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New Trends in Chemical Analysis of Disinfection By-Products

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Abstract

The disinfection by-products are special category of emergent pollutants, and their formation is widely known when the organic matter present in the catchment water reaches the disinfection agent in the water treatment plants. These kinds of compounds are close to more than 500 molecules classified in the following main families: halomethanes, haloacetic acids, haloacetonitriles and haloketones. Their adverse effects in the health are widely recognized for international health organisms and normally are in trace levels that promote the development of smart strategies for their analysis in aquatic environments where these compounds are generally not alone. In this way, the microextraction techniques for analysis of emergent contaminants in the environment which are in trace amounts have gained a lot of space because they comply fully with the objectives established in the sample preparation field: reduction in the number of steps, adaptability to field sampling, automation and reduction or total elimination of solvents required for extraction by meeting in one step the main tasks of any sample preparation technique: extraction, clean up and enrichment. There are a lot of possibilities in this field: solid phase microextraction (SPME), liquid phase microextraction (LPME), stir bar sorptive extraction (SBSE) and rotating disk sorptive extraction (RDSE).

Keywords: microextraction, disinfection by-products, halomethanes, haloacetic acids, water treatment plant, solid phase microextraction, chemical risk

1. Introduction

The sample preparation SP is the most critical step and on it is spent a lot of time in the chemical analysis, in addition herein the people make the higher number of mistakes in the whole procedure, so that in other words the SP is the "neck of bottle" of analytical procedure.

In special, this step turn off more difficult when the matrices to analyze are foods, complex materials or the target analytes are in trace amounts. Taking into account the above premises and the ideology of green chemistry based on: elimination or reduction of organic solvents, reduction of the steps number in the procedure, integration and automation of sampling and analysis in just one step, by leading to more eco-efficient and productive analytical procedures. That allows to reach the three major challenges on sample preparation: isolation, cleanup and preconcentration with better practices an optimum results [1]. In this way, the solventless microextraction techniques have gained a lot of space because fully comply with the objectives and goals above established. Additionally, they meet in one step the main tasks of any sample preparation technique: extraction, clean up and enrichment.

The disinfection by-products (DBPs) are a special kind of compounds which appear in a trace amounts during the chlorination processes in the water treatment plants (WTP). These low concentrations represent a challenge for analytical chemists. The aqueous matrices are easier to manage than sludge, air or biological fluids because the presence of interferences are low, but some of these compounds are volatile and other are nonvolatile and polar analytes, that drives to take a compromise decision for that in a single run can analyze all these compounds by facilitating the through routine in a laboratory water analysis. In this sense, the microextraction techniques help to reach the low requested detection limits for the preconcentration factor as a special characteristic of these kind of procedures. By the other side, there are the possibilities to eliminate interferences and to use a minimal amount of organic solvents. Taking into account that all this valuable merit figures are possible to do in one step, the automation operation have been reached easily.

2. Chemical formation of disinfection by-products and health implications

The disinfection process in the water treatment plant is a routine practice for microbial control risk due to the presence in raw water of the microbial pathogens. The disinfection agent more widespread is chlorine for its effectiveness, low cost, easier management and high residual effect for assurance protection along to the distribution network.

2.1. The formation reaction of disinfection by-products: natural organic matter (NOM) + Chlorine

Rook in 1974 had established that the disinfection by-products formation is due to reaction between natural organic matter NOM and chlorine [2, 3]. The NOM precedence is basically from leaching tannin compounds from leaves and soil, which have a common structure of polyphenol rings (resorcinol-type molecules) [4, 5]. The primary disinfection by-products results from breakage under chlorine influence of polyphenol ring through the next three pathways a, b and c, such as is shown in **Figure 1**.

As shown in **Figure 1**, if the breakage is by pathway *a*, it will form halomethanes, through pathway *b* with insertion of a hydroxide, the haloacetic acids and the pathway *c* will produce haloketones. From these primary DPBs and the reaction with bromine or iodine inclusively
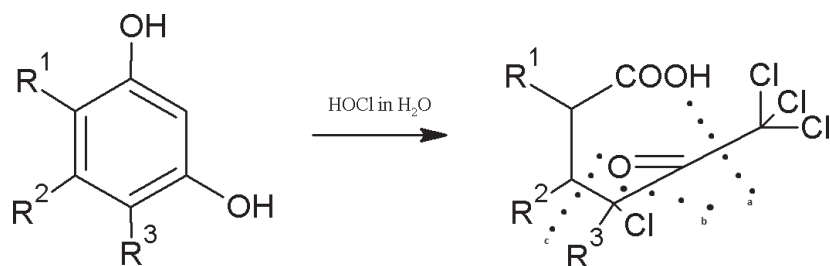
Figure 1. Mechanism of the DBP's formation.

