

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



---

# Recent Advances in the Extraction of Triazines from Water Samples

---

José A. Rodríguez, Karina Aguilar-Arteaga,  
Cristina Díez and Enrique Barrado

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/54962>

---

## 1. Introduction

The use of herbicides in agriculture has helped to improve crop quality and yield. However, the presence of such substances has also caused serious environmental pollution problems. Triazine herbicides are a group of herbicides applied in agriculture for pre- and post-emergence weed control. The first report of the use of triazine derivatives was in 1952 by J.R. Geigy from Switzerland but it was not until 1954 that chlorazine was used as a herbicide, followed by simazine in 1955 [1]. During subsequent years the amount of commercially available triazines increased. The main triazine herbicides are derived from *s*-triazine, a six member heterocycle with symmetrically located atoms in which positions 2, 4 and 6 are substituted. The stereochemical stability of *s*-triazines is large enough to persist in environmental samples from several months to many years [2].

A list of common *s*-triazines and some of their properties are given in Table 1. The two most common *s*-triazines analyzed in waters are atrazine and simazine. The chemical common name depends on the substituent in position 2 (or R1 in Table 1), when a -Cl group is contained the names end with -azine, while -SCH<sub>3</sub> and -OCH<sub>3</sub> end with -tryn and -ton, respectively. The thermodynamical properties also depend on the substitutes, the acidity decreases according the following order -OCH<sub>3</sub><-SCH<sub>3</sub><-Cl and the solubility in water are higher in acidic conditions. The *s*-triazines which contain -SCH<sub>3</sub> group are more polar than the -Cl and -OCH<sub>3</sub> compounds according to the partition coefficient between *n*-octanol and water  $K_{ow}$  (log P) [3]. The toxicity of these substances has promoted the development of new analytical methodologies to evaluate their impact to the environment and human health.

Maximum residue limits for *s*-triazines in water samples are in the  $\mu\text{g l}^{-1}$  order. This fact demands better quality and accurate analytical methodologies. Moreover, these concentration levels require performing an initial stage of concentration and purification of the analytes prior to their analysis. The analytical procedure usually is comprised of five steps: sampling, sample preparation, separation, detection and data analysis, but sampling and sample preparation are the critical steps of the analytical process. Over 80% of the analysis time is spent on these two steps. If one of these steps is not followed adequately, the performance of the procedure will be affected and the results will be inconsistent [4].

Compound	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	pK <sub>a</sub>	K <sub>ow</sub> (log P)
Atrazine	Cl	C <sub>2</sub> H <sub>5</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	1.68	2.7
Propazine	Cl	CH(CH <sub>3</sub> ) <sub>2</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	1.85	2.9
Simazine	Cl	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	1.65	2.3
Terbutylazine	Cl	C <sub>2</sub> H <sub>5</sub>	C(CH <sub>3</sub> ) <sub>3</sub>	1.88	3.1
Terbutemon	OCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	C(CH <sub>3</sub> ) <sub>3</sub>	4.20	3.6
Ametryn	SCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	4.00	3.1
Prometryn	SCH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	4.05	3.3
Simetryn	SCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	4.00	2.8
Terbutryn	SCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	C(CH <sub>3</sub> ) <sub>3</sub>	4.40	3.7

**Table 1.** pK<sub>a</sub> and K<sub>ow</sub> (log P) of common *s*-triazines herbicides

Adequate sample preparation is a requisite for analytical techniques. Analysts have responded to this challenge, so in this work recent sample extraction techniques for analysis of *s*-triazines in water samples are overviewed.

## 2. Sample preparation

The sample preparation concept is based on converting a real matrix into a sample suitable for analysis. This process involves a change in the chemical environment of the sample. An initial step in the design of an extraction method is the knowledge of the physical and chemical properties such as lipophilicity and the predominance of acid-basic species neutral or ionic.

Matrix effects are the main problem in extracting analytes. A matrix effect can be defined as the influence of a property of the sample, independent of the presence of the analyte, on the recovery efficiency. In water samples a pre-concentration step is required prior to measurement of triazines. A pre-concentration factor of several orders of magnitude (200-1000 fold) is mandatory to reach the low detection limits necessary for identification and analysis of these herbicides, especially in highly organic matter content samples such as wastewaters. The common extraction methods used for isolation of polar compounds from water matrices are the liquid-liquid extraction (LLE) and the solid phase extraction (SPE).

## 2.1. Liquid-liquid extraction

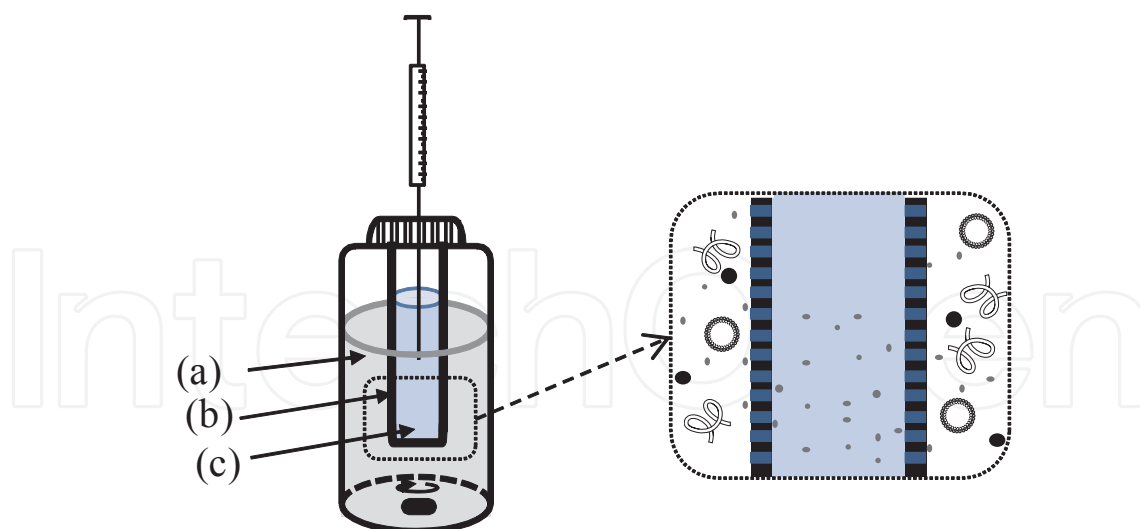
LLE has been used in the past for the extraction of triazines from environmental water samples [5]. LLE is based on the partition coefficient of the analytes between two liquid phases of low solubility. In the case of triazines the common sample volume used is 1 l (pH adjusted to 7) and it is mixed with an organic solvent, such as methylene chloride (at least 2x50 ml). The aqueous layer is then discarded, the organic phase evaporated and concentrated to a volume of 5 ml and the solvent is exchanged. The obtained extract is analyzed by a separation technique (gas or liquid chromatography). The main disadvantages of this procedure are: the use of large volumes of organic solvents, limited pre-concentration factors and tedious procedures.

In recent years, the scientific community has shown an increased interest in the development of environmentally friendly laboratory activities. Green analytical chemistry pursues the aim of replacing toxic reagents by clean ones. Also the development and improvement of new sample preparation techniques is a fast growing trend in analytical chemistry. In this context, liquid phase microextraction techniques have evolved from the use of tens of ml of solvent to the use of drop-based ( $\mu\text{l}$ ) systems. The different approaches employed for the liquid microextraction of triazine herbicides from environmental matrices are mainly: hollow fiber liquid phase microextraction (HFLME) and dispersive liquid-liquid microextraction (DLLME).

### 2.1.1. Hollow fiber liquid phase microextraction

HFLME is a membrane based separation technique. It can be sub-classified into two-phase and three-phase systems. The two-phase system is the most used system in the extraction of triazines from aqueous samples. The two-phase systems are also referred as microporous membrane extraction. It is comprised of an aqueous phase and a hydrophobic porous membrane impregnated with a suitable organic solvent (Figure 1). The aqueous phase usually contains the analyte and it is called the donor phase while the organic solvent is the receiving/acceptor phase [6].

The extraction process involves partitioning of the analyte from the aqueous sample into the organic solvent which impregnates the hollow fiber (HF) and the diffusion through the membrane into the bulk receptor/acceptor phase. These systems are suitable for extraction of compounds with large partitioning coefficients in the organic phase. Polypropylene is the material commonly used for triazines using two-phase HFLME systems.



**Figure 1.** Representation of a hollow fiber liquid phase microextraction system. (a) donor phase, (b) hollow fiber with organic phase, (c) acceptor phase.

The common steps included on the HFLME are: a) cleaning of the HF, b) conditioning of the HF impregnating it with the extraction solvent, c) adding a specific volume of the solvent into the HF, d) immersing the HF into the sample for a definite time, e) aspirating the preconcentrated sample for its analysis.

A system based on the use a polypropylene HF (1.5 cm X 0.6 mm i.d.) containing 3  $\mu\text{l}$  of toluene as organic solvent was used for the extraction of simazine, atrazine, propazine, simetryn and prometryn from 3.0 ml of water samples. The organic phase was analyzed by gas chromatography-mass spectrometry (GC-MS). The effect of salt addition, agitation, pH and exposure time were evaluated. The most critical variable was the pH value required (>4.0) which determines the formation of the suitable extractable analyte form. The method described provides good enrichment factors (<150), good precision (<3.5%, expressed as relative standard deviation, RSD) with limits of detection (LODs) in the range of 0.007-0.063  $\mu\text{g l}^{-1}$ [7].

