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Computational modeling of molecularly imprinted polymers as a green approach to the development of novel analytical sorbents

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a b s t r a c t

The development of novel molecularly imprinted polymers (MIP) sorbents for specific chemical com-pounds require a lot of tedious and time-consuming laboratory work. Significant quantities of solvents and reagents are consumed in the course of the verification of appropriate configurations of polymeri-zation reagents. Implementation of molecular modeling in the MIP sorbent development process appears to provide a solution to this problem. Appropriate simulations and computations facilitate the deter-mination of the nature of interaction between the reagents and thus the selection of the best configu-ration of chemicals for the preparation of the sorbent. The article presents literature information on major computer software used for molecular modeling, its application in the development of MIP sor-bents, as well as the advantages resulting from the implementation of computer-assisted techniques. The appropriate choice of polymerization reagents and conditions allows for a significant reduction of the adverse environmental impact of the entire laboratory process.

Keywords: Molecularly imprinted polymers, Computational modeling Green, analytical sorbents Green, analytical chemistry Basic, laboratory studies

1. Introduction

Starting from the onset of the 21st century, a clear trend can be observed in analytical chemistry that consists in the extensive development and implementation of green analytical chemistry principles in routine as well as newly developed analytical procedures. Particular emphasis is placed on such issues as: (i) significant reduction of quantities of solvents (as used both during single analysis and during the entire analytical methodology); (ii) replacement of conventional organic solvents with substances of less adverse environmental impact (surface active agents, ionic liquids, supercritical fluids, deep eutectic solvents, bio-derived solvents); (iii) use of state-of-the-art analytical instrumentation allowing for direct measurements without the need for initial sample preparation; (iv) development of novel analytical tools to increase efficacy, performance, and selectivity of isolation and/or preconcentration of the specific chemical compounds from various types of samples. New methodological and instrumentation solutions are being successively developed to significantly reduce the consumption of organic solvents at the stage of sampling, as well as isolation and/or preconcentration of analytes in environmental samples (soil and water), pharmaceuticals or samples from biological (plants, animals, humans) and food origin [1–6].

The development of novel types of sorptive materials facilitating effective and selective isolation of a specific compound or group of compounds from an array of environmental, biological or food samples is a significant element of this strategy. Most commonly, however, the materials developed (or already commercially available on the market) for use as microextraction or solvent-free extraction techniques are dedicated to determine known compounds or groups of compounds that may be present at low concentration levels in environmental samples. There is a continued demand for novel sorptive materials for the isolation of groups of compounds with their adverse environmental impact not being precisely determined while their presence in the environmental, biological or food samples being confirmed [7,8]. This demand is mainly associated with the determination of specific compounds or groups of compounds (that might be considered as a carcinogenic or toxic) in environmental, food, or biological samples (most commonly, this pertains to residues of selected pharmacological products) – samples in most cases characterized by complex matrix composition [9–11].

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The example of such sorptive materials with the capability of a selective molecular recognition are molecularly imprinted polymers (MIPs) [12]. According to the literature data, there is a growing interest (see Fig. 1) in various types of MIPs studies and applications, due to the ease of their preparation, thermal, mechanical and chemical stability, and possible recovery of sorption material for multiple use. In addition, the application of such sorbents significantly increases the selectivity and efficacy of the isolation and/or preconcentration of analytes from environmental, biological, food and pharmaceutical samples [13,14] As a result, this significantly lowered the detection and quantification limit (LOD and LOQ) values of the entire analytical procedure. In addition, MIP sorbents provide an alternative solution to the commercially available sorptive materials, facilitating the isolation and/or preconcentration of analytes in samples characterized by complex matrix composition [15–17]. Due to the number of advantages of MIP sorbents, they are applied in a wide spectrum of analytical solutions, including: (i) *in-situ* analysis and biomimetic catalysis; (ii) advanced separation techniques; and (iii) extraction or solvent-free extraction techniques (see Fig. 2) [18–21]. Although, one of the most developing research area where the use of MIP sorbents is more and more popular are the pharmaceutical and biotechnological applications. This kind of "smart materials/sorbents" might be applied in pharmaceutical laboratory or large-scale practice in the field of the extraction and purification of drugs from concentrated solutions [22–25].

A deep knowledge of the underlying process, including its advantages and limitations, is necessary for the best implementation of novel instrumentation or technical solutions in organic synthesis and analytical methodology. Moreover, it should be mentioned that in a case of green chemistry, the MIP sorbents have to be considered in a two main areas: (i) the green synthesis of MIPs – associated with the type and amount of solvents and reagents used during the preparation of the specific MIP sorbent; (ii) the green analysis using MIPs – considering the application of new type of selective MIP sorbent in developed analytical protocols.