the mixture between alone primary disinfection by-products will occur the emergent or secondary DPBs such as bromohalomethane, iodotrihalomethane, haloacetonitrile, etc. These last inclusively with a higher chemical risk for the health due to higher toxicity in the bromine and iodine atoms [6].

2.2. The pondering risk: microbial versus chemical risk

The chronic risk is associated with cancer´s presence due to intake of foods with toxic chemical compounds, this is the case of DBPs in the drinking water, and their effects normally are developed in advanced ages of human being but the acute risk related with microbial infection due to presence of the microbial pathogens show their consequences immediately and their effects can be mortally. The drinking water is a good scenery for pondering the effects and consequences of damage between the chemical associated with presence of DBPs and for the other side with microbial issues due to bacteria diseases related with bacterial contamination. The dosage application of disinfectant in the drinking water is in all development countries (emergent countries) a measure to prevent the microbial risk due to its accelerated development and tragic consequences but simultaneously formation of chemical compounds and many evidences of cancer formation has been done.

The issue in the disinfection proposals in the water treatment plants is the key for control of both risks, that means to find the ideal chlorine dosage for avoiding and diminishing the microbial problem and for other way to control the formation of DBPs in big amounts that represents a severe risk to the drinking water servers [7–9].

2.3. The disinfection by-products and regulations

The disinfection by-products DBPs are cataloged as emergent contaminants, [10] due to its recognized effects to the health and that its formation is frequently in the WTP and the exposition is high and direct by the culture of consumption of drinking water during all day without a forbidden recommendation of the authorities.

Table 1 shows the different normatives and rules with respect to control and prevention directives of DBPs under the guidance of health and technical institutions with wide knowledge in the target issue.

The most known DPBs are the trihalomethanes THMs, then the haloacetic acids HAA, allows in the importance and recognition the HAN haloacetonitrile. Nowadays, the emergent DBPs have become important in the emergent DBPs due to lower and trace amounts, meanwhile more severe and toxic health effects, such as bromohalomethanes and iodohalomethanes.

Item	Organization	DBPs	Value µg L⁻¹	IARC Health Categories*	Ref.
1	World Health Organization (WHO) $$\frac{[CH\,Cl_3]}{200} + \frac{[CH\,Cl_2\,Br]}{60} + \frac{[CH\,Cl\,Br_2]}{100} + \frac{[CH\,Br_3]}{100} = 1$$	Chloroform	200	Group 2B	[11, 14, 22]
		Bromodichloromethane	60	Group 2B	
		Dibromochloromethane	100	Group 3	
		Bromoform	100	Group 3	
		Dichloroacetic acid	50	Group 2B	
		Trichloroacetic acid	100	Group 3	
		Dichloroacetonitrile	90	Group 3	
		Dibromoacetonitrile	100	Group 2B	
		Trichloroacetonitrile	1	Group 3	
2	Environmental Protection Agency (EPA)	Chloroform	30	Group 2B	[12, 22]
		TTHMs	80	Group 3	
		Haloacetic acids	60	Group 2B	
3	European Union (EU)	Total trihalomethanes	100	Group 3	[13, 22]
4	South Korean Regulation	Total trihalomethanes	100	Group 3	[47]
		Haloacetic acids	100	Group 2B	
		Dichloroacetonitrile	90	Group 3	
		Dibromoacetonitrile	100	Group 2B	
		Trichloroacetonitrile	4	Group 3	
5	Australian Regulatory Limits	Trihalomethanes	250	Group 3	[43]
6	Colombian Regulation	Trihalomethanes	200	Group 3	[23]

*Group 1: the agent is carcinogenic to humans; Group 2A: the agent is probably carcinogenic to humans; Group 2B: the agent is possibly carcinogenic to humans; Group 3: the agent is not classifiable as to its carcinogenicity to humans; Group 4: the agent is probably not carcinogenic to humans [14].

