

Review

# Magnetic Nanomaterials and Nanostructures in Sample Preparation Prior to Liquid Chromatography

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**Abstract:** Magnetic nanomaterials and nanostructures compose an innovative subject in sample preparation. Most of them are designed according to the properties of the target analytes on each occasion. The unique characteristics of nanomaterials enhance the proficiency at extracting and enriching due to their selective adsorption ability as well as easy separation and surface modification. Their remarkable properties, such as superparamagnetism, biocompatibility and selectivity have established magnetic materials as very reliable options in sample preparation approaches. In order to comprehend the range of utilization at magnetic materials and nanostructures, this review aims to present the most notable examples in sample preparation prior to liquid chromatography (LC) to the community of analytical chemists. Primarily, the review describes the principles of the techniques in which the magnetic materials are utilized and leaned on. Additionally, there is a diligent report about the novel magnetic techniques and finally a comparison to demonstrate the total point of view.

**Keywords:** magnetic; preparation; chromatography; nanomaterials



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## 1. Introduction

While the upgrowth of advanced analytical instrumentation remains at a high level and most of the analytes can be detected, some compounds are still beyond the detection thresholds due to the restriction of instrumental detection limit and interferences of matrices. It is a vital goal to introduce sample preparation techniques prior to an analytical process so as to achieve accurate quantification and lower detection limits. The objective of sample preparation is to isolate the analyte(s) of interest from the sample matrix in the most possible concentrated form and enhance analytes' separation and/or detection [1]. Over the past several decades, considerable time has been devoted to present some widely used sample preparation techniques, such as liquid–liquid extraction (LLE) and solid phase extraction (SPE); each of these techniques bare their own advantages and disadvantages. The classical methods of sample preparation include complicated, time-consuming steps that consume high amounts of toxic organic solvents and require large sample sizes [2]. Therefore, novel microextraction protocols have been introduced to be either solvent-less or minimalize the possible amount of organic solvents. According to studies, these methods have shown great outcomes as possible replacements to the classical methods for many different applications. Recent trends are driven by the Green Analytical Chemistry (GAC), which not only encourages the minimization of the volumes used but also the use of green(er) solvents that will have a minimum impact on the environment [3,4]. Classical SPE-based approaches where the adsorbents are packed into cartridges have been applied in many effective cases; however, it is not suitable for samples containing suspended solid or fouling components, because problems of column blocking, and high pressure are frequently detected. A technique, during which the adsorbents are incubated directly with the samples, can solve the abovementioned problems [4].

Magnetic solid phase extraction (MSPE) overcomes problems such as column packing and phase separation. In this approach, magnetic materials are dispersed into an aqueous

sample and after incubation for a suitable time until the target analytes are adsorbed on the adsorbent material, an external magnetic field is applied to separate the magnetic materials from the solution in an easy way. In addition, the extraction time is shortened as suspended magnetic particles facilitate mass transfer by offering increased interfacial area between the solid adsorbent and sample solution. Overall, MSPE is a low cost, easily instrumented and quick extraction technique that has captured much attention in the field of sample preparation because of its huge upside potential and very little downside risks [5].

Dispersive liquid–liquid microextraction (DLLME) is a successful extraction developed by M. Rezaee et al. in 2006 [6]. DLLME employs low amount of extractant organic solvent normally in the order of microliters. Due to the ease in separation by centrifugation, high-density chlorinated solvents are commonly in DLLME [7]. Despite being a very common technique due to a high preconcentration factor, good extraction performance and the reduced demand for sample and organic solvents researchers have tried utilizing ionic liquids (ILs) which identify as less toxic chemicals than chlorinated solvents that exhibit high density and they are commonly used at DLLME [8]. Ionic liquids (ILs) are organic molten salts that exhibit a melting point of less than 100 °C which means they can exist as a liquid in a broader temperature range [9]. ILs comprise a good class of extraction solvents due to their unique physicochemical properties. Meanwhile, magnetic materials attract significant consideration since they are able to provide rapid and efficient separation [10]. As MSPE, MIL-DLLME correspondingly requires an external magnetic field for the phase separation. Moreover, magnetic extraction media can be easily regenerated and reused, resulting in both economic and environmental benefits. The unique combination with special separation abilities arises from the integration of magnetic materials and ILs have been thoroughly discussed in current review.