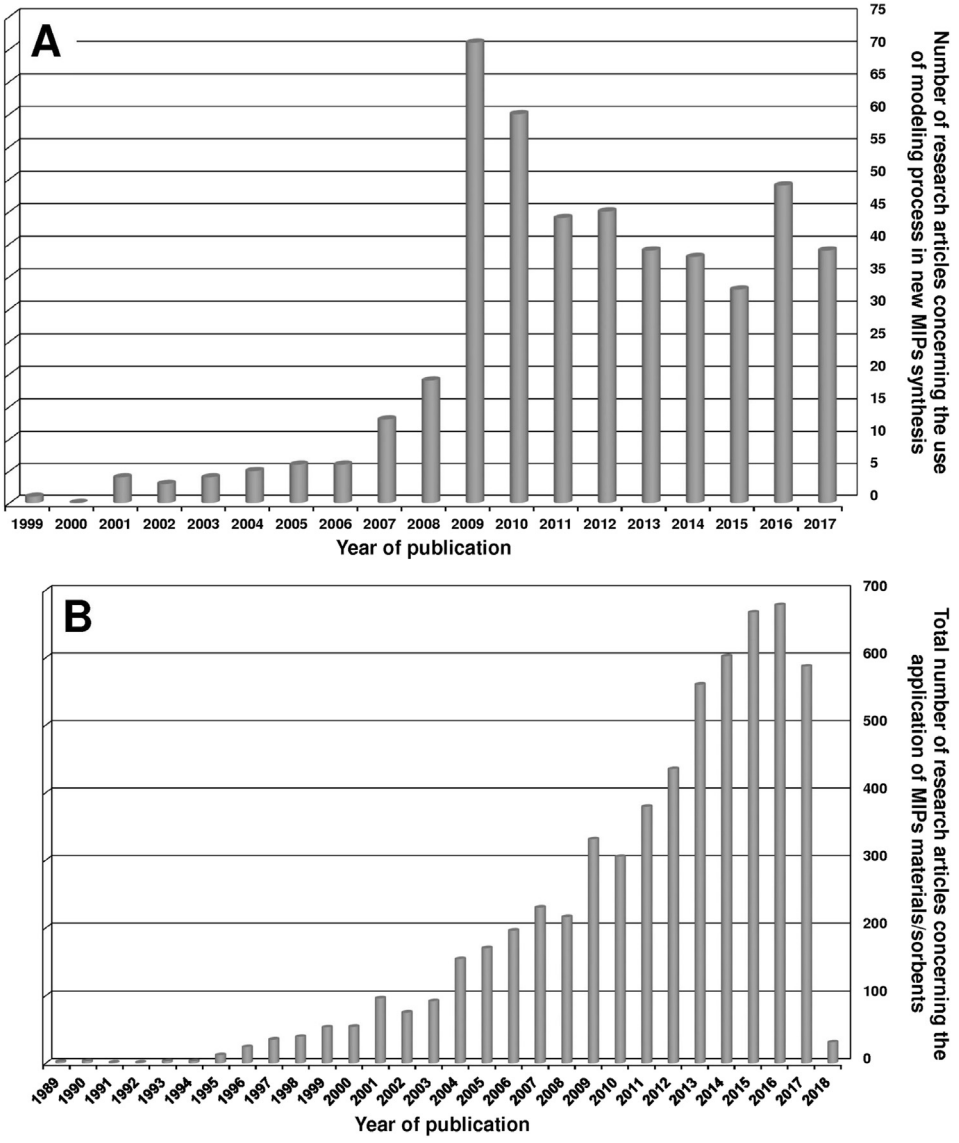

Fig. 1. The number of publications (considering research articles) on the topic of application of new type of MIP sorbents in the field of analytical chemistry: A – number of publications concerns the application of molecular modeling process in new MIPs synthesis; B – the total amount of publications concerning the new type of MIPs per year [Scopus web site data base].

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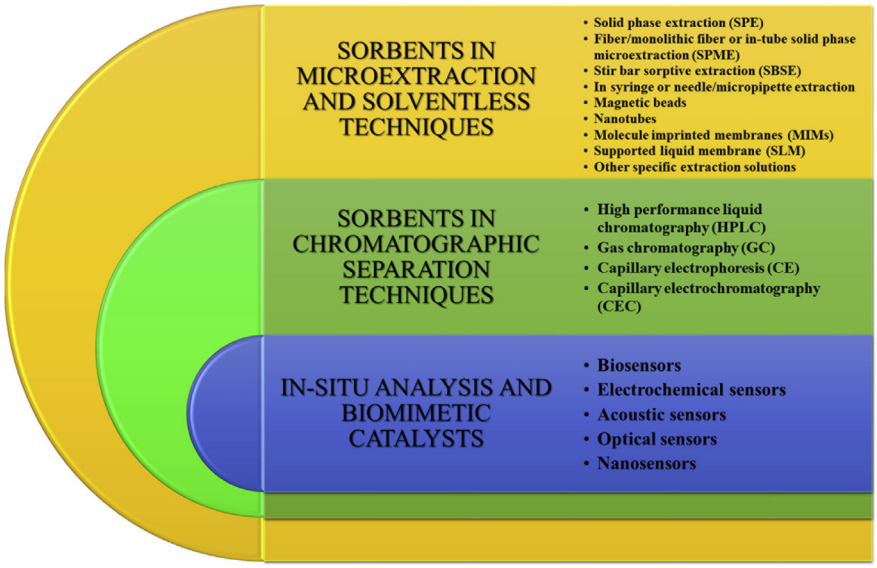

Fig. 2. General fields of application of molecularly imprinted polymers used in a wide spectrum of analytical devices and techniques employed in environmental, biological and pharmaceutical analysis.

Practical analytical use of MIP sorbents as final products ready for immediate application is with no doubt an example of green analytical chemistry. From the standpoint of the possible harmful environmental impact, a significant problem is the series of steps that need to be followed in order to obtain the appropriate high selectivity sorptive material. This causes the consumption of large quantities or solvents and some specific reagents in various configurations. The development of an optimum sorptive material requires time, appropriate instrumentation, and considerable financial input. This is due to the common requirement of a number of syntheses being carried out in various configurations that take into account the types and quantities of substrates, which may also generate significant quantities of waste products.

The solution to this problem is provided by appropriate planning and preliminary simulation of the reaction to obtain the final product from the available reagents. In this case, appropriate software is recommended to perform series of computations and carry out a simulation of the target sorptive material preparation process. Molecular modeling by means of *ab initio* or semi-empirical computational methods allows for the determination of the optimum composition of the reaction mixture, thus allowing for a significant reduction in the quantities of solvents and reagents and an increase in the likelihood of obtaining the optimum MIP characterized by high selectivity and appropriate morphological and physiochemical properties [26–29].

In the current article an attempt to gather from the literature the basic issues related to the use of computer-assisted molecular modeling as valuable support for development of a new type of polymer sorbents is presented. This short review points out the potential advantages of such combined approach for a significant reduction in the consumption of solvents and reagents during the synthesis of novel MIPs. In addition, the computer-assisted techniques allow for a significant reduction of the risk of failure in the development of MIPs sorbents (i.e. the obtained sorbents being characterized by inappropriate morphological and physiochemical properties). Furthermore, the article focuses on the use of computer-assisted molecular modeling techniques at the stage of designing the synthesis of specific selective MIP sorbents for use in the isolation and/or preconcentration of analytes in environmental, food, drug and biological fluid samples. Moreover, one of the main issues of the paper is to present the significant advantages of the interdisciplinary studies which combines aspects of green synthesis (as a part of organic and polymer chemistry), with the application of MIPs in green analytical methodologies (as a representative of analytical and environmental chemistry).

2. General information on the preparation of MIPs as selective sorbents for the solid phase extraction technique

In relation to the information presented in a graphical manner in Fig. 1b, one may observe a significant increase in the use of MIP sorbents in various types of analytical methodologies. Most commonly, novel types of sorptive materials are developed with the purpose of being used as the stationary phase in SPE. The technique is referred to as molecularly imprinted solid phase extraction (MISPE) [30,31]. To a large extent, the process of the development of an appropriate polymer MIP sorbent dedicated for a specific compound or a group of compounds is based on three basic conditions: (i) selection of appropriate reaction substrates and types of interactions to occur between the selected compounds; (ii) selection of an appropriate polymerization technique for efficient and reproductive preparation of a reliable MIP sorbent; and (iii) optimization of polymerization conditions (temperature, duration, type of initiator) [32–34].

Polymer sorbents are characterized by appropriate sorptive and physiochemical properties, like high binding capacity, large surface area and porosity (number of pores and their volumes) which are required in green analytical chemistry. This is due to, e.g. the increased selectivity and efficacy of the isolation and/or preconcentration of analytes in environmental, biological, food and pharmaceutical samples, reduced number of steps in a single analysis, and a reduced quantity of organic solvents consumed in the analysis of a single sample. However, when the process of the development and preparation of the appropriate polymer is being considered, it turns out that it requires significant amounts of time, solvents, and reagents, as well as access to appropriate laboratory instrumentation. Fig. 3 presents an outline of an overall laboratory procedure (algorithm) to be followed in the synthesis, as well as the complete morphological and physiochemical properties of the sorbent dedicated for the isolation of a particular compound.