Table 1. Rules, guides and regulation normatives to prevent and control of DBPs for drinking water (µg L⁻¹).

2.4. The health implications and evidences WHO and IARC

The epidemiological and toxicological evidences of cancer by drinking water with contents higher that mentioned guidelines in **Table 1** have been demonstrated in numerous cases, this is correlated with consumer's frequency and anatomical and physiological conditions of town server [7, 8, 11–14]. The difference among the several DBPs fill down in to the carcinogenic categories, there being two well defined kinds: possible and probable carcinogenic agent in dependence of the number of incidence and prevalence cases. In **Table 1**, this remarkable issue is shown and explained for each one DBPs.

2.5. The alternative disinfectants

Taking into account the health implications of DBP's present in the drinking water as result of the reaction between NOM and chlorine in the WTP but with the imperious necessity by controlling the action of microbial pathogens in the raw water due to uncontrolled wastewater discharges into the catchment water, has been raised the use of other alternative disinfectants with

the same or better properties than chlorine or chloride derivatives: effectiveness, low cost, easy management and big residual effect. Among candidates can be mentioned are as follows: ozone, hydrogen peroxide, UV-light, potassium permanganate, peroxyacetic acid, and so on [15].

Ozone: the ozone O_3 has a good effectiveness, high cost, technical management and low residual effect. It is properly used in the industrial deals.

Hydrogen peroxide: The hydrogen peroxide H_2O_2 has a medium effectiveness, low cost, technical management and low residual effect. Its use is widespread for catalytic experiments as $^{\bullet}OH$ promoter in Fenton or pseudo Fenton reactions.

UV-light: This physical source of disinfectant has high effectiveness, high cost, technical management and low residual effect. This is properly for condominial and individual solutions of supplier drinking water. Its drawbacks with the cost can diminish in permanent solar offer places.

Potassium permanganate: The $KMnO_4$ is a strong oxidant close to 1.1 eV. It has good effectiveness, low cost, technical management and high residual effect but to the moment are unknown its by-products formation, letting a strong flavor and taste of final drinking water and can increase the network damage due to its strong oxidation capacity.

Peroxyacetic acid: $C_2H_4O_3$ is an emergent sanitizer in the market for agricultural, medical environments, water and wastewater industry, food processing, beverage and pharmaceutical industries. It has good effectiveness, low cost, easy management and medium residual effects due to depletion into its precursors: hydrogen peroxide and acetic acid promotes by heat and bad storage and obviously letting low admissible characteristic flavor and taste to the drinking water [15].

As can inference from the mentioned alternatives disinfectants, we are so far to find soon a replacement to the chlorine.

2.6. The disinfection: Pondering between microbial and chemical risks

Some researchers like Craun [7–9] have established a basic model to pondering the weight and evolution of both risks associated and in interdependence with the chlorine dosage practice in the WTP (see **Figure 2**).

As shown in **Figure 2**, and with strict dependence of formation reaction of DBPs, there are two ways for controlling in the just measures both risks: to have good quality raw water (that means low precursors amounts and microbes) and to do a rationalize chlorine dosage practice.

2.7. Classification of disinfection by-products

There are at least 500 chemical compounds catalogued as disinfection by-products [16], which are classified in four great families:

- Halomethanes

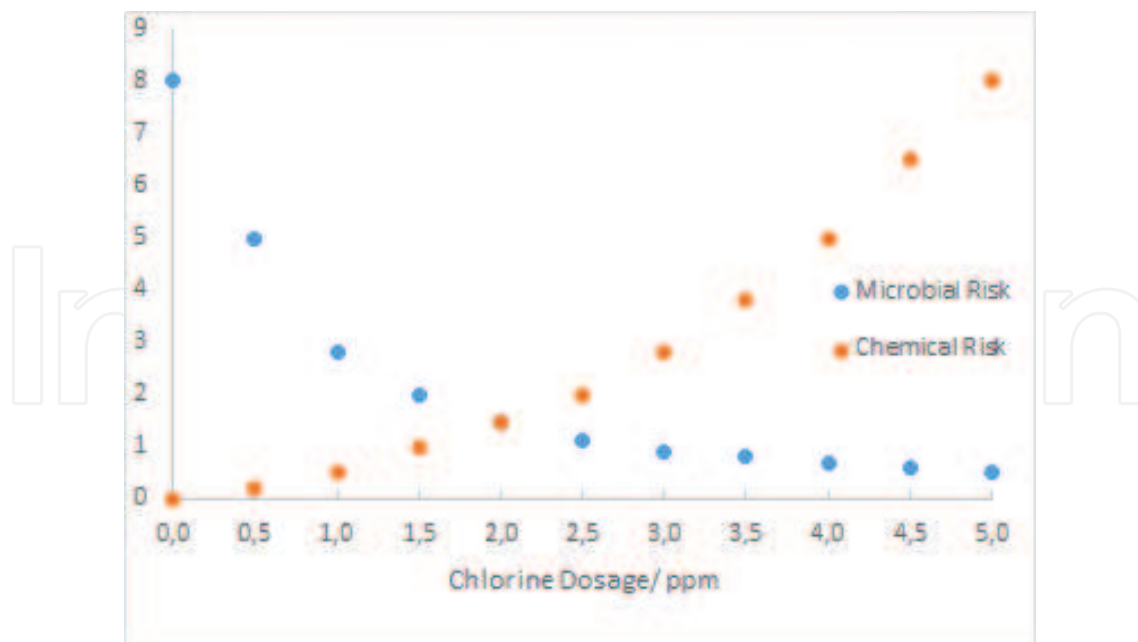- Haloacetic acids

- Haloketones

- Haloacetonitriles

Figure 2. Pondering the microbial and chemical risk in the disinfection practice with chlorine.

These compounds are also catalogued as emergent contaminants due to widespread use or formation and uncontrolled measures by sanitary authorities.

In **Table 2**, it is shown the DBPs classification containing the most cited molecules, their chemical formula and some references about found reported cases.

2.8. Routinely chemical analysis of DBPs

Due to their physicochemical condition, the most disinfection by-products are volatile and non or low polar compounds. In this sense, the proper chemical way for their analysis is the gas chromatography (GC) coupled with electron capture detection (ECD) for the presence in the molecule of electronegative atoms (halogens) or MS. In special for haloacetic acids due to their low vapor pressure and to be polar molecules is preferable the liquid chromatography by UV-detection or to derivatize to their methylesther derivatives (volatile and nonpolar compounds) with methanol under acidic conditions and catalize by anhydride chloroacetic, by doing possible their analysis by GC.

2.8.1. Liquid: liquid extraction

The USEPA method 502 established the liquid–liquid extraction (LLE) as official method for their analysis based on their physicochemical properties (**Table 2**). To 20 mL of aqueous sample to be add 5 mL of hexane, pentane or MtBE as extraction organic solvent into a 50 mL separation funnel, then the mixture is degasified by opening the key's funnel with the separation funnel slightly inclined, this operation is done by five times and then returns to initial and vertical position. Then let be the funnel in vertical position overnight to warranty the complete separation of both phases organic and aqueous, passed this time to recover the

Family	Compound	Chemical Formula	Molar mass g mol^{-1}	CAS	B.p. °C	Log P	Ref.
Halomethanes	Chloroform	$CHCl_3$	119.37	67-66-3	61.2	1.83	[41]
	Dibromochloro methane	$CHBr_2Cl$	208.28	124-48-1	119	2.13	[41]
	Bromodichloro methane	$CHCl_2Br$	163.82	75-27-4	90	1.98	
	Bromoform	$CHBr_3$	252.731	75-25-2	149.1	2.28	
Haloacetic Acids	Monochloroacetic acid (MCA)	$C_2H_3ClO_2$	94.49	79-11-8	189.3	0.31	[48]
	Bromochloroacetic acid (BCA)	$C_2H_2Cl_2O_2$	128.94	79-43-6	194	1.06	
	Dichloroacetic acid (DCA)	$C_2HCl_3O_2$	163.38	76-03-9	196	1.53	
	Trichloroacetic acid (TCA)	$C_2H_3BrO_2$	138.948	79-08-3	208	0.50	
	Monobromoacetic acid (MBA)	$C_2H_2Br_2O_2$	217.844	631-64-1	128	0.70	
	Dibromoacetic acid (DBA)	$C_2HBr_3O_2$	296.74	N/A	245	1.98	
	Tribromoacetic acid (TBA)	$C_2H_2BrClO_2$	173.39	5589-96-8	210	0.79	
	Dichlorobromoacetic acid (DCBA)	$C_2HBrCl_2O_2$	207.83	71133-14-7	N/A	1.68	
	Dibromochloroacetic acid (DBCA)	$C_2HBr_2ClO_2$	252.29	5278-95-5	N/A	1.83	
Haloketones	1,1-dichloropropanone (1,1-DCP)	$C_3H_4Cl_2O$	126.96	513-88-2	118	1.39	[22, 48]
	1,3-dichloropropanone (1,3-DCP)	$C_3H_4Cl_2O$	126.96	534-07-6	173	1.18	
	1,1,1-trichloropropanone (1,1,1-TCP)	$C_3H_3Cl_3O$	161.41	918-00-3	134	1.86	
Haloacetonitrile	Monochloroacetonitrile (MCAN)	C_2H_2ClN	75.5	107-14-2	124	0.37	[47]
	Monobromoacetonitrile (MBAN)	C_2H_2BrN	119.949	590-17-0	60	0.56	[48]
	Dibromoacetonitrile (DBAN)	C_2HBr_2N	198.845	3252-43-5	67	0.68	
	Dichloroacetonitrile (DCAN)	C_2HCl_2N	109.94	3018-12-0	110	1.12	
	Trichloroacetonitrile (TCAN)	C_2Cl_3N	144.38	545-06-2	83	1.59	
	Bromochloroacetonitrile (BCAN)	$C_2HBrClN$	154.39	83463-62-1		0.77	

