilibrium of the analytes between the two phases [474]. To study this variable, the mass of MNPs added into the tablets was varied in the range of 10 to 250 mg. Figure 32 shows that the extraction efficiencies

increase up to 50 mg of MNPs and reach a plateau afterward. Therefore, the tablets were prepared by mixing 0.2 g of fumaric acid, 0.1 g of Na_2CO_3, and 50 mg of MNPs as the optimum extraction medium.

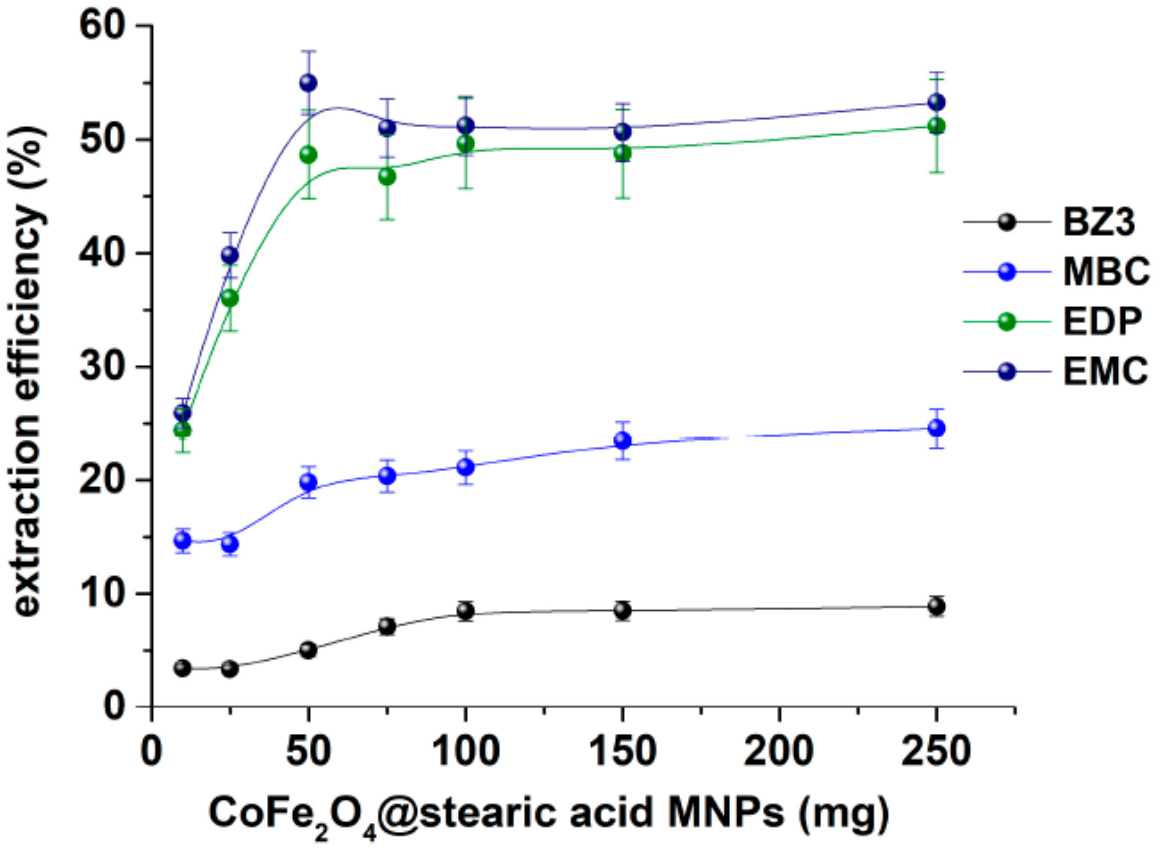

Figure 36: Effect of the mass of CoFe2O4@stearic acid on the extraction efficiency of UV filters.

4.4. Optimization of the Desorption Process

An essential step in the performance of microextraction methods is the desorption of the analytes from the surface of the nanosorbent. In that regard, the elution of analytes was tested using various organic solvents of different polarities, under various mixing conditions, and at different elution times. The results in Figure 33a show that methanol was the most efficient elution sorbent, offering higher extraction efficiencies than ethanol, propanol, and their aqueous mixtures. The elution solvent was mixed with the sorbent by manual shaking, vortex agitation, and ultrasound irradiation to improve the extraction efficiency. The agitation of the sorbent in a vortex mixer during desorption was the most efficient method for eluting the analytes (Figure 33b). Finally, 5 min of vortex agitation was adequate to elute the analytes (Figure 33c), while longer vortexing times offered no improvement as evidenced by the results of ANOVA, which showed no significant difference at the $p < 0.05$ level ($F_{(6.37)} = 2.37 > F_{Calculated} = 0.005$, $p = 0.99$).