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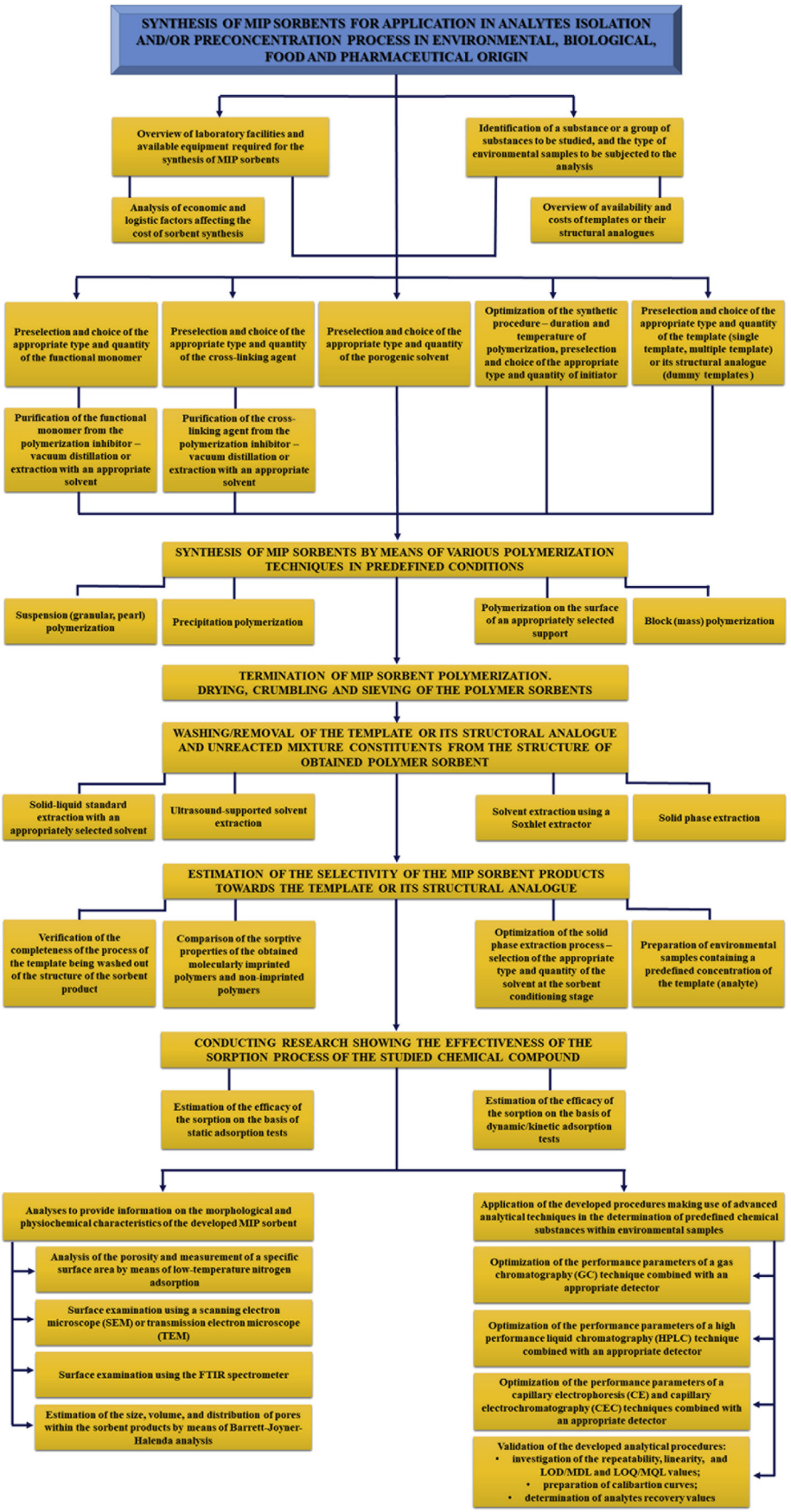

Fig. 3. General laboratory protocol commonly used to develop and characterize the new type of analytical MIP sorbents.

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The appropriate polymer sorbent is obtained mainly by the proper selection of the functional monomer, the template or its structural analogue and the porogenic agent (solvent). Appropriate types and quantities of the cross-linking agent and the reaction initiator should also be selected [35]. The synthesis of MIP sorbents may be pursued in different manners depending on the nature of the bonds to be formed between the functional monomer and the template or its structural analogue. In order to obtain a precisely defined MIP sorbent, one should also take into consideration the solubility of the template or its structural analogue in the polymerization mixture (mainly in the porogenic solvent) and the nature of functional groups of compounds (substrates) comprising the polymerization mixture [36]. Earlier analysis of the economic aspects of the polymerization reaction, mainly in relation to the instrumentation maintenance costs and the availability and cost of the template or its structural analogue are also important [37,38].

As a consequence of all these factors, a large number of operations must be conducted and a large number of substrate configurations (in relation to both the type and the quantity of individual substrates, as well as ranging from appropriate purification of substrates to appropriate setup of analytical instrumentation at the stage of final determinations) must be tested to achieve a satisfactory final outcome, i.e. a new type of sorptive material [39]. In addition, the sorptive material must be dried, fragmented and washed with the solvent after the completion of polymerization so as to remove/wash out the residue template or its structural analogue. This also allows for the elimination of potential unreacted chemicals. Purification of the newly prepared sorptive material is another source of waste materials. Only after all the above steps are completed may the obtained sorptive material be used for further research aimed at a full determination of its morphological and physiochemical properties [19]. A detailed characterization of individual polymerization techniques and methods for the preparation of MIP sorbents were presented in earlier literature reports [15,17,40–42].

3. Basic software applied in a computational modeling of molecules in the field of development of new MIPs sorbents

Molecular modeling *in silico* [43,44], e. g. using computer as a research tool enables carrying out a high number of calculations and simulations in order to select the most suitable structure and composition of functional monomer: template (or its structural analogue – reference substance): porogen/solvent. This approach leads to a significant reduction of the amounts of solvents and chemical reagents during the polymerization process with a parallel decrease of financial costs. As a result, molecular modeling supported production of a new type sorbent acquire a "greener feature or character".

Molecular modeling of MIP-type sorption materials using computer as a tool is related to finding a specific relation between the functional material, template (reference compound) and a porogen/solvent. The core of such calculations is based on input data related to chemical composition, structure at atomic scale, distribution of electrostatic charges leading to dipole formation, as well as weak, long range dispersion interactions governed by hydrophobic type van der Waals forces. All these factors contribute to direct picture of a molecular associate and the corresponding interaction energy [45–47].