CAS: Chemical Abstracts Service; B.p: Boiling point.

Table 2. Disinfection by-products classification and physicochemical properties.

organic extract in the overhead (less dense phase) by releasing the aqueous phase, opening the key's funnel and exactly closing when in the funnel there have been just the organic phase, from this phase to take and direct inject into chromatograph equipped with electron capture detection ECD. The yield of this method is calculated in the equation [1]

$$[S]_1 = \frac{[S]_0 V_1}{V_1 + V_2 D} = [S]_0 \left(\frac{1}{1 + D\frac{V_2}{V_1}} \right) \tag{1}$$

where

$[S]_1$ = Concentration of solute in the phase 1

$[S]_0$ = Initial concentration of solute

V_1 = Aqueous volume phase

V_2 = Organic volume phase

D = Distribution relation

This operation is possible to do n times reaching better results, because in an exhaustive method, in dependence on the next equation [2]

$$[S]_1 = [S]_0 \left(\frac{1}{1+D\frac{V_2}{V_1}} \right)^n \qquad (2)$$

2.8.2. Solid phase extraction SPE

This procedure is properly for concentration and cleanup method for nonvolatile compounds [17]. The cartridges available for extraction are SDB, NH_2, C18, C8, HLB, SAX and SCX sorbents. The whole SPE procedure includes four steps: conditioning, loading, wash and elution. It has been used for solid-phase extraction of 35 DBPs with analysis by GC-ECD and GC–MS [18, 19] (**Figure 3**).