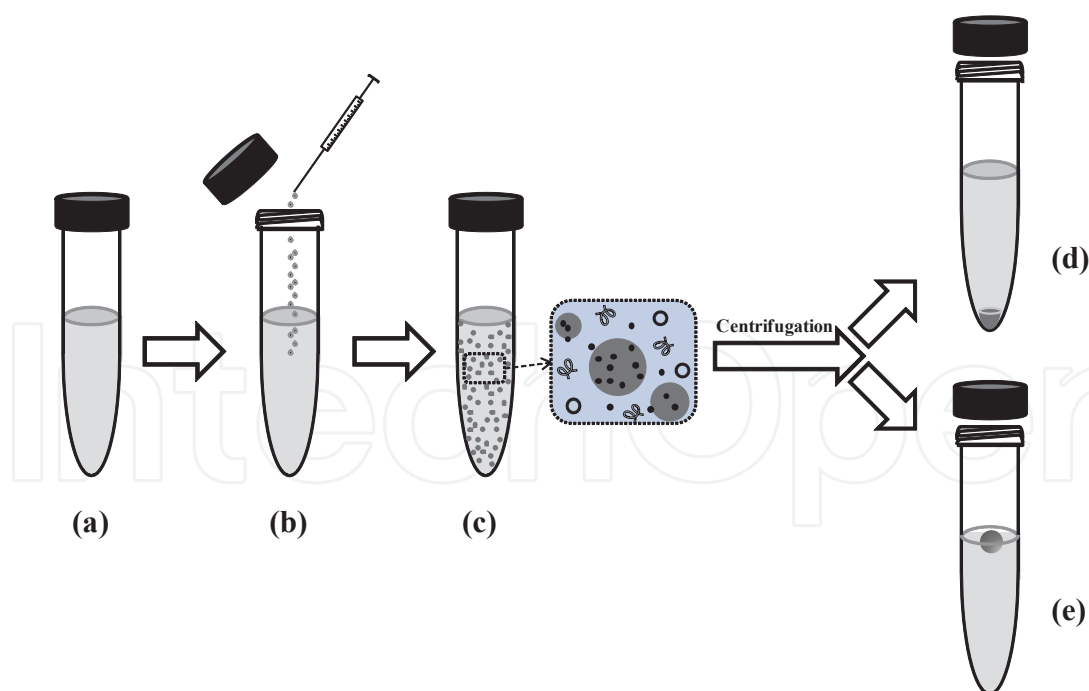
The use of phosphorus-oxygen compounds as co-extraction solvents has been proposed for isolation of pesticides from water samples including triazine herbicides. Atriazine, simazine and propazine were extracted using a polypropylene HF (3.3 cm X 0.3 mm i.d.) filled with a *n*-dihexylether solution containing 10% of tri-*n*-octylphosphine oxide ( $(\text{C}_8\text{H}_{17})_3\text{PO}$ ) and 10% of tri-*n*-butylphosphonate ( $(\text{C}_4\text{H}_9\text{O})_3\text{PO}$ ). The dipolar moment from the P-O bond increases the polarity of the extraction solvent, allowing the isolation of the triazines and the other pesticides evaluated. The extraction was optimal when the donor pH was fixed to 8.0, using the organic phase, above mentioned and a contact time of 4 h in a 250 ml of a water sample. The system was coupled to high performance liquid chromatography- mass spectrometry (HPLC-MS) as separation and detection technique. Under these conditions LODs from 0.061 to 0.26 were obtained for triazine compounds [8].

Over the past decades, carbon nanotubes have elicited interest due to their chemical and physical properties. At the nanoscale, an increase of the contact surface area is observed.

Following the new tendencies, a polypropylene HF (3.0 cm X 0.6 mm i.d.) was impregnated with a suspension composed by n-octanol and multiwalled carbon nanotubes, intended for simazine, simetryn, propazine, and prometryn isolation. The HF was immersed into the sample (15.0 ml) containing 30  $\mu$ l of chlorobenzene and 2.25 g of NaCl for 20 minutes. Then, the HF was washed with water and immersed in 50  $\mu$ l of methanol for elution of the analytes. The analysis of the methanolic solution by HPLC with ultraviolet detection (HPLC-UV) gives a LOD of in the range of 0.08-0.15  $\mu$ g l<sup>-1</sup> [9].

### 2.1.2. Dispersive liquid-liquid microextraction

DLLME is a miniaturized LLE technique based on a ternary component solvent system composed of a certain amount of the sample, a disperser solvent and an extraction solvent. The extraction steps involved on the DLLME are (Figure 2): a) a volume of the sample is placed in a tube with conic bottom, b) the disperser and extraction samples are injected into the sample, c) the mixture is then mixed and a cloudy solution is formed in the test tube. A higher contact area between the organic-aqueous phases is obtained due to the formation and dispersion of micro-drops of organic phase. Subsequently, equilibrium state is achieved quickly, resulting in a reduction in the extraction time. The final step is the centrifugation and depending on the density of the extraction solvent, d) it sediments at the bottom of the test tube or e) floats at the top of the solution. Finally, a definite volume of the pre-concentrated sample is recovered and analyzed.



**Figure 2.** Representation of the dispersive liquid-liquid microextraction methodology

Chlorobenzene is a suitable extraction solvent for triazine isolation, and it was applied for DLLME of atrazine, simazine, prometryn, propazine and simetryn from water samples. The

methodology uses 5.0 ml of water samples containing 4% (w/v) of sodium chloride mixed with 12.0  $\mu\text{l}$  of chlorobenzene and 1.0 ml of acetone (disperser solvent). The mixture was centrifuged and a 2  $\mu\text{l}$  sample was analyzed by GC-MS. The method proposed has a LODs between 0.021 and 0.12  $\mu\text{g l}^{-1}$  with a precision <5%, expressed as RSD [10].

The search for new extraction solvents is a key trend in the solvent extraction evolution. In this sense, ionic liquid, which is an ionic media resulting from the combination of organic cations with various anions has attracted attention for its special features such as: low-vapour pressure, high viscosity, dual polarity and a wide range of miscibility with water and other organic solvents [11].

The ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate has been evaluated as extraction solvent of atrazine, prometryn, and simazine. The proposed methodology prepared a solution mixing water sample (10 ml) and the ionic liquid (60  $\mu\text{l}$ ) in a conical test tube. The test tube was heated in water bath at 70 °C for 5 min and was thereafter cooled with ice for 30 min until the solution became turbid. The dispersion was centrifuged for 10 min at 3800 rpm, the upper aqueous phase was removed and the ionic liquid phase was dissolved in 100  $\mu\text{l}$  of methanol for HPLC-UV analysis. Under optimal condition the LODs of the reported method are in the range from 0.46 to 0.89  $\mu\text{g l}^{-1}$ , with precisions below 10% (RSD) [12].

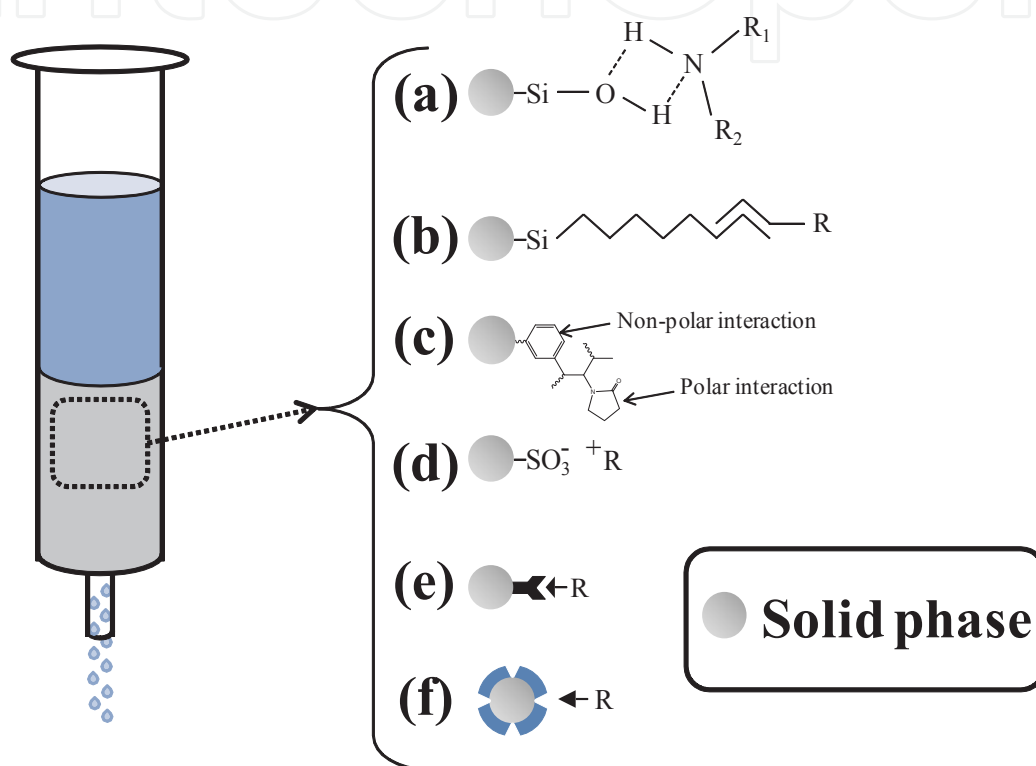
Following the same tendency, a DLLME method coupled to microwave assisted extraction (MAE) was design for extracting ametryne, prometryne, and terbutryn. A 10 ml microwave tube was filled with 5.0 ml of water sample. Then, 40  $\mu\text{l}$  of 1-butyl-3- methylimidazolium tetrafluoroborate and 500  $\mu\text{l}$  of a 0.2 g  $\text{ml}^{-1}$  disperser solution of lithium bis[(tri-fluoromethane)sulfonyl]imide were added. The suspension was irradiated under microwave power of 30 W during 90 seconds. After cooling, the suspension was centrifuged at 5000 rpm for 6 minutes. The aqueous phase was removed and the ionic liquid phase was stored for HPLC-UV analysis. The LODs were between 0.52 and 1.30  $\mu\text{g l}^{-1}$  with precisions <10%, as RSD [13].