During the production of a new polymeric material the most sensitive issue is how to optimize the selection of the optimal template (reference compound). At the early stage of planning the economic issue (high cost of template related to its unique structure or properties) and logistic issue (availability of defined chemical compound, including its solubility in porogens/solvents) could be critical. Selection of a proper template (reference compound), which is the most expensive chemical used, has a direct impact on the costs of the entire procedure of new sorption material production. In case of failure of the synthesis or its low yield or quality new wastes are generated and the loss of template results in additional costs. Therefore, if possible, one should use the so-called alternative chemicals which exhibit similar physicochemical properties and three-dimensional structure to the optimal chemical compound. In many cases structural analogues of selected template are significantly cheaper, easier to obtain or purchase and better soluble in common solvents – porogens.

On the other hand, searching for a proper chemical compound as replacement of the defined template (reference compound) is not so easy and fast and it requires performing several trial reactions. As result, additional costs are created and sizable amounts of reagents and solvents are wasted. One of the proposed solution in this case is the introduction of molecular modeling as initial stage of polymer sorbent synthesis design. It makes possible getting an important knowledge about the optimal chemical compound which could be a structural analogue for the template (reference compound). In addition, conducting computer experiments "*in silico*" could decrease the number of syntheses on a "*try-and-error*" basis in order to get the desired sorbent exhibiting the optimal physicochemical and morphological properties. Such approach could lead to a significant decrease of costs and amounts of chemicals and reagents, as well as the unwanted waste materials. There is another benefit of using molecular modeling – an estimation of the best structural analogue of potential template capable of formation of the most stable complex with functional monomer. Molecular modeling of MIP type sorbents is based on selection of the suitable method of calculation including *ab initio* Hartree-Fock (HF), or significantly more accurate second order Moller-Plesset (MP2) which treats correlation energy but is computationally expensive. The best choice in terms of accuracy and efficiency is density functional theory (DFT) [26,48,49]. The second component of molecular modeling is related to a choice of a suitable basis set. There is another trade-off allowing accurate modeling of small molecules with relatively flexible and saturated basis sets and the use of small basis sets for large molecular systems. Thus, small Pople type basis sets (3-21G, 6-31G*) are preferred for larger molecular systems or for fast and very approximate calculations. On the other hand, Dunning [50] – or Jensen-type [51] correlation-consistent and polarization-consistent basis sets are well-suited for characterization of small molecules with chemical accuracy (±1 kcal mol^{-1}), in particular using advanced correlation methods [21,52–56].

The initial step of molecular modeling is related to a simple building of three-dimensional (3D) structure of a free (in vacuum) molecule using a graphical program [44]. Besides, an initial structure could be taken from X-ray studies, including libraries of known structures and partly modified. The input data created in a graphical program (sometimes also manually) is submitted to a program capable of iterative search for the lowest energy by changing the structural parameters (bond lengths, angles between bonds and dihedral angles) in so-called full (unrestricted) optimization procedure. As result, an equilibrium geometry, e. g., a structure corresponding to the global energy minimum is obtained. However, to verify this in the next step a vibrational analysis should be performed. A stable structure is referred to the situation where only positive (not imaginary) frequencies are calculated. This procedure should be applied to both the template and its possible structural analogues, important for the polymerization process. Besides, it is important to model a "reasonable fragment" of the polymer and the corresponding complex and its composition. This means a selection of the smallest unit of the studied polymer which contains all the functional groups and structural fragments, in many cases capped

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with hydrogen atoms for modeling and the small molecule, forming an associate (complex). Since SCF-Hartree-Fock and density functional theory calculations heavily depend on the number of atoms (like N^4, where N is the number of basis functions) the size of complex should be kept small to facilitate meaningful modeling. This solution could give a valuable information about the optimal molar ratio of functional monomer to template (reference substance) molecule [57]. Next, for different (allowable) geometries of the formed complex are optimized the structures and calculated interaction and/or binding energies (ΔE_{inter} or ΔE_b, in kJ mol^{-1} or kcal mol^{-1}; defined in vacuum conditions) [53]. On the basis of the strongest interaction (the most negative energy) one selects the most stable complex formed by the template (reference compound) and the functional monomer. The interaction energy is calculated as a difference of complex total energy and the reagents energy [58,59] (1):

$$\Delta E = E_{(template-monomer)} - \left[E_{(template)} - \sum E_{(monomer)}\right] \quad (1)$$

where:

$E_{(template\ -\ monomer)}$ – the total energy of template – functional monomer complex;
$E_{(template)}$ – the energy of the template;
$\Sigma E_{(monomer)}$ – the sum of energy of the functional monomers (in defined molar ratio).

Obviously, the calculated above interaction energies are obtained for molecules in the gaseous phase (vacuum) and no solvent effects are included. However, real experiments (conducted under real laboratory conditions) are carried out in the condensed phase, e. g. in the presence of solvent and therefore, the solvent/porogen impact should be included in a more accurate modeling. According to the literature data the quantum mechanical calculations the functional monomer with highest value of binding energy (ΔE_{inter}) to the template is mostly suitable for the future preparation of new polymeric sorption material (new MIP sorbent) [60]. Obviously, such calculations should help in selection of the most suitable functional monomer which shows the largest binding energy (with negative sign) for the potential polymeric sorption material. The criterion of highest interaction energy is also valid for the composition, e. g. the number of molecules forming the complex.

In addition, the estimation of interaction energy in complexes formed by strong hydrogen bonding or weaker dispersion forces suffers from the so-called basis set superposition error (BSSE) [61,62]. In such cases the description of electron density of individual components of a complex is overestimated due to overlap of wave functions and this results in apparently stronger binding (it is equivalent to the use of better quality basis sets) [63,64]. The use of counterpoise correction (CP) could alleviate the problem of BSSE, but is computationally expensive [65–67].

The second stage of molecular modeling involves a selection of optimal solvent as a porogen agent for a new MIP sorbent. In most cases the impact of porogen/solvent on the formation of MIP sorbent is computer modeled *via* polarizable continuum model (PCM) [68,69]. It takes into account solvent dielectric constant and the solute size using van der Waals radii. The results of computational molecular modeling using PCM are more reliable and closer to experimental data. The corresponding porogen/solvent impact (solvation energy in kcal mol^{-1}) is given as [66] (2):

$$\Delta E_{(solvent\ interaction\ energy)} = \Delta E_{(monomer-template\ complex\ in\ solution)} - \Delta E_{(complex\ in\ a\ gaseous\ phase)} \quad (2)$$

where:

$\Delta E_{(monomer\ -\ template\ complex\ in\ solution)}$ – the total energy of template – functional monomer complexes in the presence of porogen/solvent solution;
$\Delta E_{(complex\ in\ a\ gaseous\ phase)}$ – the total energy of complexes in the gaseous phase.