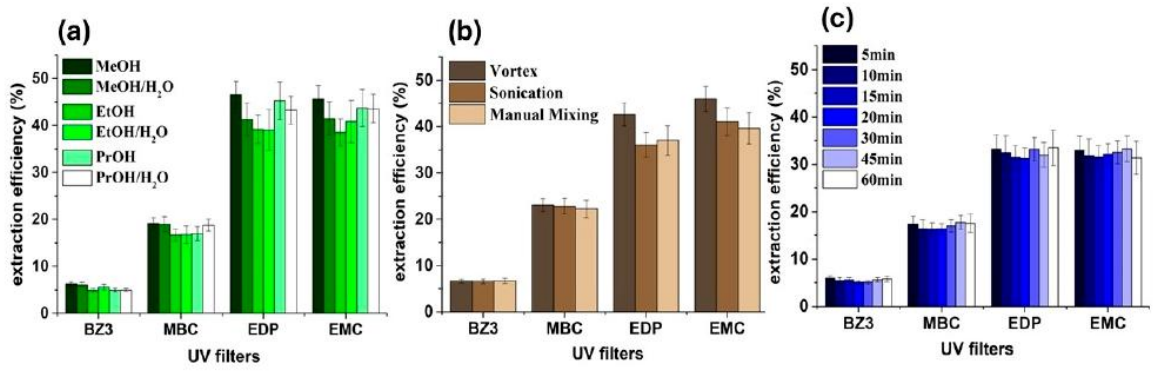

Figure 37: Optimization of desorption conditions (a) selection for elution solvent (elution time 10 min, manual mixing) (b) examination of mixing method (elution solvent: methanol, elution time: 10 min), (C) effect of elution time (elution solvent: methanol, vortex agitation).

4.5. Analytical Characteristics of the Method

Under the optimum conditions, the analytical quality parameters of the method, such as linearity, limits of detection (LOD), repeatability, and reproducibility, were evaluated. The results summarized in Table 19 show that a high level of linearity was obtained for all examined UV filters. The employed working range expanded by almost two orders of magnitude and was set from 0.5 to 10 μg mL^{-1} for BZ3 and from 0.1 to 10 μg mL^{-1} for the other UV filters with regression coefficients (r^2) > 0.995. As can also be seen in Table 18, the LODs (calculated as 3 × Sy/x/a, where Sy/x and a are the residual standard deviation and the slope, respectively, of the calibration curve) were found to be in the low μg mL^{-1} level ranging from 0.16 to 0.32 μg mL^{-1} (0.5 μg mL^{-1} for BZ3). The lower linear range and the higher LOD for BZ3 can be attributed to the lower hydrophobicity of BZ3 compared to the other UV filters. The extraction efficiencies exhibited a statistically significant correlation with the target UV filters' octanol-to-water partition coefficient (log K_{ow}) ($r = 0.75$, $p = 0.05$), indicating that less polar compounds are more effectively extracted. A significant improvement in the LODs of the method may be accomplished by resorting to more sensitive detectors employing mass spectrometric (MS) detection [475], [476]. Further improvement in sensitivity to meet the demand for even higher sensitivity can conceivably be accomplished by scaling up the method to extract larger sample volumes and/or by preconcentrating the eluate to a lower volume; both approaches can increase the preconcentration ratio and improve the sensitivity of the method.

The repeatability and reproducibility, expressed as relative standard deviation (RSD %), were evaluated by extracting replicate samples (standard aqueous solutions containing the target analytes) on the same day (intra-day) and five consecutive days (inter-day), respectively. Values were between 1.8 and 11%, showing the method's high precision.

4.6.Application to the Analysis of Genuine Water Samples

The reliability of the method was evaluated by employing recovery experiments. Three natural water samples were fortified with the target analytes at 0.5 μg mL^{-1} and extracted under the optimum experimental conditions. The calculated recoveries (Table 20) show that satisfactory recoveries are obtained. On many occasions, the extraction efficiencies were higher than 100%, which can be attributed to the presence of matrix components that may be coextracted with the target analytes but cannot be discriminated from the (single wavelength) UV detector. Moreover, natural waters have a buffering capacity (mainly attributed to carbonate and bicarbonate species), which may affect the effervescence process, the pH, and the ionic strength of the solution.

Table 20: Recovery of UV filters from three water samples spiked with 0.5 μg mL−1 (n = 3).

UV Filter	Tap Water	River Water	Lake Water
BZ3	78.4 ± 7.1	105.2 ± 5.8	84.7 ± 6.3
MBC	102.1 ± 9.8	102.8 ± 7.9	127.1 ± 10.4
EDP	98.0 ± 8.4	105.0 ± 9.0	117.3 ± 12.4
EMC	101.6 ± 7.3	107.5 ± 9.2	112.4 ± 8.8

5. Conclusions

In this thesis, an effervescence-assisted magnetic micro solid phase extraction method was developed to extract UV filters from water samples. Except for its role in dispersing the sorbent, the influence of effervescence on the physicochemical conditions of extraction was examined by testing various acid/base combinations. It was found that the duration of effervescence, the ionic strength, and the pH of the solution, which are essential parameters in extraction, are all affected simultaneously and influence extraction efficiency. Since the properties of the analytes mainly determine the optimum pH, the combination of effervescence reagents should be limited to those that do not alter the pH beyond the optimum range. Once this is established, the ionic strength and effervescence time should be optimized, considering that ionic strength lower than 0.35 M should offer a compromise between the salting out effect and the viscous resistance effect, which has a reversibly proportional influence on the extraction efficiency, and ensure an adequate extraction time. Based on these observations, the extraction of UV filters, as model non-polar organic compounds, was demonstrated with satisfactory analytical features. Overall, the study provides a general pathway for selecting the appropriate experimental conditions for effervescence-assisted microextraction and aids in simplifying and streamlining the method optimization.

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