It is remarkable that magnetic composites have been also introduced in sample pre-treatment methodologies also including ionic liquid-linked dual magnetic microextraction (IL-DMME) [11], stir bar sorptive extraction (SBSE) [12], SPME and single drop microextraction (SDME) [13].

## 2. Magnetic Sample Preparation Methods

The separation mechanism using magnetic nanoparticles (MNPs) depends on the type of sorbent, and is related to the interaction of analyte molecules with the surface functional groups, as in the classical solid phase extraction (SPE). Magnetic nanomaterials used in MSPE are usually designed according to the molecular structures and properties of the targets [14].

### 2.1. Magnetic Solid Phase Extraction (MSPE)

Du Q. et al. described a novel MSPE utilizing magnetic molecularly imprinted polymers (MMIPs) using triallyl isocyanurate as functional monomer. The study revealed that the monomer was successfully used for the enrichment and determination of stigmatocystin (STG) in wheat samples [15]. MMIPs use magnetic nanoparticles as the core covered by MIPs shell. The MMIPs can be separated from the solvent by external magnetic field due to the magnetic properties of magnetic nanoparticles [16]. It is worth reporting that their low toxicity combined with the skills above make MMIPs a qualified option in the fields of purification and separation [17]. Magnetic solid phase extraction, based on the MMIPs, combined with high-performance liquid chromatography (MSPE-HPLC) at optimal conditions was successfully used for the extraction of STG. The recovery of this method gave very satisfactory results at 87.6–96.9% and the limit of detection (LOD) was 0.63 ng·g<sup>-1</sup>.

An interesting study carried out by Ning T. and his collaborators [18] concerning an in vitro assessment for human skin exposure to parabens (PBs) was introduced. PBs are esters of p-hydroxybenzoic acid primarily used as antibacterials and preservatives in medicine, cosmetics and food. Their advantages, such as low cost, stability in wide pH range, negligible direct toxicity caused broad production and consequently extensive

utilization lead to serious endocrine function disorders [18]. Despite the fact that the penetration capacity of parabens in cosmetics by the skin has been studied for years, the human skin remains a very difficult biological matrix and hard to be sampled [19]. According to Tao Ning, a novel magnetic porous carbon (MPC) derived from discarded cigarette butts (DCBs) was proposed as an adsorbent of magnetic solid phase extraction (MSPE) by preparation following a one-step strategy. Five parabens were monitored in hand cream and their residual amount on hand, based on the MPC materials, which lead to a highly sensitive in vitro assessment. Agarose gel was used, replacing the skin of living tissues in order to conduct in vitro assays to study the absorption of human skin to parabens. In conclusion, this novel MSPE provides a very fast and efficient sample preparation technique which was easy to be coupled with high-performance liquid chromatography at optimal conditions. The proposed approach exhibited limits of detection between 0.25 and 0.34 ng mL<sup>-1</sup> and satisfactory range for recoveries at 85.8–112.6% for the spiked samples [20].

Ye Z. et al. [21] reported the synthesis of an efficient highly fluorinated and boron-rich adsorbent (FBA) for the determination of fluoroquinolones (FQs) in environmental water and milk samples. The study revealed satisfactory extraction capability for FQs through fluorophilic and B–N coordination interactions. Moreover, the synthesized FBA also exhibited strong magnetic responsiveness and a good lifespan. This novel MSPE performed prior to high-performance liquid chromatography at optimal conditions (HPLC-DAD) to quantify trace levels of FQs in the examined matrices. Low limits of detection which ranged from 0.0049 to 0.016 µg/L in water samples and 0.010–0.046 µg/kg in milk samples were reported, while the respective recovery rates with regard to the analysis of target FQs in real samples were in the ranges of 80.1–120% and 78.9–119% for water and milk samples accordingly [21].