2.8.3. Head space extraction HSE

Due the volatility of the major DPBs one very affordable technique for their analysis is the head space extraction, there are in the market two automatized possibilities: with transference line [20–22], and high volume syringe [23, 24]. In both cases, the stirring and heating are promoted by the same equipment, two of the most important and critical variables in the extraction process. In addition and with the similarity concept from Schdmidt's group has come the device coined in tube extraction (ITEX), in this case the high volume syringe are coated with specific sorbent material with big affinity for the target analytes [25].
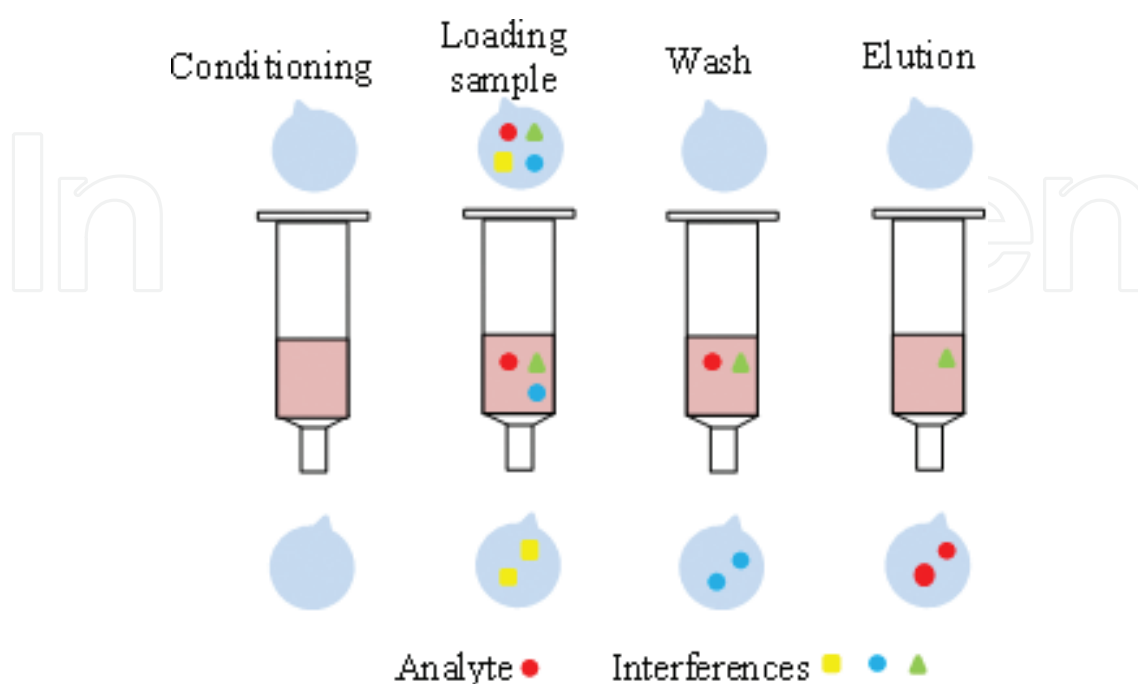

Figure 3. Steps of solid phase extraction SPE.

2.9. New trends in chemical analysis of DBPs

Based on the green chemistry ideology, the new trends in chemical analysis of DBPs advice to lead the sample preparation in route of miniaturization, automation and lower solvent amounts. The first attempts to meet these criteria have been done by Pawliszyn et al. (1989) with the solid phase microextraction (SPME) development [26]. Also, Jeannot [27] in 1997 did miniaturize the liquid–liquid extraction in the form of single drop microextraction (SDME). Then, simultaneously from different origins and countries were developed in 1999: the stir bar sorption extraction (SBSE) and the liquid phase microextraction with hollow fiber (HF-LPME) by Sandra [28] and Pederssen [29], respectively. In 2009, Richter [30] has discovered the rotating disk sorption extraction (RDSE). Thus, in the last three decades smart devices have been invented giving compliment to the goals of the new trends in chemical analysis.

The thermodynamic principles that rules the distribution of analyte from aqueous phase (1) to organic phase (2) are summarized in the next three equations.

$$K = \frac{a_{S_2}}{a_{S_1}} = \frac{[S]_2}{[S]_1} \tag{3}$$

$$R = \frac{K V_2}{K V_2 + V_2} \tag{4}$$

$$EF = \frac{V_1 R}{100 V_2} \tag{5}$$

where

K = distribution or partition constant

$aS_1 = [S]_1$ = Activity or concentration of analyte in aqueous phase

$aS_2 = [S]_2$ = Activity or concentration of analyte in organic phase

V_1 = Volume aqueous phase

V_2 = Volume organic phase

R = Recovery

EF = Enrichment factor

The next extraction techniques to study are equilibrium processes, that means their distribution constants are on strong dependence of temperature, time, ionic force and stirring speed.

2.9.1. Solid phase microextraction SPME

This device consists of a sorbent polymer coating over thin stainless steel wire. It is a robustness, selectivity and powerful technique for volatile compounds, in special for DBPs compounds. There are two working modes: in headspace HS and direct immersion DI. For nonvolatile analytes is possible to lead the derivatization reaction in fiber or out fiber (**Figure 4**).

There are a wide range of polarities of sorbents polymer coatings from nonpolar until polar moieties, allowing a great spectrum of affinities by polarity for extraction of several kinds of molecules, for example, polydimethylsiloxane PDMS, polydivinylbenzene DVB, carboxen [26], and nowadays has been gone gain a lot of terrain, the greener sorbents such as modified clays, cork, agarose, chitosan, magnetite, nanoparticles or nanotubes [31].

2.9.2. Liquid phase microextraction LPME

It is the miniaturization of liquid–liquid extraction (LLE). The basic principle is the distribution or partition of the analyte between aqueous phase and organic phase. The amount of organic phase used is micro amounts from 5 until 30 μL.