In the case of DLLME using extraction solvents with lower density than water, there has been reported the use of DLLME based on the solidification of a floating organic droplet for analysis of atrazine and simazine in water samples. The conditions proposed for the sample treatment are: 10  $\mu\text{l}$  of 1-undecanol ( $\rho=0.83 \text{ g ml}^{-1}$ ) as extraction solvent, 100  $\mu\text{l}$  of acetonitrile as disperser solvent, NaCl 5% (w/v) and 5ml of water sample. The mixture was then centrifuged for 3 min at 400 rpm and then transferred into an ice bath. After 5 minutes the extraction solvent solidified and was transferred into a clean conical tube, where it melts quickly at room temperature. The extract was then analyzed by GC-MS. The LODs reported were in the range of 0.52-1.30  $\mu\text{g l}^{-1}$  with precisions <5.0%, as RSD [14].

Simultaneous DLLME and microwave assisted extraction was also applied in the analysis of cereal samples. The method involved the use of 1-dodecanol, methanol and water in order to extract the solid sample. Although the technique reported does not involve the analysis of water samples, it is an interesting example of coupled techniques which generates a dynamic and simple methodology for extraction of triazines from complex samples [15].

## 2.2. Solid phase extraction

Solid phase extraction (SPE) is the main separation technique used for trace enrichment of triazines from aqueous samples. The use of cartridges or disk forms, allows a high degree of flexibility. In the last years, there has been a considerable interest in designing new selective and sensitive stationary phases for extracting triazine compounds. Selectivity is related with the extraction mechanism used during isolation of the analytes. The most important interactions between the solid phase and the analytes are represented in Figure 3.



**Figure 3.** Representative interactions mode between the solid phase and the analytes during SPE

SPE using polar solid phases (Fig 3.a) has been applied for isolation of atrazine, ametryn, prometryn, terbuthylazine, terbutryn and simazine. Initially, a solution of 10 ml of water sample, 50 ml of acetonitrile and 10 g of NaCl was prepared. Then a 25 ml portion of the mixture was evaporated to dryness in a vacuum evaporator at 50 °C. The residue was dissolved in hexane and it was then subjected to SPE clean-up with Florisil cartridges using hexane and acetone/hexane (80:20) as condition and elution solvents. The sample extract was analyzed by HPLC-MS, achieving limits of quantification (LOQs) in the range of 0.02-0.05 mg l<sup>-1</sup> with precisions < 10% [16].

SPE, based on C18 and polymeric phases (Fig 3.b and c), has been widely used for determination of triazine in water samples [17-23]. The common amount of water sample passing through the cartridge is 100 ml, followed by a drying step. Triazine compounds are eluted with a few ml of a solvent such as acetonitrile, ethyl acetate or methanol. The LODs achieved depend



on the type of separation technique (GC or HPLC) and the detector used (MS, UV, etc.). In some cases it is reported limits in the  $\text{ng l}^{-1}$  when sensitive detectors are used.

Strong cation exchange SPE (SCX-SPE, Fig 3.d) has been proposed for ametryn, atrazine, propazine, prometryn, simazine, simetryn and terbutryn isolation. The positive charge of the acid form of triazines allows the isolation of the analytes. Elution was performed by adding a 0.07 M KCl aqueous-methanolic solution. The obtained extract was analyzed by HPLC-UV. The LODs reported using spikes water samples was  $0.01 \mu\text{g l}^{-1}$  [24].

In order to increase the selectivity of extraction, the use of immunosorbents was reported (Fig. 3.e). The production of polyclonal antibodies was done by immunization of rabbits with caprolyl-atrazine. The immunosorbent was applied in the analysis of ametryn, atrazine, propazine, prometryn, simazine, simetryn and terbutryn in water samples. The system could be used in off- or on-line modes. The pre-concentration of 50 ml water samples and the use of methanol 70% (v/v) as elution solvent prior to HPLC-UV analysis provided LODs of  $1\text{-}2 \mu\text{g l}^{-1}$  [25-26].

A highly specific method for atrazine isolation was developed using a molecularly imprinted polymer (MIP, Fig 3.f). The MIP was synthesized using atrazine : methacrylic acid: ethylene glycol dimethyl methacrylate in a molar ratio of 1:4:20. The polymer exhibited a high selectivity to atrazine isolation, achieving LOD of  $0.5 \mu\text{g l}^{-1}$  when it is coupled to HPLC-UV [27].

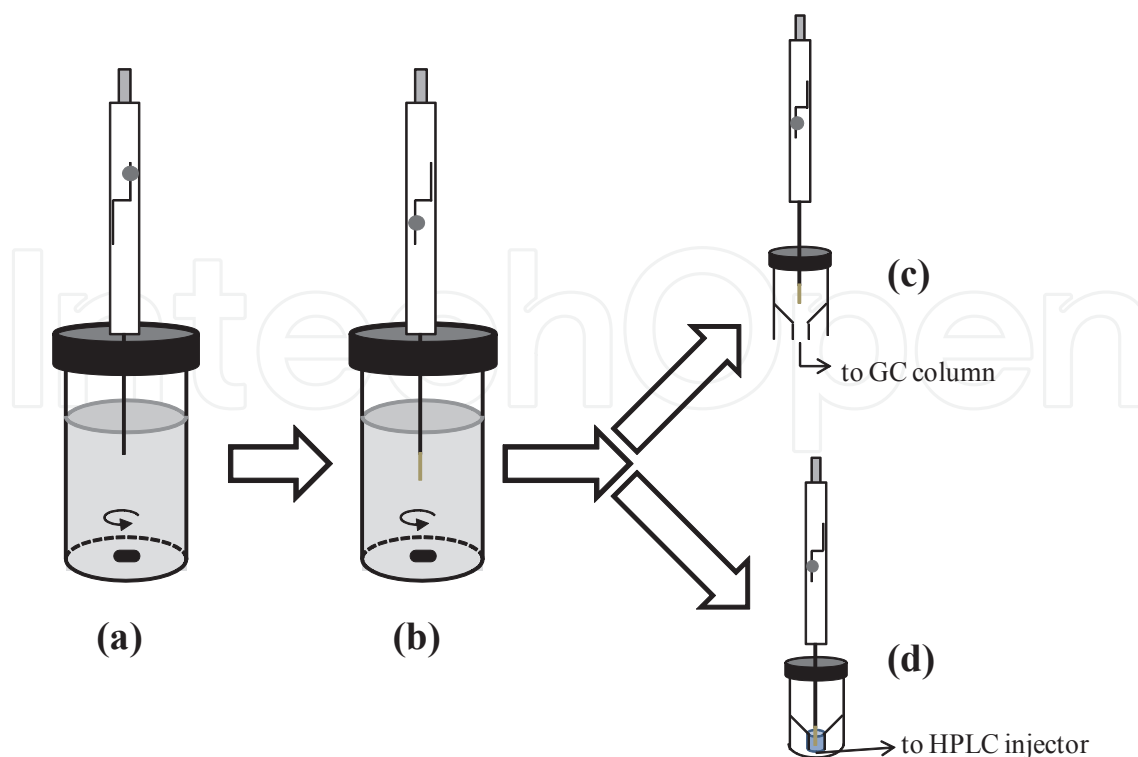
Multiwalled carbon nanotubes have been evaluated as adsorbent for atrazine and simazine isolation. The atrazines were retained on the solid phase in their neutral form and they were eluted from the solid using acetonitrile or acetone. The methodology was tested using different geometries (disk and cartridge) and volumes (200 and 500 ml) and also different detection methods (GC-MS and HPLC-DAD). The LODs were in the  $\mu\text{g l}^{-1}$  order [28-29].

During the last decades, different techniques have been proposed to improve the SPE. Extraction of triazines has been usually carried out by solid phase microextraction (SPME), stir bar sorptive extraction (SBSE) and dispersive solid phase extraction (DSPE).

### 2.2.1. Solid phase microextraction

SPME (Figure 4) has become popular for the analysis of organic compounds because it combines sampling and pre-concentration in a single step. In this technique a fused silica fiber coated with a polymeric film is immersed into the sample (Fig. 4.a and b). The analytes are adsorbed into the stationary phase and later desorbed for its ulterior analysis (Fig. 4.c and d). SPME has the following advantages: (i) the extraction time is reduced, (ii) it provides good results over a wide range of analyte concentrations and (iii) it can be easily automated. Obviously, the composition of the fibers is a great importance in this methodology.