Selection of the optimal (most stable) template (reference compound) – functional monomer in solution is based on the interaction energy criterion – $\Delta E_{(solvent\ interaction\ energy)}$. Optimization of substrate selection procedure in new MIP sorbents design is performed using dedicated software packages. These programs contain routines allowing selection of method of calculation and libraries of common basis sets [66]. More recent basis sets could be downloaded from special libraries *via* internet [70–72]. Among the parameters most often predicted are equilibrium geometries of ground and transition states, molecular energy, including atomization energy, proton affinity, harmonic and anharmonic vibration frequencies, dipole moments, partial charges and NMR parameters [73–76]. Some general information on several popular commercial and free software applied in computational molecular modeling [77] in the field of analytical chemistry methodologies were listed in Table 1.

For a chemist working in the laboratory it is important to know the software performance, what is shortly mentioned in Table 1. Therefore, in most cases, the use of highly sophisticated "non-commercial" packages needs only a free "user license". However, it is not trivial to use it. Besides, such programs (for example *Dalton* or *CFOUR*) are dedicated to very accurate calculations in case of small molecular systems. At the other end is a commercial program *Gaussian* (and *GaussView*, which is a graphical tool for building models and analysis of results). It is a very easy to use tool designed to model small, medium size and large molecular systems. It works in a very intuitive way and is very popular in the computational chemists community. Moreover, it is easy to implement at various platforms, starting from a small netbook to desktop, mackintosh and unix supercomputer. *ADF* is more demanding and better suitable for density functional calculations on molecular systems including metal ions (in catalysis). Besides, *Material Studio* is suitable for modeling fairly large molecular systems.

4. Development of a new type of MIP sorbent in laboratory conditions – basic laboratory studies

The development of novel sorptive materials as part of basic research studies (i.e. studies conducted in laboratory settings) consists of two basic stages: (i) computer-assisted molecular modeling to design the theoretical configuration of reaction substrates (types, quantities, and molar ratios of substrates) to ensure the preparation of an appropriate sorptive material; and (ii) synthesis being carried out in laboratory conditions and followed by tests to determine the full characteristics of the new sorptive material.

Basic research does not involve studies aimed at demonstration of applicability of the newly developed sorptive materials for the selective isolation and/or preconcentration of specific chemicals from the samples characterized by the complex matrix in real life (field) conditions. The first stage of basic research the available graphical software dedicated to the design of 3D structures of selected chemical compounds are used to develop (e.g. by means of the semi-empirical (SE) quantum mechanical approach) optimum structures and configurations of potential reaction substrates, mainly the functional monomers, predefined template or its

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Table 1
General characterization of computational techniques (software) used to perform the quantum chemical calculations in the field of environmental chemistry.

Software name	Characterization of software	Web page/references
Commercially available software		
HyperChem	Popular program package for creating molecular models, performing molecular mechanics, molecular dynamics, semi-empirical, *ab initio* and density functional theory calculations aiming at predicting structural and spectroscopic parameters, as well as interaction energies. Allows direct visualization and analysis of calculation results. Designed for handling small, medium and large molecular systems.	http://www.hyper.com/ [78]
Gaussian	Commonly used professional program package for *ab initio* and density functional theory calculations aiming at accurate predicting structural and spectroscopic parameters as well as interaction energies. Designed for handling small and medium size molecular systems and allows prediction of energy with chemical accuracy (± 1 kcal mol^{-1}) using advanced correlated methods.	www.gausian.com [70]
GaussView	For building molecular models and visualization of Gaussian calculation results.	www.gausian.com [79]
Materials Studio	Allows modeling large molecular systems at DFT level (in material science and pharmacy). It is used in advanced research of various materials, such as polymers, carbon nanotubes, catalysts, metals, ceramics.	http://accelrys.com/ [80]
Discovery Studio	Allows modeling large molecular systems at DFT level (in material science and pharmacy).	
Molpro	Molpro version 2015.1 is a comprehensive system of *ab initio* programs for advanced molecular electronic structure calculations, similar to Gaussian.	https://www.molpro.net/ [81]
Free software		
GAMESS – US	Similar to Gaussian, applicable to small, medium and large molecular systems, no cost license.	http://www.msg.ameslab.gov/gamess/ [82]
CFOUR	Very Professional, similar to Gaussian but more sophisticated, applicable to small and medium molecular systems, no cost license.	www.cfour.de [83]
Dalton	Very Professional, similar to Gaussian but more sophisticated, applicable to small and medium molecular systems, no cost license.	http://daltonprogram.org/ [84]
NWChem	Similar to Gaussian, highly parallelized.	http://www.nwchem-sw.org/index.php/Main_Page [85]
Molden	A pre- and post-processing program of molecular and electronic structure	http://www.cmbi.ru.nl/molden/ [86]

potential structural analogue, as well as the solvents likely to be used as porogenic agents. According to the literature, the SE method takes advantage of pre-calculated data from previous empirical research, disregarding the core electrons and only the valence electrons being taken into consideration. Moreover, the method disregards or parameterizes two-electron integrals. The SE method provides the potential user with standard information regarding the molecules and is relatively faster than other quantum mechanical methods [87]. The second stage after the determination of appropriate structures and configurations of polymerization substrates consists in the use of more advanced computational packages. These packages are used to perform series of *ab initio* calculations in order to obtain datasets including the approximate numerical values of interaction (bonding) energies. At this stage, appropriate assumptions and approximations are used to obtained information on the energies of bonding in individual molecules (functional molecules or templates) and numerical values of interaction energies within the potential functional monomer-template complexes. The obtained value is defined as the binding score – the amount of energy necessary for a molecule to be taken apart into atoms. The use of the aforementioned advanced computational packages facilitate the estimation and generation of highly probable information on the stable conformation and vibrational frequencies of atoms, molecules, and reactive systems, optimum functional monomer: template ratios, and the nature of interactions. One should also note that computations/simulations of monomer-template interactions are carried out in two potential reaction environments, i.e. in a vacuum and in the presence of a solvent [88–92].

After 3D visualizations of selected structures are rendered and a series of computations are performed using computer-assisted molecular modeling systems, a detailed analysis of the generated dataset is performed. This leads to the pre-selection of a set of chemical compounds (functional monomer – template – porogenic agent) which might provide appropriate substrates for the polymerization reaction leading to the formation of a specific polymer sorbent dedicated to selectively bind a predefined substance. After this information is obtained, simultaneous synthesis of the specific MIP sorbent and a non-imprinted polymer sorbent is carried out in the laboratory. Block polymerization is most commonly used for this purpose due to the simplicity of the technique. The preparation of the new polymer sorbent is followed by standard operations described above and presented in Fig. 2; these operations are related to the drying and purification of the sorptive material. Next, the obtained polymer sorbent is subjected to a series of tests aimed at the characterization of its morphological and physicochemical properties. The tests include the determination of: (i) adsorption capacity (a study of sorption isotherms); (ii) porosity, pore size distribution and specific surface area; and (iii) binding ability, as well as (iv) characterization of the binding sites. In addition, advanced analytical techniques are used to obtain analytical information on the degree of washout/elimination of residual template molecules from the structure of the sorptive material. The series of tests to characterize the physiochemical and morphological properties are carried out using MIP as well as NIP (non-imprinted polymer) so that the potential of the new sorbent for the selective binding of a specific type of compound may be demonstrated [93–97]. Table 2 lists data on basic laboratory studies conducted at numerous research sites with the aim of designing, preparing and fully characterizing new types of MIP sorbents. Data presented in Table 2 pertain to MIP sorbents obtained in laboratory settings as the final outcome of basic studies that demonstrate the significant applicability of computer-assisted molecular modeling in the design of specific MIP sorbents. In the future, it is possible that the newly developed sorbents will find practical applications in analytical methodologies used in the determination of specific compounds present at low levels in environmental, biological fluids, and pharmaceutical samples.