2.9.2.1. LPME with protected membrane

In this specific technique, the solvent is supported by a porous polymer membrane. The HF is made in hydrophobic polypropylene (300 μm internal diameter ID; 1.2 mm wall thickness, and 0.2 μm pore size), and act as a filter due to its microporous constitution less than 0.2 μm size pore (**Figure 5**).

2.9.2.1.1. HF-LPME two phases HF-2-LPME

With porous membrane (hollow fiber) used as support for the extractant solvent, there are two specific working modes: in two and three phases. In two mode, the solvent is filled into the hollow fiber (HF) and also dipped into the pores, in other words the solvent is
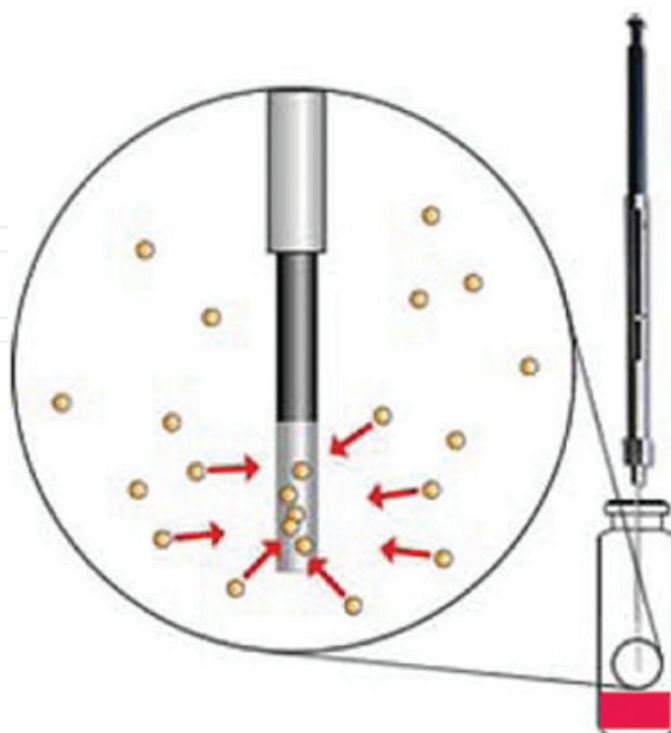

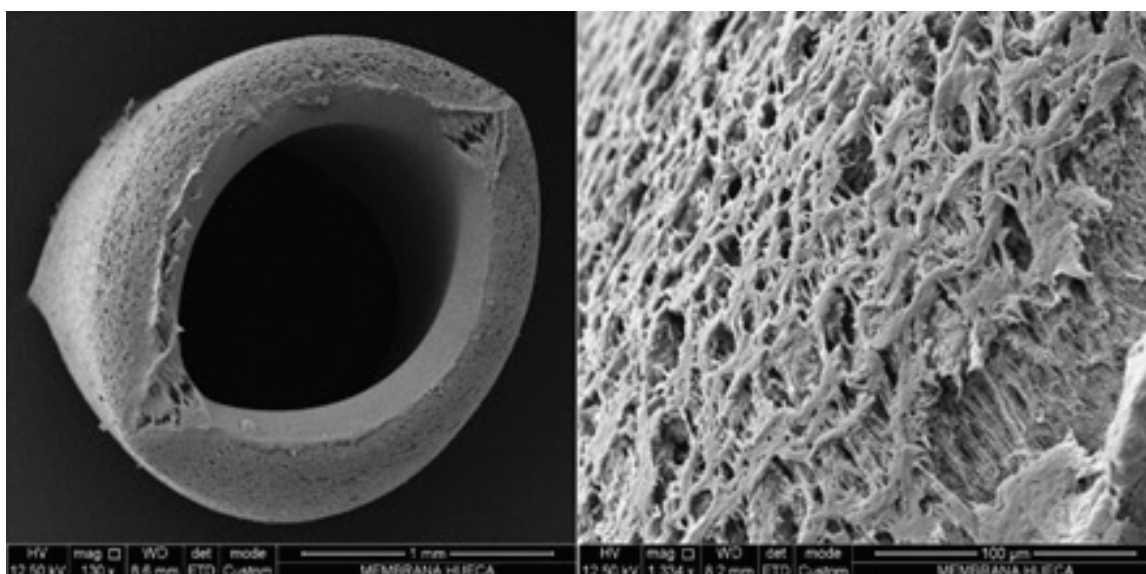**Figure 4.** Schematic representation of extraction device by SPME. Source: [26].