Atrazine, simazine, terbuthylazine and terbutryn have been extracted from water and soil samples using SPME with a carbowax-divynilbenzene fiber. Extraction was carried out by direct immersion of the fiber into the sample (3.0 ml) containing 10% of NaCl to adjust the ionic force. The mixture was stirred for 30 min and desorption of the herbicides was carried out at  $240 \text{ }^\circ\text{C}$  in the hot GC-MS injector. The LODs were below  $0.1 \mu\text{g l}^{-1}$  with precision intra-



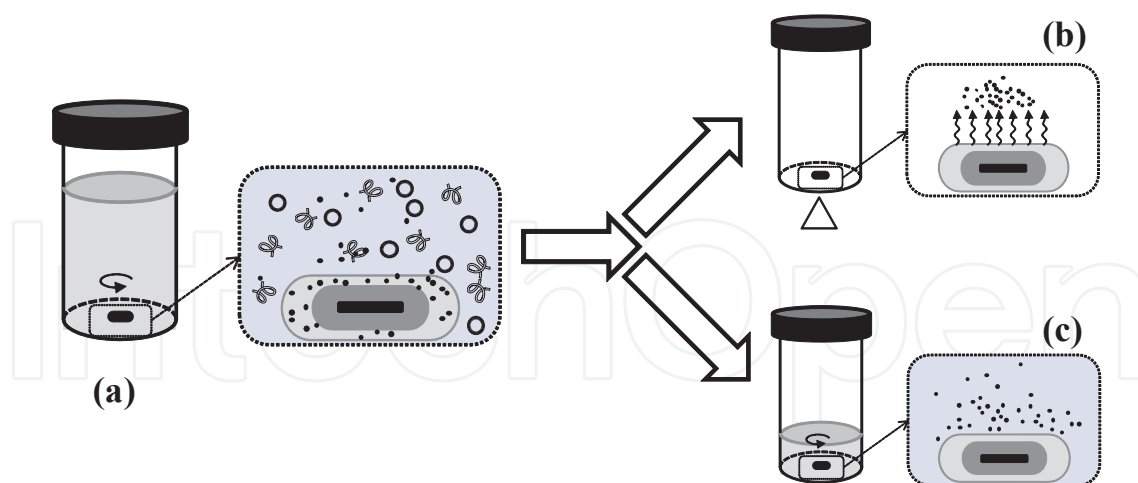
**Figure 4.** Representation of the solid phase microextraction methodology

and inter-day below 10 and 20%, respectively. The absence of organic solvent during sample preparation was the main advantage of the proposed method [30].

Carbon solids are one of the most important adsorption materials since they exhibit high isolation capacity for organic compounds. Graphene is a novel carbon material with large delocalized  $\pi$ -electron system that can form strong  $\pi$ -stacking interaction with the aromatic ring presented in the triazine structure. Atrazine, ametryn, prometon and prometryn were extracted using iron fibers coated with graphene. The fiber was immersed into 10 ml water sample solution for 30 min with stirring at 950 rpm. Afterwards, the extracted analytes on the SPME fiber were desorbed with 50  $\mu$ l of acetone. The extract was then analyzed by HPLC with diode array detection (HPLC-DAD). The LODs of the method were in the range of 0.05-0.2  $\mu$ g l<sup>-1</sup> with precision <5%, as RSD [31].

### 2.2.2. Stir bar sorptive extraction

SBSE is a relatively new technique. It has been used with success for the extraction of organic compounds from aqueous, food, biological and environmental samples. In SBSE the sample is stirred for a given time with a stir bar coated with a sorbent (Fig. 5.a), until the analyte reaches equilibrium between the polymer and the aqueous phase according to their distribution constant. The sorbed analytes are then desorbed by high temperatures into the injector port of the GC (Fig. 5.b) or by liquid removal for HPLC analysis (Fig. 5.c). The main disadvantage of SBSE is the high extraction time required during sample treatment.



**Figure 5.** Representation of the solid phase microextraction methodology

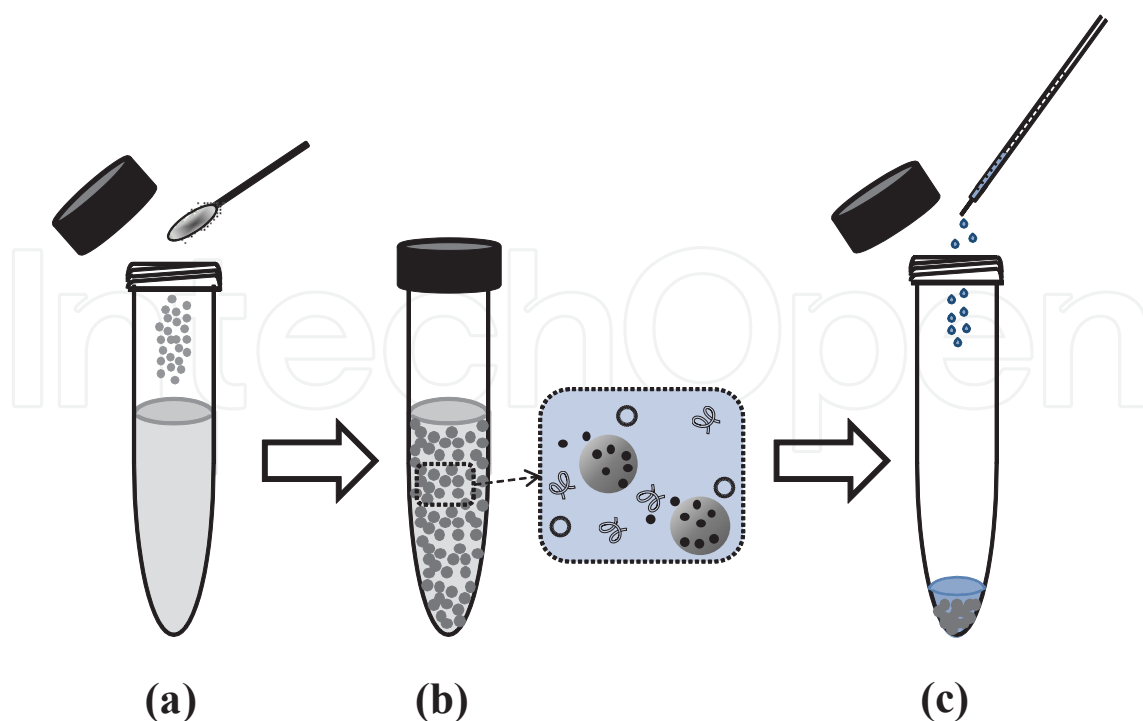
A stir bar of 10 mm length and 0.5 mm polydimethylsiloxane was used to extract ten triazines from water samples. The SBSE step was carried out by introducing the stir bar into a vial containing 20 ml of the sample, 30% of NaCl and stirred ( $31.4 \text{ s}^{-1}$ ) during 60 min. The stir bar was washed with water and then thermally desorbed and analyzed by GC-MS. The LODs obtained were in the range from 0.2 to  $3.4 \text{ ng l}^{-1}$  [32].

The use of thermal desorption requires a cold trap during elution process. The hyphenation of SBSE with HPLC-DAD using solvent desorption was applied to atrazine, simazine and terbuthylazine in environmental water samples. A polyethylene bar impregnated with activated carbon (15 mm length and 0.5 mm thickness) was used to extract 10 ml of water samples. The extraction time required was 16 h, followed by desorption of the analytes using acetonitrile as solvent. The reported LODs were around  $0.1 \text{ } \mu\text{g l}^{-1}$  with precision  $<15\%$ , as RSD. This method was an alternative to the analysis of analytes with polar characteristics [33].

### 2.2.3. Dispersive solid phase extraction

DSPE involves a sorbent addition to a water sample to form a dispersion (Fig. 6.a and b). The solid used has been derivatized to produce a bound organic phase (e.g., octadecyl, MIP, etc.) on its the surface similar to those used for packing SPE columns. The contact between the analytes and the support is higher than in traditional SPE, increasing the equilibrium rate and providing higher extraction yields. After centrifuging the suspension, the solid phase sediments are at the bottom of the test tube. An appropriate organic solvent is then used to elute the analytes from the solid sorbent prior to the organic extract analysis (Fig. 6.c).