5. Application of the developed new types of MIP sorbents in analytical methods in real life conditions

Due to the possibility of optimum sorptive materials being designed without the need to carry out series of syntheses

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Table 2
General information about the applied software and chemical compounds used for synthesis of MIP sorbent in laboratory modeling conditions.

Analyte	Sample type	Applied software	Template: functional monomer molecular ratio	Functional monomer type	Template type	Solvent/porogen type	Analytical technique used to the analysis of MIP recognition properties	Ref
Cholate salts	Laboratory modeling studies	Software: SYBYL 7.0 (Tripos Inc., St. Louis, MO, USA) using LEAPFROG algorithm	1:4	N-(3-aminopropyl)-methacrylate hydrochloride; N,N-diethylamino ethyl methacrylate; ethyleneglycol methacrylate phosphate	Cholic acid	Dimethyl sulfoxide	UV spectroscopy	[23]
Gallic acid	Laboratory modeling studies	Software: Gaussian 03; Chem 3D Ultra 8.0.3 (Cambridgsoft Corporation, USA) Method: DFT (B3LYP/6-31G*)	1:4	Acrylic acid	Gallic acid	Acetonitrile	UV spectroscopy	[39]
Serotonin	Laboratory modeling studies	Software: Spartan 08 SYBYL; MOPAC12 Method: DFT (ωB97xD/6-31++G**)	1:4	Acrylamide	Serotonin	Dimethyl sulfoxide	FT-IR analysis	[57]
4-nitrophenol	Laboratory modeling studies	Software: Materials Studio 5.0 (Accelrys, San Diego, CA, USA) using force fields COMPASS, Universal, and Dreiding	1:4	4-vinylpyridine	4-nitrophenol	Chloroform	HPLC system	[58]
Benzo[α]pyrene	Laboratory modeling studies	Software: HyperChem Release 8.0 Method: Hartree-Fock (HF) with 6-31G basis set; Moller-Plesset second order perturbation theory (MP2)	1:4	Methacrylic acid	Benzo[α] pyrene	Acetonitrile	GC System	[87]
Homoveratrylamine	Laboratory modeling studies	Software: Gaussian 03 Method: DFT (B3LYP/6-311+G**)	n. m.	Methacrylic acid	Homoveratrylamine	Methanol	UV spectroscopy	[88]
Oxalic acid	Basic laboratory research Defined amount of analyte dissolved in aqueous solution	Software: Gaussian 03; AVOGADRO Method: DFT (B3LYP/6-311+G**//B3LYP/6-31G*)	1:4	Acrylamide	Oxalic acid	Acetonitrile	UV spectroscopy	[89]
Veterinary drugs residues	Laboratory modeling studies	Software: GROMACS 3.3; Gaussian 03 Method: DFT (B3LYP/6-31G*, and B3LYP/ 6-311+ G**)	1:5	Methacrylic acid	Sulfadimidine	Acetonitrile	UV spectroscopy	[90]
Adenosine triphosphate	Laboratory modeling studies	Software: NWChem v.6.3 package Method: DFT using 6−31 G* or 6−31G**	1:5	3-vinyl-benzoic acid	Tri-O-acetyl adenosine	Benzene	n.m.	[91]
Diisopropyl urea	Laboratory modeling studies	Software: Gaussian 03; GaussView 3.09 Method: DFT (B3LYP/6-311++G**)	1:1; 1:2	Methacrylic acid	1,3-diisopropylurea	Dichloromethane Chloroform	NMR and IR methods	[92]
2,6-dinitrotoluene	Laboratory modeling studies	Software: Gaussian 03; Molekel 5.3 Method: 6-31G**	1:1	Methacrylic acid	2,6-dinitrotoluene	Chloroform	FT-IR analysis	[93]
Enrofloxacin	Laboratory modeling studies	Software: Gaussian 09 Method: DFT (B3LYP/6-31G**)	1:7	Trifluoromethacrylic acid	Enrofloxacin	Acetonitrile	Hydrogen nuclear magnetic resonance	[94]
Chicoric acid	Basic laboratory research Chicorium intybus L. Medicinal plant samples	Software: Gaussian 03; GaussView 5.0 Method: HF/6-31G*	1:4	4-vinylpyridine	Chicoric acid	Dimethyl sulfoxide	HPLC system FT-IR analysis	[95]

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Table 2 (*continued*)

Analyte	Sample type	Applied software	Template: functional monomer molecular ratio	Functional monomer type	Template type	Solvent/porogen type	Analytical technique used to the analysis of MIP recognition properties	Ref
Ephedrine enantiomer (−)-Ephedrine	Laboratory modeling studies	Software: SYBYL 6.7 (Tripos Inc., St. Louis, MO, USA) using LEAPFROG algorithm; Gasteiger–Huckel computational method	1:10	Hydroxyethyl Methacrylate Methacrylic acid	(−)-Ephedrine	Chloroform	HPLC system	[96]
Phenoxyacetic Acids (phenoxyacetic herbicides)	Laboratory modeling studies	Software: Gaussian 03 Method: DFT with 6-311G**	1:1	4-vinylpiridine	2-methylphenoxyacetic acid	Water/methanol	HPLC system	[97]
Tryptophan	Laboratory modeling studies	Software: Gaussian 09; GaussView 5.0 Method: Moller-Plesset theory (MP2) at 6-311++g** level; DFT at B3LYP employing 6-31+g (2d, 2p) level	1:1; 1:2	p-nitrophenyl acrylate	Tryptophan	Dimethyl sulfoxide	FT-IR analysis	[98]
Cinchona alkaloids	Laboratory modeling studies	Software: Gaussian 03 Method: B3LYP/6-31+G(d, p)	1:4; 1:2	Chiral self-synthetized monomers: N-Acryloyl-l-phenylalanine; N-Acryloyl-l-alanine	Hydroquinidine	Trichloromethane	FT-IR analysis HPLC system UV spectroscopy	[99]
Abacavir – HIV-1 reverse transcriptase inhibitor	Laboratory modeling studies	Software: SYBYL 6.9 (Tripos Inc., St. Louis, MO, USA) using LEAPFROG algorithm	1:4 1:2	Acrylamide; itaconic acid N,N-methylenebisacrylamide	Abacavir	N,N-dimethylformamide	n. m.	[100]