#### 2.1.1. On-Line MSPE

On-line sample preparation methods provide some notable advantages over the off-line ones. They are faster, more precise with reduced sample and reagent consumption, but most importantly they can significantly eliminate errors from human sources and thus simplify the method. Compared with off-line MSPE, the sensitivity of on-line MSPE can be enhanced by 30–400 times [22].

In a study carried out by P. Montoro Lea and his research group, an on-line preconcentration system based on two knotted reactors containing Fe<sub>3</sub>O<sub>4</sub> nanoparticles functionalized with [1,5-bis(2-pyridyl) 3- sulfophenylmethylene] thiocarbonohydrazide (PSTH-MNPs) was introduced. The novel system was combined with inductively coupled plasma mass spectrometry (ICP-MS) for the determination of As(III) and As(V) in natural waters (seawater, lake and well-water). The complexity of the samples especially in the case of arsenic where chloride ions could hinder its detection as well as the low concentrations in which the analytes are present makes the speciation of trace elements in aqueous environmental samples very difficult [23]. In this work, enrichment factors were 1.9 for As(III) and 2.1 for total As. The working range was 0.01 to 50 µg L<sup>-1</sup> for As (III) and 0.03 to at least 100 µg L<sup>-1</sup> for total As. Sampling frequency was 14.4 h<sup>-1</sup> while sample and eluent consumption was 9.6 mL and 3.6 mL, respectively.

#### 2.1.2. Solid Phase Microextraction (SPME)

SPME is a modern alternative technique to traditional sample preparation technology introduced by Arthur and Pawliszyn [24]. The method has shown incredible benefits such as greenness, sensitivity, robustness, easy miniaturization or automation and coupling with instrumental techniques. Although SPME's most important drawback is the limited range of stationary phases' polarity, which are commercially available. Furthermore, the bending and stripping of fibers in combination with the ease for coating damage can reduce the fiber's lifetime [25,26]. With these disadvantages being known, H. Heidari et al. developed a novel SPME fiber based on a glass tube coated with ceramic/carbon-coated Fe<sub>3</sub>O<sub>4</sub> MNP

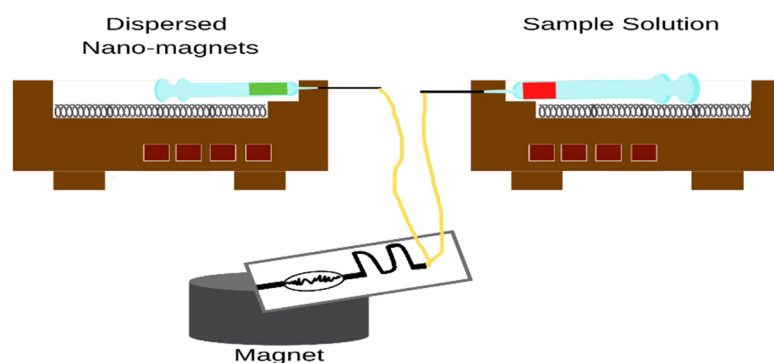
composite ( $\text{CeFe}_3\text{O}_4/\text{C}$  MNP), which was synthesized by sol–gel technique. A simple hydrothermal reaction used to synthesize the carbon coated  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles and the produced powder was mixed with sol–gel precursors to prepare  $\text{C–Fe}_3\text{O}_4/\text{C}$  MNP. A simple method was employed for the deposition of  $\text{CeFe}_3\text{O}_4/\text{C}$  MNP on the surface of the glass tube as new substrate. The results demonstrate that this method is a reproducible and straightforward procedure for preparing MNP coated SPME fibers.