DSPE has been applied to determine atrazine, prometryn, simazine, terbumeton and terbuthylazine in lettuce and corn acetonitrile extracts. Although this method is not used in water matrices, it is a good example for the isolation of triazine herbicides by DSPE. A MIP was synthesised using methacrylic acid, ethylenglycol, dimethacrylate, dithioester compounds and atrazine. The retention mechanism is based on the electrostatic interaction between the acid monomer and the basic properties of the target molecule. 100 mg of the MIP were dispersed



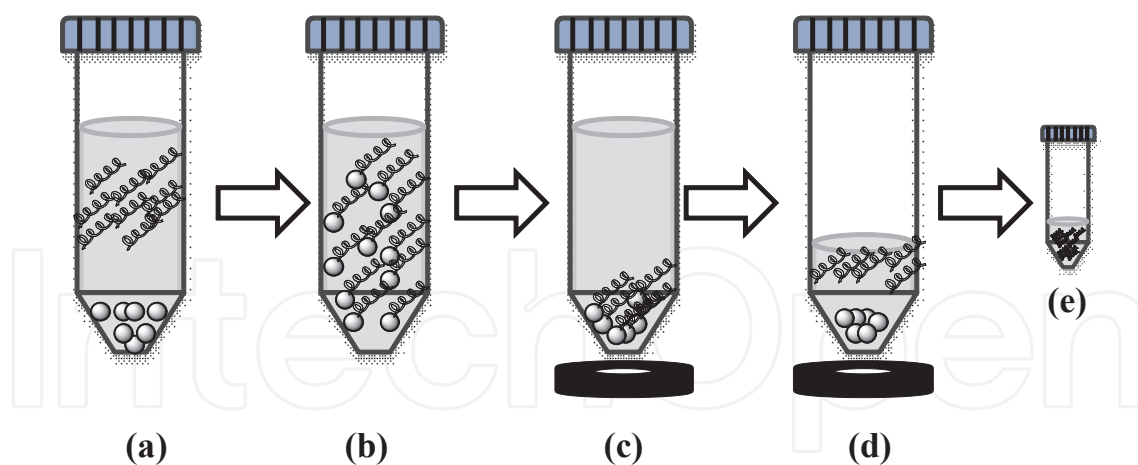
**Figure 6.** Representation of the dispersive solid phase extraction methodology

in 5 ml of sample solution for 1 hour. Once the extraction was concluded, the solid phase was collected in a membrane filter. The solid was washed with methanol and then the atrazine was eluted with 5 ml of desorption solvent (methanol/acetic acid, 9:1 v/v). The extract was dried and redissolved in acetonitrile before its analysis by HPLC-UV. The LOD reported was  $2.8 \mu\text{g l}^{-1}$  with precisions  $<10\%$  [34].

#### 2.2.4. Magnetic solid phase extraction

Recovery of the solid phase in DSPE requires the use of filtration or centrifugation techniques that may lead to a solid phase loss and the subsequent decrease in precision and accuracy. The use of magnetic solids is an alternative for the selective preconcentration of different chemical species. It offers adequate surface area, the possibility of functionalization and paramagnetic properties. Their application as dispersed sorbents in liquid samples is so-called magnetic solid phase extraction (MSPE, Fig. 7). This technique has demonstrated several advantages such as: the decrease in sample treatment time, the decrease in solvent use, and the easy treatment of high volume samples. MSPE has been applied for the selective separation of many organic contaminants including antibiotics, anti-inflammatory drugs, pesticides, etc. which are present in different matrices [35].

MSPE has been applied for the extraction of atrazine, prometon, propazine and prometryn in environmental water samples using graphene- $\text{Fe}_3\text{O}_4$  nanoparticles. The effect of the amount of magnetic solid, extraction time and pH of the sample were evaluated. 20 mg of the magnetic support was dispersed into a 250 ml aqueous sample solution for 20



**Figure 7.** Representation of the magnetic solid phase extraction methodology

minutes. The solid was isolated from the sample solution using a magnet. The liquid phase was discarded and the solid was vortexed with acetone to desorb the analytes prior to its analysis by HPLC-DAD. The LODs of the method ranged between 0.025 and 0.040  $\mu\text{g l}^{-1}$  with reproducibilities <5.2% [36].

In this study, the effect of polarity of the solid phase on the interaction between triazines with magnetic supports used as part of a MSPE system coupled to HPLC-UV was evaluated. The developed methodology was used to determine atrazine and simazine in surface water samples.

### 3. Experimental conditions

#### 3.1. Reagents and solutions

Ferrous sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), ammonium solution ( $\text{NH}_3$  25%, w/w), sodium hydroxide 99%, and hydrochloric acid 36% were purchased from J.T. Baker (Phillipsburg, NJ, USA). Triton X-100, cetyltrimethylammonium bromide (CTAB), tetramethoxysilane (TMOS), phenyltrimethoxysilane (PTMS), octyltriethoxysilane (C8-TEOS), chlorotrimethylsilane (CTMS), and methanol (HPLC grade) were obtained from Sigma-Aldrich (St. Louis, MO, USA). 1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine standard 99.5% (atrazine) and 6-chloro-*N,N'*-diethyl-1,3,5-triazine-2,4-diamine standard 98.5% (simazine) were provided by Dr. Ehrenstorfer GmbH (Augsburg, Germany).

Stock solutions of triazines were prepared at a concentration of 250  $\text{mg l}^{-1}$  in deionized water. These solutions were protected from light and stored under refrigeration (4 °C) until use to avoid possible decomposition. Calibration standards were prepared at concentrations of 5-1000  $\mu\text{g l}^{-1}$  by mixing adequate volumes of each standard solution in deionized water.

### 3.2. Equipment

Magnetic solids were characterized by X-ray diffraction in a PHILIPS PW1710 (Almelo, The Netherlands) instrument equipped with a Cu anode, automatic divergence slit and a graphite monochromator under the following experimental conditions:  $\text{CuK}\alpha$  radiation, 1.54 Å; generator tension, 40 kV; generator current, 30 mA; intensity ratio ( $\alpha_2/\alpha_1$ ), 0.500; divergence slit, 1°; receiving slit, 0.1; start angle ( $2\Theta^\circ$ ), 5; end angle ( $2\Theta^\circ$ ), 70. A JEOL JSM-820 (Tokio, Japan) scanning electron microscope (SEM) was used for obtaining the magnetic solid microphotographs.

The separation and analysis were performed using HPLC equipment consisting of a Gilson (Middleton, WI, USA) model 302 pressure pump, a Rheodyne mod. 7525 injection valve and a UV–VIS diode array HP8453 spectrophotometer (Hewlett Packard, Palo Alto, CA, USA). The absorbance of atrazine and simazine was monitored at 220 nm [37]. The quantification of triazines was made by comparison of peak height with those of the standards. The chromatographic separation was achieved with a Scharlau C18 column (5  $\mu\text{m}$ ; 150 mm $\times$ 4.6 mm i.d.) (Barcelona, Spain). The mobile phase consisted of methanol-deionized water (2:1, v/v). A flow rate of 1.0 ml  $\text{min}^{-1}$  was established at 25 °C.

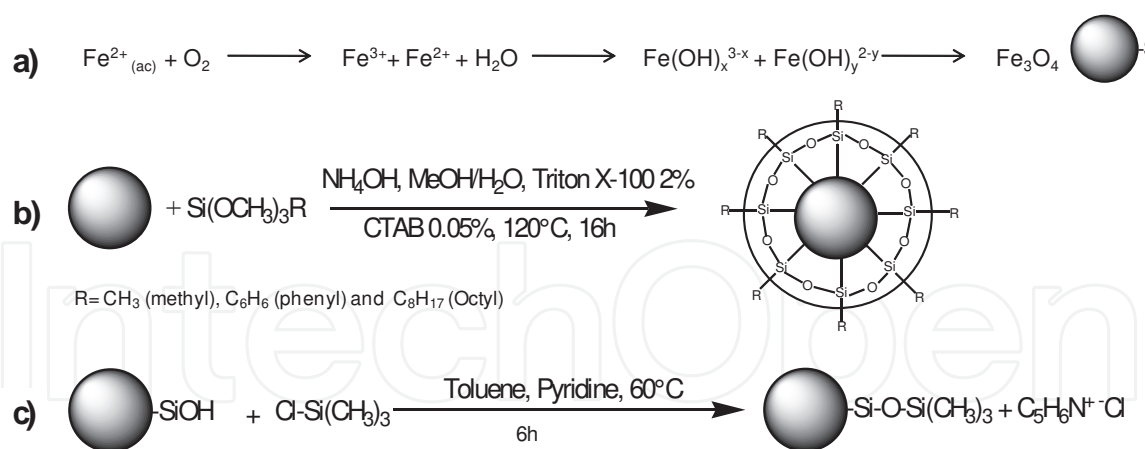
### 3.3. Analytical method

#### 3.3.1. Synthesis and characterization of magnetic supports

The magnetic solids were synthesized by emulsion polymerization. Magnetite particles  $\text{Fe}_3\text{O}_4$  were synthesized by a co-precipitation method [38] (Figure 8.a). The magnetite obtained was washed three times with 50 ml portions of deionized water and added to a flask containing a mixture methanol/water 3:1, Triton X-100 2%, CTAB 0.05% and the precursors indicated in Table 2. The mixture was heated and refluxed at 120 °C for 16 h with stirring (Figure 8.b). The solids were washed with two portions of 20 ml of deionized water and then a portion of 20 ml of ethanol then were dried at 60 °C. In order to block superficial silanol groups ( $-\text{Si}-\text{OH}$ ), the solids obtained in the previous process were derivatized using a mixture of 0.9 g of chlorotrimethylsilane (CTMS), and 1 ml of pyridine per gram of support in 50 ml of toluene (Figure 8.c). The supports were then washed with 20 ml portions of each of the following solvents: toluene, ethanol and deionized water until the washing liquid was colorless. The obtained magnetic particles were dried at 60 °C for 24 h [39]. Subsequently, all the magnetic solids were characterized by different techniques like SEM, X-ray diffraction and infrared spectroscopy.

#### 3.3.2. Sampling and sample treatment

Surface water samples were collected from an agricultural area in Zamora, Spain in October 2009. Polypropylene bottles previously washed with deionized water and  $\text{H}_2\text{SO}_4$  solution of 2% (v/v) were used. Once at the sampling site, the bottles were rinsed several times with the water to be collected and the temperature was measured. The samples were stored at 4°C before analysis. They were filtered through 0.45  $\mu\text{m}$  cellulose acetate filters (Sartorius,



**Figure 8.** Synthetic methodology for magnetic supports preparation; a) magnetite preparation by co-precipitation method, b) silica polymerization onto magnetite particles by emulsion polymerization, c) silanol block reaction.