DFT – density functional theory; B3LYP – Becke, three-parameter, Lee-Yang-Parr hybrid density functional; n. m. – not mentioned.

including the consumption of high quantities of solvents and reagents, specific MIP sorbents can be applied in a number of analytical procedures. Thanks to the computer-assisted design of specific polymer sorbents combined with proper synthetic procedures, MIPs that facilitate the isolation of characteristic chemical compounds from samples with complex matrix compositions became available in analytical chemistry. Due to the fact that such sorbents are dedicated to specific chemical compounds (selective for a predefined analyte or group of analytes), their main application fields include medicine, biotechnology, food samples, biological fluids and pharmacology. They are commonly used in a wide spectrum of new types of electrochemical biosensors (ECBSs) based on molecularly imprinted polymer films [101]. According to the literature data the ECBSs are defined as a high selectivity and sensitivity electrochemical analytical tools characterized by mechanical and chemical stability, reusability, facile preparation and low exploitation costs. Such small-scale MIP-based electrochemical devices might be used in medical diagnose, biological analysis, environmental monitoring and food safety evaluation, i.e. to selective assay of dimethoate in real samples (flour samples); determination of imidacloprid residue in brown rice samples, detection of dodecyl gallate in aqueous solutions or detection of ascorbic acid in series of vitamin C beverages [102–105]. One of the main drawbacks of MIP-based electrochemical devises is the preparation process of MIP sensors – problems to update the MIP films, low binding capacity and selection of an appropriate and most effective way for immobilization and MIP renewal from the solid support medium, like fibers/glass, carbon nanomaterials (carbon nanotubes or graphene), silica particles, magnetic nanoparticles or polystyrene nanoparticles. The characteristic and fields of applications of new types of ECBSs based on molecularly imprinted polymer films were the main issue of valuable review papers published by Gui et al., 2018 [106] and Ansari, 2017 [107] and were described there in detail.

The use of selective sorptive materials such as MIP sorbents in analytical procedures extends the limits of the detection and quantitation of specific analytical procedures. This opens up the possibility for the determination of hazardous chemicals present within various types of environmental, biological, food and pharmaceutical samples at low or very low concentrations [108]. Table 3 lists the literature data on MIP sorbents being used in analytical procedures (most commonly as the fillings of SPE columns) and obtained with the use of computer-assisted molecular modeling at the stage of designing the synthetic product. When interpreting the data presented in Table 3, one may notice that the sorbents are dedicated to very specific chemicals that may be present in the listed environmental samples. The very high analyte recovery rates may provide an appropriate confirmation of the hypothesis stating that the developed sorptive material may be successfully used in the particular analytical procedure at the stage of analyte isolation and/or preconcentration. The reduction of LOD and LOQ values (for a defined analytical instrumentation), and high recoveries achieved with MIP sorbents (listed in Table 3) are related to metrological aspects and, unlike other aspects such as significant reduction of consumption of solvents and reagents, they cannot unequivocally be considered as green aspects of analytical procedures.

6. Summary and future perspectives

From the perspective of users, novel MIPs dedicated for the selective binding of analytes in environmental, biological, pharmaceutical and food samples characterized by complex composition of the matrix provide an ideal solution for everyday analytical practice, whereas the preparation of reliable sorptive materials with appropriate characteristics poses a significant challenge. Therefore, computer-assisted molecular modeling appears to provide an answer to the current demand of research sites and teams involved in the development of new types of MIP sorbents. The use

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Table 3
General information about the main software, chemical compounds and basic validation factors concerning developed analytical protocols using MIPs sorbents at the stage of isolation and/or preconcentration of specific analytes from real environmental samples.

Analyte	Sample type	Applied software	Template: functional monomer molecular ratio	Functional monomer type	Template type	Solvent/porogen type	LOD value	Recovery value [%]	Analytical technique used to the analysis of MIP recognition properties	Ref
Amphetamine analogue (3,4-methylenedioxymethamphetamine)	Human plasma samples	Software: Gaussian 03; GaussView 4.1 Method: DFT (B3LYP/6-31-G**)	1:3	Methacrylic acid	3,4-methylenedioxymethamphetamine	Chloroform	1.0 ng/mL	71–81	HPLC system	[60]
Furosemide	Human plasma samples	Software: Gaussian 03 Method: Hartree-Fock (HF/6-31G*)	1:3	Acrylamide	Furosemide	Acetone	12 ng/mL	76	HPLC system	[64]
Allopurinol	Human plasma samples	Software: Gaussian 98 Method: HF/6-31G*	1:3	Acrylamide	Allopurinol	Acetone	0.028 μM	92–96	HPLC system	[66]
Baicalein	*Scutellaria baicalensis Georgi* (SB) – Chinese medicine	Software: Gaussian 09 Method: DFT (B3LYP/6-31G**)	1:4	Acrylamide	Baicalein	Tetrahydrofuran	0.30 ng/mL	94	HPLC system	[109]
Tyramine	Bovine serum albumin sample	Software: Gaussian 09 Method: DFT (B3LYP/6-311+G**)	n. m.	Methacrylic acid	2-(4-methoxyphenyl) ethylamine	Methanol	0.76 μmol/L	95	HPLC system	[110]
Norfloxacin	Pharmaceutical wastewater	Software: Discovery Studio (DS, v2.5); CHARMm (Chemistry at Harvard Macromolecular Mechanics); MMFF94 (Merk Molecular Force Field)	1:3	Methacrylic acid	Norfloxacin	Ethanol	0.010 μg/mL	87–99	HPLC system	[111]
Voriconazole	Basic laboratory research Defined amount of analyte was dissolved in methanol	Software: Discovery Studio 3.1; Gaussian 09 Method: DFT (B3LYP/6-311+G**)	n. m.	Isopropenylbenzene	1-(2,4-diuorophenyl)-2-(1h-1,2,4-triazol-1-yl)ethanone	Chloroform	0.58 μmol/L	n. m.	UV spectroscopy	[112]
Dimethoate Omethoate Monocrotophos Methidathion Malathion Fenthion	Commercially available samples of olive oil	Software: SYBYL 7.3 (Tripos Inc., St. Louis, MO, USA); Method: LEAPFROG algorithm	1:4	Methacrylic acid Itaconic acid	Dimethoate Omethoate	Dimethylformamide	0.012 μg/g	94	HPLC system	[113]
S-warfarin	Plasma samples	Software: Gaussian 03	1:3	Methacrylic acid	S-warfarin	Acetonitrile	8.6 ng/mL	92	HPLC system	[114]

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Table 3 (*continued*)