The applicability of the designed SPME fiber was examined by some selected polycyclic aromatic hydrocarbons (PAHs). The analytes were extracted by SPME and desorbed using acetonitrile as eluent [27]. The determination of the target analytes was performed using HPLC-FLD. As shown by the presented results, the proposed method based on this novel fiber had wide dynamic linear range ( $0.01\text{--}350\ \mu\text{g L}^{-1}$ ) with good linearity ( $R^2 > 0.990$ ) and remarkably low detection limits ( $0.7\text{--}50\ \text{pg mL}^{-1}$ ). The fibers have been effectively used for the analysis of spiked water samples [28].

### 2.1.3. Dispersive Magnetic Solid Phase Microextraction on Microfluidic Devices

In the past few years, an underlying technology known as microfluidics has been introduced due to their utility to the preparation of miniaturized devices [29]. Plenty of advantages, such as really low consumption of reagents/samples, minimum intervention and simple miniaturization have grown rapid interest in the research community. Moreover, remarkable preconcentration could be accomplished by the utilization of sorptive materials that exhibit increased capacity and ratio between the sorbent's surface and volume used that could result in efficient miniaturization in combination with good enrichment and sensitivity [30,31].

In their study, Farahmandi et al. introduced a pioneer system based on microfluidics with an extraction channel at 80 mm length that was employed for separation and preconcentration of parabens. In order to achieve efficient extraction and separation of sorbent particles the researchers managed to synthesize magnetite nanoparticles and coat them with polyaniline. The aid of a hydrophobic surfactant was efficient to ensure the good dispersion of the solid particles within the extraction channel. The microfluidic platform that was used consisted of a relatively long spiral microchannel that was prepared using laser-cutting and multi-layered assembly. The stability of the dispersed nanoparticles in the aqueous solution was increased after suitable investigation and optimization of various chemical and instrumental parameters. Optimal conditions lead to calibration curves that were linear in the range of  $5.0\text{--}1000.0\ \text{mg L}^{-1}$  for propyl paraben and  $8.0\text{--}1000.0\ \text{mg L}^{-1}$  for methyl- and ethyl paraben with coefficients of determination  $\geq 0.992$ . The proposed method was successfully applied in the extraction of parabens from real samples (including fruit juice, cosmetic cream and urine). The recoveries obtained were profitable and the standard deviations from the real sample analysis indicated that the procedure is practicable with regard to efficiency of the extraction and dispersion maintenance at complicated sample matrices [32]. Despite all the advantages of such systems, major problems might occur, mostly regarding the dispersion and maintenance of particle dispersibility during the extraction. The aid of a counter (or simultaneous) flow of sample solution with the input of magnetic beads into the device inlet facilitates the struggle at the initial dispersion. However, this disadvantage still remains unsolved in long microchannels. Figure 1 illustrates the representation of the extraction set up.



**Figure 1.** Schematic representation of the extraction set up for MSPE on microfluidic device.

#### 2.1.4. Dispersive Micro-Solid Phase Extraction (D- $\mu$ -SPE)

A variety of nanomaterials have been applied for SPE among which zeolitic imidazolate frameworks (ZIFs) and layered double hydroxides (LDHs) have gained popularity due to their unique morphologies and properties. Recently, pioneer nanocomposites consisting of a wide variety of nanomaterials was introduced to improve the characteristics of sorbents and boost their applicability in sample preparation methods. For example, in a work carried out by Xin Di et al., a magnetic layered double hydroxide ( $\text{Fe}_3\text{O}_4$ @LDH/ZIF) was synthesized and used for the D- $\mu$ -SPE of endocrine disruptors from milk samples prior to their determination by ultra-high performance liquid chromatography coupled with tandem mass spectrometry. The proposed protocol exhibited low limits of detection ( $3\text{--}15\text{ ng L}^{-1}$ ) and good linearity. This work reveals promising results for the fabrication of new adsorbents towards the improvement of the performance of analytical protocols [33].

#### 2.2. MIL-DLLME

Simplicity, low-cost, rapidity, reduced amount of chemicals solvents, good recoveries and high enriching ability are the main benefits that attained the attention of researchers. The majority of MIL-based microextractions protocols are conducted utilizing DLLME and the goal is to describe an illustrative point of view at this section.