Magnetic Solid Name	Ratio SiO <sub>2</sub> monomer-Fe <sub>3</sub> O <sub>4</sub> (w/w)
Polar 1 (P1)	1:1 / TMOS
Polar 2 (P2)	1:2 / TMOS
Phenyl 1 (PH1)	1:1 / PTMS
Phenyl 2 (PH2)	1:2 / PTMS
Octyl 1 (C8-1)	1:1 / C8-TEOS
Octyl 2 (C8-2)	1:2 / C8-TEOS

**Table 2.** SiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> ratio (w/w) and functionalized monomers for magnetic supports used such as adsorbents in MSPE for atrazine and simazine isolation

Göttingen, Germany) in a glass filtration device connected to a hand-operated vacuum pump (Sartorius, Göttingen, Germany).

Parameters such as the water samples' pH and the nature of the functionalized magnetic solids (mainly polarity) were modified to find the adequate extraction conditions. All the experiments were carried out with five replicates.

The optimal developed MSPE procedure involves the following steps: First, 1 ml of methanol is added to 0.1 g of the magnetic support (PH1) for activation and the magnetic solid is washed with 5 ml of deionized water. After addition of a known volume of water sample (0.2, 0.5 or 1.0 l) and pH adjustment to a value of 5 with HCl 1 M, the mixture is dispersed in an ultrasonic bath for 10 min. Then, a neodymium magnet is placed on the bottom of the beaker providing the isolation of the magnetic supports with the adsorbed analytes from the solution. The water sample is then eliminated by decantation. After the adsorption process, the solid is rinsed twice with 10 ml of deionized water. Finally, 1 ml of methanol was added to the magnetic solid and dispersed in an ultrasonic bath for 10 min. A neodymium magnet was placed on the bottom

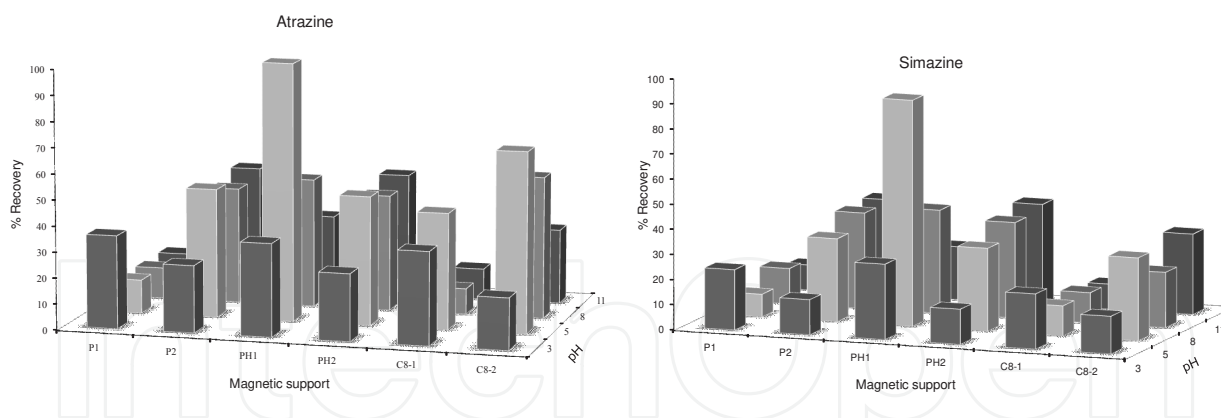
of the beaker, and using a syringe the extract was isolated, dried, redissolved in 50  $\mu\text{l}$  of methanol and injected into the HPLC system for their separation and analysis.

The SPE procedure for comparison was performed as described [40]: C18 SPE cartridges (500 mg, Bound Elut, Varian, Netherlands) were conditioned using 5 ml of ethyl acetate, 5 ml of methanol and 5 ml of deionized water at a flow rate around 2  $\text{ml min}^{-1}$ . Water samples (1 l) were flowed through the cartridges with a flow rate between 10-15  $\text{ml min}^{-1}$  under vacuum and the loaded cartridges were rinsed with 3 ml of methanol:water (5:95, v/v). The elution was performed with three aliquots (1 ml) of ethyl acetate at a flow-rate of about 1  $\text{mL min}^{-1}$ . The combined aliquots were evaporated to dryness by a gentle stream of nitrogen and the residues were dissolved in 50  $\mu\text{l}$  of methanol and injected into the HPLC system.

## 4. Results and discussion

### 4.1. Triazine extraction by MSPE

Figure 9 shows the effect of the polarity of the magnetic solid and the pH value of the aqueous phase on the recovery of each analyte. The results obtained demonstrate the high affinity achieved by phenyl based supports. The best extractions were observed when using the PH1 solid at pH 5 with recoveries of 90% and 100% for simazine and atrazine, respectively. Based on this performance, solid PH1 and pH 5 were selected for further experiments.



**Figure 9.** Effect of magnetic solid polarity and sample pH value on the triazine recoveries in spiked surface water (10  $\text{ng ml}^{-1}$ )

The adsorption of analytes on the solid surface depends on acid-base interactions (hydrogen bonds),  $\pi$ - $\pi$  interactions, and Van der Waals forces (hydrophobic interactions). However, it has been observed that solid absorbent with aromatic groups improve the adsorption of triazines, due to  $\pi$ - $\pi$  interactions, improving significantly recovery percentages [41-43]. This type of interaction has been reported for adsorption of triazines on mineral oxides coated with surfactants, the hydrophobic interaction between adsorbents and analytes improve the adsorption [44]. On the other hand, the acid-base equilibrium has an important role during



adsorption, in this case is evident that the better adsorption onto the surface solid is presented at pH 5. In these conditions the triazines are neutral without electric charges increasing the hydrophobic interactions. At pH values  $>7.0$  the remaining surface silanol groups acquire a negative charge, increasing the repulsions between the surface of magnetic solid and the triazines decreasing the percentage recoveries for both analytes [45].

#### 4.2. Characterization of magnetic solids

The magnetic solid characterization has been previously reported [39]. In this paper, we focus on the characterization of the most adequate solid for the selected triazine preconcentration. The magnetic particle morphology is spherical with core-shell type, where the core particle is magnetite, with super paramagnetic properties ( $20\text{-}50\text{ emu g}^{-1}$ ) [46]. On the other hand, the shell is formed by silica phase functionalized with phenyl groups. The micrograph shown in Figure 10 confirms the spherical morphology of magnetic particles, with an approximated diameter of  $2\text{ }\mu\text{m}$ . The diffraction pattern shows the magnetite line diffraction (m) and a broadband signal between  $2\Theta^\circ$  of  $10^\circ$  and  $40^\circ$ , corresponding to the amorphous silica phase. The physiochemical and magnetic properties of the magnetic particles were adequate for their application as adsorbents in MSPE.

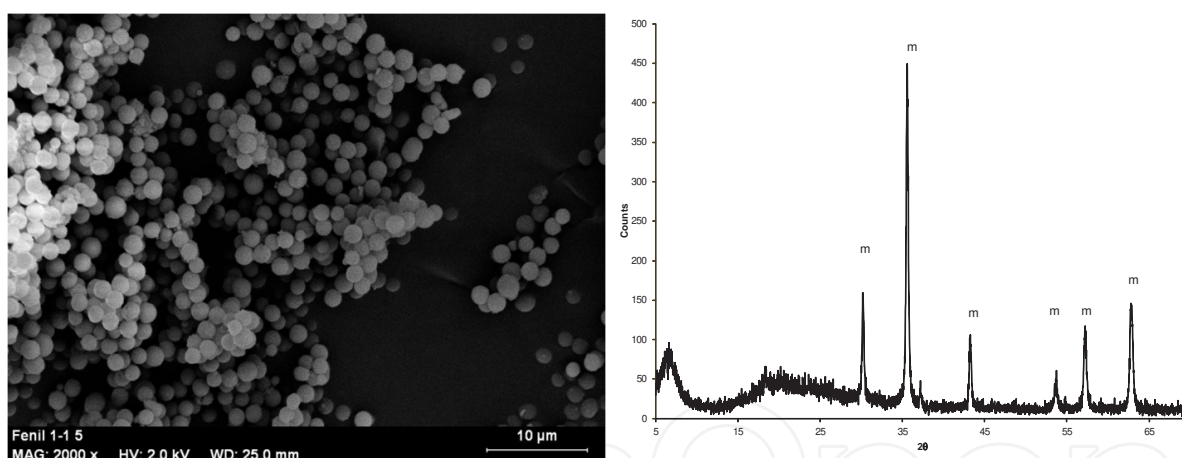


Figure 10. Microphotography and diffraction pattern of PH1 support

#### 4.3. Analytical parameters of the MSPE

In the optimized conditions, the analytical parameters and precision data were determined using spiked tap water samples. Different volumes of spiked surface water samples ( $0.2$ ,  $0.5$  and  $1.0\text{ l}$ ) with an interval concentration of  $10\text{-}1000\text{ }\mu\text{g l}^{-1}$  were used. The results obtained are listed in Table 3. The limits of detection (LODs) were calculated for a signal/noise relation equal to ( $S/N = 3.29$ ). The limits of quantification (LOQ) were determined using a signal/noise relation equal to  $10$  ( $S/N = 10$ ). The calibration curves were constructed from the high signal versus concentration  $\mu\text{g l}^{-1}$ .