Analyte	Sample type	Applied software	Template: functional monomer molecular ratio	Functional monomer type	Template type	Solvent/porogen type	LOD value	Recovery value [%]	Analytical technique used to the analysis of MIP recognition properties	Ref
Methadone	Plasma and saliva samples	Method: DFT (B3LYP/6-31+G**) Software: Gaussian 03 Method: DFT (B3LYP/6-31+G**)	1:2	Methacrylic acid	Methadone	Acetonitrile	2.5 ng/mL for plasma samples; 2.1 ng/mL for saliva samples	>85 for plasma samples; >90 for saliva samples	GC system	[115]
(R,S)-octopamine	Basic laboratory research Spiked human serum albumin	Software: Gaussian 09; Discovery Studio 4.0. Method: DFT (B3LYP/6-311+G**)	1:4	4-vinylbenzoicacid	(R,S)-2-amino-1-phenylethanol	Methanol	2.5 μmol/L	70–86	HPLC system	[116]
Deltamethrin	Basic laboratory research Spiked olive oil samples	Software: GAMESS (US); Method: DFT with 6-31G* basis set	1:4	Acrylamide	Deltamethrin	Dichloromethane	n.m.	94	HPLC system	[117]
Oxytetracycline	Basic laboratory research Spiked aqueous media samples	Software: SYBYL 7.3 (Tripos, St Louis, MO, USA) Method: LEAPFRO algorithm.	1:4.5; 1:9	2-acrylamido-2-methylpropane sulfonic acid 2-hydroxyethyl methacrylate	Oxytetracycline hydrochloride	Dimethyl sulfoxide	n.m.	Nearly 100	UV spectroscopy	[118]
Biogenic amine – histamine	Wine samples	Software: SYBYL 7.0 (Tripos Inc., St. Louis, MO, USA) Method: LEAPFRO algorithm.	1:6	Itaconic acid	Histamine	Dimethylsulfoxide	0.090 mg/L	93–99	HPLC system	[119]
antimalarial drug – artemisinin	*Artemisia annua* L. – plant that is used in Chinese medicine	Software: SYBYL 7.3 (Tripos Inc., St. Louis, MO, USA) Method: LEAPFRO algorithm.	n. m.	Artemisinin	N,N-methylenebisacrylamide	Dimethylformamide	n. m.	87	HPLC system	[120]
Organophosphate insecticide- Fenthion	Olive oil samples	Software: SYBYL 7.3 (Tripos Inc., St. Louis, MO, USA) Method: LEAPFRO algorithm.	1:4	Acrylamide	Fenthion	Dimethylformamide	0.0050 mg/L	96	HPLC system	[121]
Potassium-sparing diuretics: amiloride, triamterene	Human urine samples	Software: SYBYL 7.3 (Tripos Inc., St. Louis, MO, USA) Method: LEAPFRO algorithm.	n. m.	Itaconic acid	Amiloride; Triamterene	Dimethylformamide	n. m.	99–102	HPLC system UV spectroscopy	[122]
Methocarbamol	Human plasma samples	Software: Gaussian 03 Method: DFT (B3LYP/6-31G**)	1:3	Acrylic acid	Methocarbamol	Tetrahydrofuran	0.025 μg/mL	94–98	Differential pulse voltammetry (DPV)	[123]
							0.065 μg/mL	96–98	HPLC system	

DFT – density functional theory; B3LYP – Becke, three-parameter, Lee-Yang-Parr hybrid density functional; n. m. – not mentioned.

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of molecular modeling as a complementary tool in synthesis of novel MIP sorbents was discussed. The *in silico* studies could increase the speed of possible subtracts selection for their "optimal" laboratory preparation. This could result in shortening the time of typical try-and-error approach in traditional laboratory, as well as decrease the amount of necessary chemicals and solvents. The user-friendly Gaussian program, associated with *GaussView* for structure building and analysis of calculation results is recommended. In contrary to noncommercial programs, for example *CFOUR* or *Dalton*, suitable for very accurate calculations of small molecular systems, *Gaussian* is also fairly versatile and allows studies of significantly larger molecular systems. Appropriate series of computer simulations reduce the time required to obtain the appropriate MIP sorbent and the costs associated with the reagents (porogens and templates), as well as significantly reduce the consumption of organic solvents. Thanks to all these factors, the process of the preparation of new MIP sorbents is associated with a lower environmental impact, which influence on an increase in its "greenness level". Thus, the use of MIP sorbents in analytical practice is an important element of the compliance with the principles of green analytical chemistry.

In addition, one should also remember that in the constant development of novel analytical techniques, including the stages of sample preparation and final determination, it is important that advanced computer-assisted techniques (process simulations, chemometric techniques, molecular modeling, etc.) be introduced into everyday analytical practice. The software used for this purpose does not require very expensive and efficient hardware, with standard desktop or portable personal computers being entirely sufficient. An investment in an appropriate computer system contributes to future reduction of the economic/logistic factors in the MIP sorbent synthesis processes. Nevertheless, there are no ideal solutions, characterized by the lack of limitations or drawbacks. In a case of application of computer-assisted molecular modeling, the user is obliged to have the skills to use the advanced software in a correct way. Moreover, the user should have the appropriate knowledge and experience to proper implementation of the input data and correct interpretation of obtained data base. Appropriately developed input data base requires time and prior consultation in the field of organic, physical and analytical chemistry. Additionally, in some cases, it is necessary to use a professional computer set, if the input data base is characterized by a large number of variables. This also influence on the time to wait for the final result of the computer calculations and very often the costs associated with the possibility of use of such advanced high-performance computer hardware.

As for another benefit in relation to the MIP sorbents preparation process is the fact, that computer-assisted molecular modeling facilitates the appropriate selection of functional monomers and the solvent (porogenic agent), and estimation of the type of interactions between the template and the functional monomer. Due to this the obtained sorptive material selectively and efficiently retains the molecules of the defined analytes on its surface. By applying appropriate assumptions for model studies, it is possible to develop MIP sorbents facilitating the selective isolation and/or preconcentration of very specific compounds present in samples with complex matrix compositions, as well as effective elution of the compounds from the sorption medium. Thus, in response to another postulate of green analytical chemistry, the use of selective MIP sorbents in the analytical methodology significantly lowers the values of LOD/MDL and LOQ/MQL of the particular procedure.

Computer-assisted molecular modeling in analytical chemistry is also useful in selecting appropriate structural analogues of specific templates (dummy templates). This is extremely useful when the cost of the template is significant, or when the template is poorly soluble in porogenic agents commonly used in the synthesis. In the future, the use of computer-assisted molecular modeling as one of the stages of analytical procedures might significantly reduce the number of low quality sorptive materials being obtained in the synthetic process. In the context of the design and preparation of the new type of selective MIPs, analytical methods involving multi-criteria decision making (MCDM) models such as simple additive weighing (SAW) or technique for order preference by similarity to ideal solution (TOPSIS) appear very interesting [124]. They would allow for the complete characterization of the environmental impact of individual elements of the MIPs preparation process.

The implementation of molecular modeling into everyday analytical practice, as presented in this article, provides a good illustration of interdisciplinary research. It is a very good example of different branches of chemistry (organic chemistry, physical chemistry, molecular modeling science, environmental chemistry, polymer chemistry, and analytical chemistry) complementing one another with significantly broadening research horizons.

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