A recently found class of magnetic ionic liquids (MILs) made of a single component was discovered and is now in the forefront of research in MIL-DLLME. These chemicals owe their magnetic property to complex ions of metals overcoming the need for external magnetic supports. In sample preparation MILs are important media due to their physiochemical properties that results in a strong counter force to external magnetic fields. Typically, for the extraction of the target analytes ultrasound irradiation can be employed for the uniform dispersion of MILs in the sample [34]. The majority of the initially synthesized MILs exhibited hydrophilicity and were expected to result in good extraction performance when used in hydrophobic media. MILs are composed of a plethora of functional groups including esters and protonated primary amines and as a result they are water miscible. Moreover, MILs are miscible with polar solvents after a very staminal shake which restricts their applications, while they are not miscible with non-polar solvents (e.g., n-hexane) [11]. The first application of MILs in DLLME was introduced in 2014 by Yuanpeng Wang et al. In this study, a MIL-based DLLME was proposed for the extraction of triazine herbicides from vegetable oils prior to their analysis by liquid chromatography. An aliquot of 1-hexyl-3-methylimidazolium tetrachloroferrate ( $[\text{C}_6\text{mim}]$ ) was employed as the extractant. In order to ensure the rapid magnetic separation, carbonyl iron powder was added to form carbonyl iron powder (CIP)-MIL. Overall, the method showed better performance followed by good precision and sensitivity, as well as low limits of detection and limits of quantification for the target analytes [35].

Aiming to expand the applicability of MILs in aqueous media, a demand for the preparation of hydrophobic MILs arose. Thus, it was necessary to take some actions so the hydrophobic character can be urged in MILs. Typical approaches that can be employed to improve the hydrophobic character of MILs include either the replacement

of hydrolysis susceptible  $\text{FeCl}_4^-$  anion with other transition metal-based anions or the use of long aliphatic alkyl chain-based organic cations. Taking that into account, to avoid the limitations related with  $\text{FeCl}_4^-$ , MILs with  $\text{MnCl}_4^{2-}$  were introduced in DLLME. In a study carried out by Merib J, manganese-based MILs were used for the extraction of the hormones from urine samples. This work is innovative because it reported on an application of manganese-based MILs compatible with HPLC for the extraction of analytes of biological interest. The hydrophobic MILs trihexyl-tetradecylphosphonium tetrachloromanganate (II) ( $[\text{P}_{6,6,6,14}^+]_2[\text{MnCl}_4^{2-}]$ ) and aliquat-tetrachloromanganate (II) ( $[\text{Aliquat}^+]_2[\text{MnCl}_4^{2-}]$ ) were used. Under optimum sample preparation conditions, an amount of 5 mg of MIL and 5  $\mu\text{L}$  of methanol (disperser solvent) were used. As such, good overall method performance was achieved. The proposed method can be characterized as reliable and environmentally friendly, while it overcame the need for a centrifugation step [36].

As it was previously mentioned, ILs utilize organic solvents, which are toxic and can affect health and cause environmental problems. That being said, there is a need for the use of safer and greener chemicals for the replacement of conventional solvents that exhibit high toxicity. Recently, an ionic liquid-linked dual magnetic microextraction (IL-DMME) developed by Yilmaz and Sylak with magnetic nanomaterials was proposed as a new extraction media. This novel method demonstrates that IL-DLLME and dispersive  $\mu$ -magnetic nanoparticle solid phase extraction (D- $\mu$ -SPE) is an effective combination that assisted in overcoming the abovementioned limitations. By using vortex mixing, 1-butyl-3-methylimidazolium hexafluorophosphate [ $\text{C}_4\text{mim}$ ][ $\text{PF}_6$ ] was employed for the extraction of lead-pyrrolidine-dithiocarbamate (Pb-PDC) complex. Following the IL-DMME step, an amount of 50 mg of  $\text{Fe}_3\text{O}_4$  MNPs was used for extracting the IL and Pb-PDC complex. Under optimum sample preparation conditions, the method presented low detection limit ( $0.57 \mu\text{g L}^{-1}$ ) and good repeatability ( $<7.5\%$ ,  $n = 10$ ). The proposed methodology was finally employed for the determination of lead in hair, plant and water samples [37].