According to the results from Table 3, it is possible to observe that the LODs decrease when higher initial sample volumes are used. The lowest limits of detection were reached between 0.01 and 0.02  $\mu\text{g l}^{-1}$  using 1 l of initial sample. LOD and LOQ obtained by the method are comparable to those reported by other methods.

Sample volume (l)	Analyte	LOD ( $\mu\text{g l}^{-1}$ )	LOQ ( $\mu\text{g l}^{-1}$ )	Repeatability		Reproducibility	
50 $\mu\text{g l}^{-1}$	100 $\mu\text{g l}^{-1}$	50 $\mu\text{g l}^{-1}$	100 $\mu\text{g l}^{-1}$				
0.2	Simazine	4	12	2.8	6.2	4.8	2.8
	Atrazine	3	9	2.3	5.1	3.2	2.6
0.5	Simazine	1	3	2.4	6.7	2.5	2.9
	Atrazine	1	3	1.6	5.6	4.2	2.2
1.0	Simazine	0.01	0.03	1.4	2.8	1.5	2.0
	Atrazine	0.02	0.06	1.6	3.9	1.2	1.5

**Table 3.** Analytical parameters for different sample volumes, repeatability and reproducibility (%RSD, n = 5) for two concentration levels.

The precision of method expressed as the repeatability and reproducibility values (%RSD < 5%) and the high recoveries obtained make the proposed method a viable alternative to be routinely implemented in the analysis of simazine and atrazine in water samples, without the necessity of expensive or difficult access equipment.

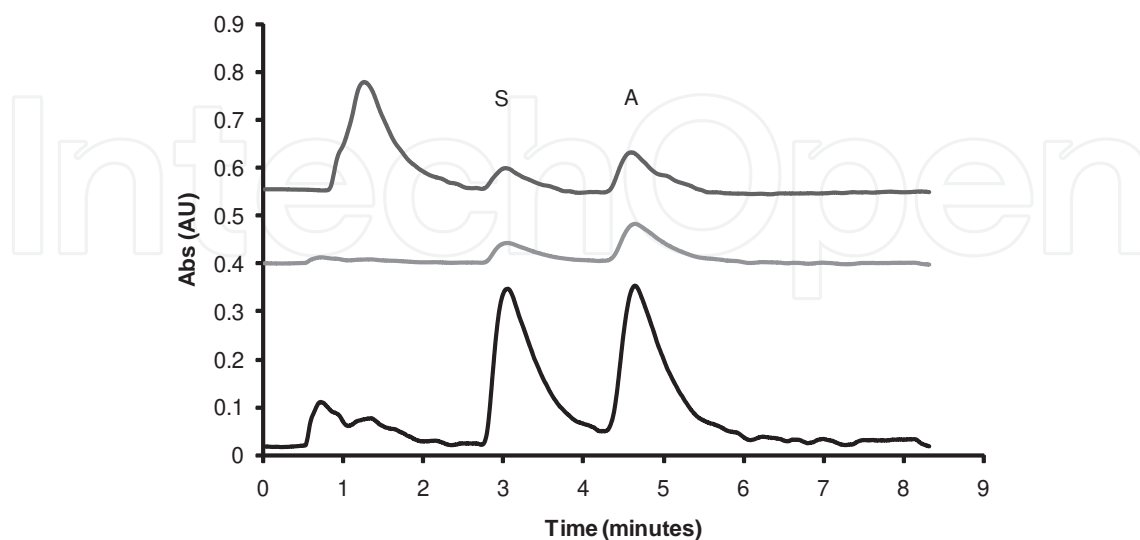
#### 4.4. Analysis of superficial water samples

The developed method was applied to the determination of triazines in surface water samples from agricultural lands in Zamora, Spain. Only one of the four samples analyzed showed contamination by triazines, being this water sample was collected in a waterhole near a corn field, which shows that pesticides applied to crops, migrate to nearby water bodies.

The concentrations found with the MSPE-HPLC (mean and %RSD, n=5) method were 9.9(3.0) and 12.2(2.5)  $\mu\text{g l}^{-1}$  for simazine and atrazine, respectively. The concentrations determined using the SPE-HPLC were 9.8(3.0) and 11.8(2.3  $\mu\text{g l}^{-1}$ ). The average of each analyte (determined by both methods) was compared by a t-test for comparison of means, assuming comparable variances (verified by a F-test). Calculated t values were compared with the tabulated t value for 8 degrees of freedom and a significance level of  $\alpha=0.05$  ( $t=2.30$ ). Thus, the null hypothesis was accepted meaning that there were no significant differences between the results provided by both methods.

Figure 11 showed the chromatogram of surface water sample collected from Zamora, Spain, extracted with MSPE and SPE and a standard chromatogram. The clean-up process results for

both preconcentration methods are similar, showing that MSPE can be used as an alternative method for the determination of atrazine and simazine.



**Figure 11.** Chromatograms obtained at the optimized conditions: (a) surface water sample obtained by MSPE pre-concentration method, (b) surface water sample obtained by SPE pre-concentration method and (c) simazine and atrazine standard solution  $20 \mu\text{g l}^{-1}$ . S: simazine and A: atrazine.

## 5. Conclusions

Due to the wide application of herbicides, it is necessary to develop fast and reliable methods for their determination in different analytical matrices providing a correct risk assessment to human health and the environment.

The results obtained by the optimized and validated MSPE method are comparable with other reported methods, concluding that the developed MSPE-HPLC procedure can be used for the screening and quantification of atrazine and simazine in water samples.

Although there are more sensitive methods, they require expensive and inaccessible instrumentation such as mass spectrometry, representing the MSPE-HPLC-DAD a rapid and low cost determination method of atrazine and simazine in water samples.

## Acknowledgements

The authors wish to thank the CONACyT (project 61310) and Consejería de Educación, Junta de Castilla y León (project VA023A10-2) and MCINN project AIB2010PT-00234 for the financial support.

## Author details

José A. Rodríguez<sup>1</sup>, Karina Aguilar-Arteaga<sup>1</sup>, Cristina Díez<sup>2</sup> and Enrique Barrado<sup>3</sup>

1 Universidad Autonoma del Estado de Hidalgo, Mexico

2 University of Geneva (Analytical Pharmaceutical Chemistry) and Food Authority Control (SCAV), Switzerland

3 Universidad de Valladolid, Spain

## References

- [1] Crafts AS. *The Chemistry and Mode of Action of Herbicides*. New York: Wiley; 1965
- [2] LeBaron HM, McFarland, Burnside, OC. *The Triazine Herbicides. 50 Years Revolutionizing Agriculture*. Hungary: Elsevier; 2008
- [3] Pacakova V, Stulik K, Jiskra J. High-Performance Separations in the Determination of Triazine Herbicides and Their Residues. *Journal of Chromatography A* 1996;754 17-31
- [4] Mitra S. *Sample Preparation Techniques in Analytical Chemistry*. New Jersey: Wiley; 2003.
- [5] U.S. Environmental Protection Agency, EPA 500 Series, Method 507 (revision 2.0). *Determination of Nitrogen- and Phosphorus-Containing Pesticides in Water by Gas chromatography with a Nitrogen-Phosphorus Detector*. 1989
- [6] Chimuka L, Michel M, Cukrowska E. Buszewski. *Advances in Sample Preparation Using Membrane-Based Liquid-Phase Microextraction Techniques*. *Trends in Analytical Chemistry* 2011; 30(11) 1781-1792
- [7] Shen G, Lee HK. Hollow Fiber-Protected Liquid Phase Microextraction of Triazine Herbicides. *Analytical Chemistry* 2002; 74 648-654
- [8] Trtic-Petrovic T, Dordevic J, Dujakovic N, Kumric K, Vasiljevic T, Lausevic M. Determination of Selected Pesticides in Environmental Water by Employing Liquid-Phase Microextraction and Liquid Chromatography-Tandem Mass Spectrometry. *Analytical and Bioanalytical Chemistry* 2010; 397 2233-2243
- [9] Wu C, Liu Y, Wu Q, Wang C, Wang Z. Combined Use of Liquid-Liquid Microextraction and Carbon Nanotube Reinforced Hollow Fiber Microporous Membrane Solid-Phase Microextraction for the Determination of Triazine Herbicides in Water and Milk Samples by High-Performance Liquid Chromatography. *Food Analytical Methods* 2012; 5 540-550

- [10] Nagaraju D, Huang S. Determination of Triazine Herbicides in Aqueous Samples by Dispersive Liquid-Liquid Microextraction with Gas Chromatography-Ion Trap Mass Spectrometry. *Journal of Chromatography A* 2007; 1161 89-97
- [11] Zaijun L, Xiulan S, Junkang L. Ionic Liquids as Novel Solvent for Extraction and Separation in Analytical Chemistry. In: Kokoron A. (ed.) *Ionic Liquids: Applications and Perspectives*. Rijeka: Intech; 2012. p153-180
- [12] Wand S, Ren L, Liu C, Ge J, Liu F. Determination of Five Polar Herbicides in Water Samples by Ionic Liquid Dispersive Liquid-Phase Microextraction. *Analytical and Bioanalytical Chemistry* 2010; 397 3089-3095
- [13] Zhong Q, Su P, Zhand Y, Wang R, Yang Y. In-situ Ionic Liquid-Based Microwave-Assisted Dispersive Liquid-Liquid Microextraction of Triazine Herbicides. *Microchimica Acta* 2012; 178 341-347
- [14] Sanagi MM, Abbas HH, Ibrahim WAW, Aboul-Enien HY. Dispersive Liquid-Liquid Microextraction Method Based on Solidification of Floating Organic Drop for the Determination of Triazine Herbicides in Water and Sugarcane Samples. *Food Chemistry* 2012; 133 557-562
- [15] Wang H, Li G, Zhang Y, Chen H, Zhao Q, Song W, Xu Y, Jin H, Ding L. Determination of Triazine Herbicides in Cereals Using Dynamic Microwave-Assisted Extraction with Solidification of Floating Organic Drop Followed by High-Performance Liquid Chromatography. *Journal of Chromatography A* 2012; 1233 36-43
- [16] Mou R, Chen M, Cao Z, Zhu Z. Simultaneous Determination of Triazine Herbicides in Rice by High-Performance Liquid Chromatography Coupled with High Resolution and High Mass Accuracy Hybrid Linear Ion Trap-Orbitrap Mass Spectrometry. *Analytica Chimica Acta* 2011;706 149-156
- [17] Dean JR, Wade G, Barnabas IJ. Determination of Triazines Herbicides in Environmental Samples. *Journal of Chromatography A* 1996; 733295-355
- [18] Molto JC, Pico Y, Font G, Mañes J. Determination of Triazines and Organophosphorus Pesticides in Water Samples Using Solid-Phase Extraction. *Journal of Chromatography* 1991; 555 137-145
- [19] Chavez-Moreno CA, Guzman-Mar JL, Hinojosa-Reyes L, Hernandez-Ramirez A, Ferrer L, Cerda V. Applicability of Multisyringe Chromatography Coupled to On-Line Solid-Phase Extraction to the Simultaneous Determination of Dicamba, 2,4-D, and Atrazine. *Analytical and Bioanalytical Chemistry* 2012; 403 2705-2714
- [20] Ollers S, Singer HP, Fassler P, Muller SR. Simultaneous Quantification of Neutral and Acidic Pharmaceuticals and Pesticides at Low.ng/l Level in Surface and Waste Water. *Journal of Chromatography A* 2001; 911 225-234
- [21] Benvenuto F, Marin JM, Sancho JV, Canobbio S, Mezzanotte V, Hernandez F. Simultaneous Determination of Triazines and Their Main Transformation Products in Surface and Urban Wastewater by Ultra-High-Pressure Liquid Chromatography-Tandem Mass Spectrometry. *Analytical and Bioanalytical Chemistry* 2010; 397 2791-2805

- [22] Bester K, Lamani X. Determination of Biocides as Well as Some Biocide Metabolites From Facde Run-Off Waters by Solid Phase Extraction and High Performance Liquid Chromatographic Separation and Tandem Mass Spectrometry Detection. *Journal of Chromatography A* 2010; 1217 5204-5214
- [23] Lissalde S, Mazzella N, Fauvelle V, Delmas F, Mazzellier P, Legube B. Liquid Chromatography Coupled with Tandem Mass Spectrometry Method for Thirty-Three Pesticides in Natural Water and Comparison of Performance Between Classical Solid Phase Extraction and Passive Sampling Approaches. *Journal of Chromatography A* 2011; 1218 1492-1502
- [24] Battista M, DiCorcia A, Marchetti M. Extraction and Isolation of Triazine Herbicides from Water and Vegetables by a Double Trap Tandem System. *Analytical Chemistry* 1989; 61 935-939
- [25] Pichon V, Chen L, Hennion MC, Daniel R, Martel A, LeGoffic F, Abian J, Barcelo D. Preparation and Evaluation of Immunosorbents for Selective Trace Enrichment of Phenylurea and Triazine Herbicides in Environmental Waters. *Analytical Chemistry* 1995; 67 2451-2460
- [26] Pichon V, Chen L, Durand N, LeGoffic F, Mennion MC. Selective Trace Enrichment on Immunosorbents for the Multiresidue Analysis of Phenylurea and Triazine Pesticides. *Journal of Chromatography A* 1996; 725 107-119
- [27] Muldoon MT, Stanker LH, Molecularly Imprinted Solid Phase Extraction of Atrazine from Beed Liver Extracts. *Analytical Chemistry* 1997; 69 803-808
- [28] Zhou Q, Xiao J, Wang W, Lui G, Shi Q, Wang J. Determination of Atrazine and Simazine in Environmental Water Samples Using Multiwalled Carbon Nanotubes as the Adsorbents for Preconcentration Prior to High Performance Liquid Chromatography with Diode Array Detector. *Talanta* 2006; 68 1309-1315
- [29] Katsumata H, Kojima H, Kaneco S, Suzuki T, Ohta K. Preconcentration of Atrazine and Simazine with Miltiwalled Carbon Nanotubes as Solid-Phase Extraction Disk. *Microchemical Journal* 2010; 96 348-351
- [30] Hernandez F, Beltran J, Lopez FJ, Gaspar JV. Use of Solid-Phase Microextraction for the Quantitative Determination of Herbicides in Soil and Water Samples. *Analytical Chemistry* 2009; 72 2313-2322
- [31] Wu Q, Feng C, Zhao G, Wand C, Wang Z. Graphene-Cated Fiber for Solid-Phase Microextraction of Triazine Herbicides in Water Samples. *Journal of Separation Science* 2012; 35 193-199
- [32] Sanchez-Ortega A, Unceta N, Gomez-Caballero A, Sampedro MC, Akesolo A, Goicolea MA, Barrio R. Sensitive Determination of Trizazines in Underground Waters Using Stir Bar Sorptive Extraction Directly Coupled to Automated Thermal Desorption and Gas Cromatography-Mass Spectrometry. *Analytica Chimica Acta* 2009; 641 110-116

- [33] Neng NR, Mestre AS, Carvalho AP, Nogueira JMF. Powdered Activated Carbons as Effective Phases for Bar Sorptive Micro-Extraction (BS $\mu$ E) to monitor levels of triazine herbicides in environmental water samples. *Talanta* 2011; 83 1643-1649
- [34] Xu S, Li J, Chen L. Molecularly Imprinted Polymers by Reversible Addition-Fragmentation Chain Transfer Precipitation Polymerization for Preconcentration of Atrazine in Food Matrices. *Talanta* 2011; 85 282-289
- [35] Aguilar-Arteaga K, Rodriguez JA, Barrado E. Magnetic Solids in Analytical Chemistry: A Review. *Analytica Chimica Acta* 2010; 647 157-165
- [36] Zhao G, Song S, Wang C, Wu Q, Wang Z. Determination of Triazine Herbicides in Environmental Water Samples by High-Performance Liquid Chromatography using Graphene-Coated Magnetic Nanoparticles as adsorbent. *Analytica Chimica Acta* 2011; 708 155-159
- [37] Katsumata H, Kaneco S, Suzuki T, Ohta K. Determination of Atrazine and Simazine in Water Samples by High-Performance Liquid Chromatography After Preconcentration with Heat-Treated Diatomaceous Earth. *Analytica Chimica Acta* 2006; 577 214-219
- [38] Barrado E, Rodríguez JA, Prieto F, Medina J. Characterization of Iron Oxides Embedded in Silica Gel Obtained by Two Different Methods. *Journal of Non-Crystalline Solids* 2005; 351 906-914
- [39] Aguilar-Arteaga K, Rodriguez JA, Miranda JM, Medina J, Barrado E. Determination of Non-Steroidal Anti-Inflammatory Drugs in Wastewaters by Magnetic Matrix Solid Phase Dispersion-HPLC. *Talanta* 2010; 80 1152-1157
- [40] Ma WT, Fu KK, Cai Z, Jiang GB. Gas Chromatography/Mass Spectrometry Applied for the Analysis of Triazine Herbicides in Environmental Waters. *Chemosphere* 2003; 52 1627-1632
- [41] Bagheri H, Khalilian F, Naderi M, Babanezhad E. Membrane Protected Conductive Polymer as Micro-SPE Device for the Determination of Triazine Herbicides in Aquatic Media. *Journal of Separation Science* 2010; 33 1132-1138
- [42] Bruzzoniti MC, Sarzanini C, Costantino, Fungi M. Determination of Herbicides by Solid Phase Extraction Gas Chromatography-Mass Spectrometry in Drinking Waters. *Analytica Chimica Acta* 2006; 578 241-249
- [43] D'Archivio AA, Incani A, Mazzeo P, Ruggieri F. Adsorption of s-Triazines onto Polybenzimidazole: A Quantitative Structure-Property Relationship Investigation *Analytica Chimica Acta* 2009; 650 175-182
- [44] Moral A, Sicilia MD, Rubio S, Perez BD. Multifunctional Sorbents for the Extraction of Pesticide Multiresidues from Natural Waters. *Analytica Chimica Acta* 2008; 608 61-72
- [45] Nawrocki J. The Silanol Group and Its Role in Liquid Chromatography. *Journal of Chromatography A* 1997; 779 29-71
- [46] Gupta AK, Gupta M. Synthesis and Surface Engineering of Iron Oxide Nanoparticles for Biomedical Applications. *Biomaterials* 2005; 26 3995-4021