### 2.3. Single Drop Microextraction (SDME)

SDME is a sample preparation mode based on solvent microextraction (SME), which is often combined with GC or HPLC [38]. SDME has two separate modes, namely "direct immersion" and "headspace". A standard execution includes the utilization of a few microliters of an organic solvent microdrop that is kept on the tip of a microsyringe, which is placed directly in the liquid matrix or in the headspace above the sample in order to achieve the extraction of the target analytes. After a certain period of time, the microdrop is withdrawn inside the syringe and further analyzed by an analytical technique [39]. Limitations of this sample preparation technique includes the instability of the microdrop during the immersion in the liquid sample, as well as the long microextraction times [40].

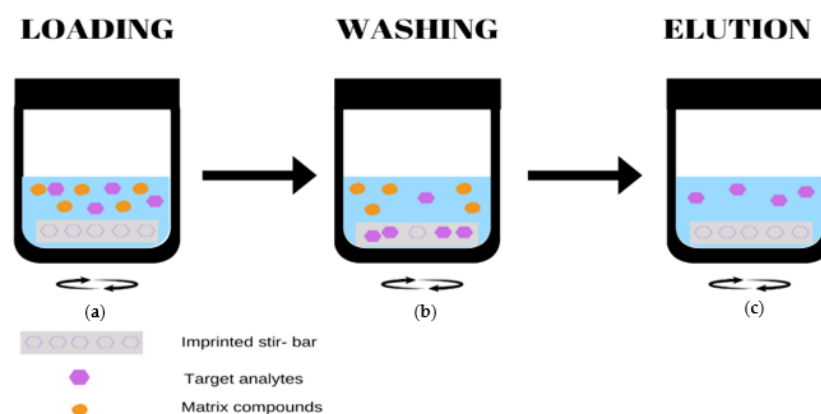
A recent study indicates the parallel-SDME/MIL-based (Pa-SDME) analytical methodology that is able to take advantage of the magnetic properties, drop stability and extraction capacity of the trihexyl (tetradecyl) phosphonium tetrachloromanganate (II) ( $[\text{P}_{6,6,6,14}^+]_2[\text{MnCl}_4^{2-}]$ ) MIL. The proposed scheme was coupled with a 96-well plate to provide high throughput and low cost. As proof-of-concept, the proposed analytical strategy was used for the extraction of methylparaben, ethylparaben, propylparaben, bisphenol A, butylparaben, benzophenone and triclocarban. In order to stabilize the magnetic IL droplets during the parallel sample handling, the 96-well plate contained a set of magnetic pins. As such, a sample throughput of less than 1 min per sample was achieved. Among the benefits of this technique over conventional SDME approaches is its ability to maintain a stable solvent microdrop to facilitate high throughput. The extracts were analyzed by HPLC-DAD under optimal conditions. The results were satisfactory and promising with low LODs and good linearity [41].

### 2.4. Stir Bar Sorptive Extraction (SBSE)

SBSE can be considered as an alternative to the SPME technique. In this regard, SBSE increases the typical low capacity of conventional SPME fibers and is based on the partitioning of the desired compounds between the stationary phase-coated magnetic stir

bar and the sample solution. More specifically, in comparison with SPME coatings, the coating of SBSE occupy a significantly higher volume resulting in increased extraction capacity and extraction efficiency. For years, the only commercially available stir bar coatings were polydimethylsiloxane (PDMS) and a PDMS/Ethylene glycol copolymer limiting the applicability of this technique to the extraction of hydrophobic target analytes. Although the demand for coatings with high affinity towards a bigger group of analytes, especially the polar ones, was the guidance for the fabrication of novel stir bars coated with novel magnetic composites [42].

A work developed by M. Díaz-Álvarez et al. was based on the entrapment of modified magnetic nanoparticles within an imprinted polymer monolith for creating molecularly imprinted stir bars. As the first step, modification of the surface of the MNPs by oleic acid took place, followed by encapsulation in a silica network. For this purpose, vinyl groups were grafted onto the particles' surface. Moreover, a glass vial insert was employed as the mold for the subsequent copolymerization. As a result, the obtained imprinted monolith presented magnetic properties allowing its use as magnetic stir bar. The main factors affecting the polymer morphology were optimized. The technique of SBSE utilized these top notch imprinted stir bars for efficient extraction of triazines from soil sample extracts. The recoveries ranged from 2.4 to 8.7% but despite that observation, high selectivity was obtained allowing the determination of the target analytes with detection limits lower than  $7.5 \text{ ng g}^{-1}$  [43]. Figure 2 illustrates the main steps of the proposed MI-SBSE.



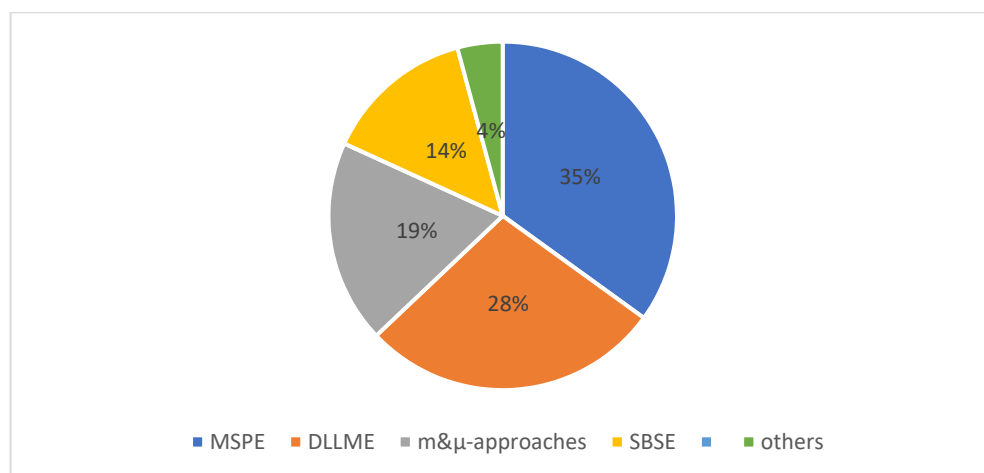
**Figure 2.** Scheme of the proposed MI-SBSE. (a) Matrix compounds—orange; (b) Target analyte—purple; (c) Imprinted stir bar—grey.

### 3. Epilogue

This current review article focused on the applications of magnetic nanomaterials and magnetic nanostructures in sample preparation prior to liquid chromatography. Their unique properties gave the opportunity to extract analytes from matrices even at low concentration levels that back in day researchers were unable to achieve. The illustrative point of view that this article demonstrates is that the most noteworthy applications occurred in either MSPE or DLLME as shown in Figure 3.

MSPE is a dispersed SPE format that utilizes magnetic materials as sorbents which reveals all the advantages mentioned above and combined with liquid chromatography provokes good results in terms of accuracy and sensitivity. Furthermore, the development of current technology gave the opportunity for more automated methods such as the online-SPE providing the researchers with even bigger ambitions for more elucidating assays.

MILs are good extraction solvents for a plethora of target analytes in a wide variety of complex samples. MILs combine the physicochemical properties of ILs with the magnetic susceptibility, overcoming the need for additional external supports. They have been used in many microextraction techniques with most applications in DLLME and even though MILs already show great performance, their technology is susceptible to big development, both in synthesis and their interaction with the analytes.



**Figure 3.** Consolidated summary of the magnetic applications in sample preparation methods.

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