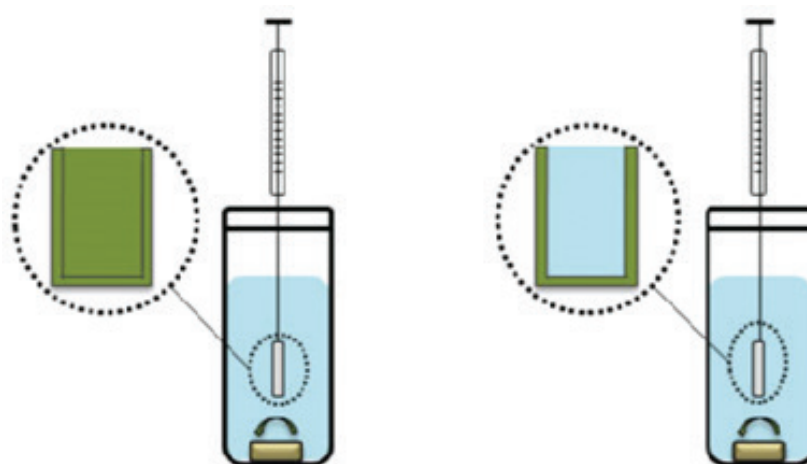**Figure 5.** SEM micrographs of HF.

Figure 6. HF liquid phase microextraction modes: Two phases (left); three phases (right). Source: [1].

immobilized in the membrane pore's and filled inside it (**Figure 6**, https://drive.google.com/drive/folders/1dE94Qe_VhY-U3x0909WPIOWpoPtIvVHg). The force that facilitates the transfer mass is the mass gradient.

2.9.2.1.2. HF-LPME three phases HF-3-LPME

As shown in **Figure 6**, the three phases mode implied the immobilization of the organic solvent into the membrane pores, then outsider and insider of HF, both phases are aqueous, normally in this mode is necessary put a pH gradient to enhance the transfer mass. In the donor phase (outsider), the type of pH (acidic o basic aqueous phase) is on dependence of pKa target analyte, in any case herein is important to assure the molecular or neutral form of target molecule to reach higher affinity with organic solvent, and in the insider phase should turn on to ionic form of the analyte in study to avoid the back extraction.

In 2014, we developed the new microextraction technique on hollow fiber liquid phase micro-extraction (HF-LPME) basis [32, 33]. The enhancement consisted in the functionalization of the HF as solvent bar because the stirring promotes a better mass transfer. For this accomplishment, we put a small stainless steel wire into the HF prior to fill it with extracting solvent (preferably 1-octanol). The new approach was coined hollow fiber solvent bar microextraction (HF-SBME) (see **Figure 7** and https://drive.google.com/drive/folders/1dE94Qe_VhY-U3x0909WPIOWpoPtIvVHg), by adding to the early advantages the possibilities to reduce the Nernst's layer diffusion and enhancing the analyte transfer from aqueous to organic phases.

2.9.2.1.3. Electromembrane extraction EME

The EME is a one class of three phase LPME mode, but now the driven force to assure the transfer mass is the external electric force impost under power supply. The electrodes are made in platinum and the electric field necessary is the 10 V. This kind of technique is especially for ionic or ionizable compounds and biological matrices [29].

The extraction process with electromembrane has been carried out with two platinum electrodes 5 cm in length and applying a 10 V potential with power supply Enduro™ 300 V (Labnet International Inc.), through the semipermeable membrane of 50 mm in length (50 µL acceptor medium). Several liquid extractants that served as supporting liquid membrane (SLM) have been analyzed, for example, ionic liquid hexadecyl methylimidazolium hexafluorophosphate $[C_6MIM][PF_6]$, 1-octanol, 2-nitrophenyl octyl ether (NPOE). For analytes with high values of pKa, a conventional reverse electrode arrangement has been used as shown in **Figure 8** and an acidic acceptor medium has been used, while maintaining the analyte ionized at pH near 7 in the donor media.

2.9.2.2. LPME without protected membrane

Is the classic liquid–liquid extraction LLE but using microvolumes of organic solvent. There are two special techniques:
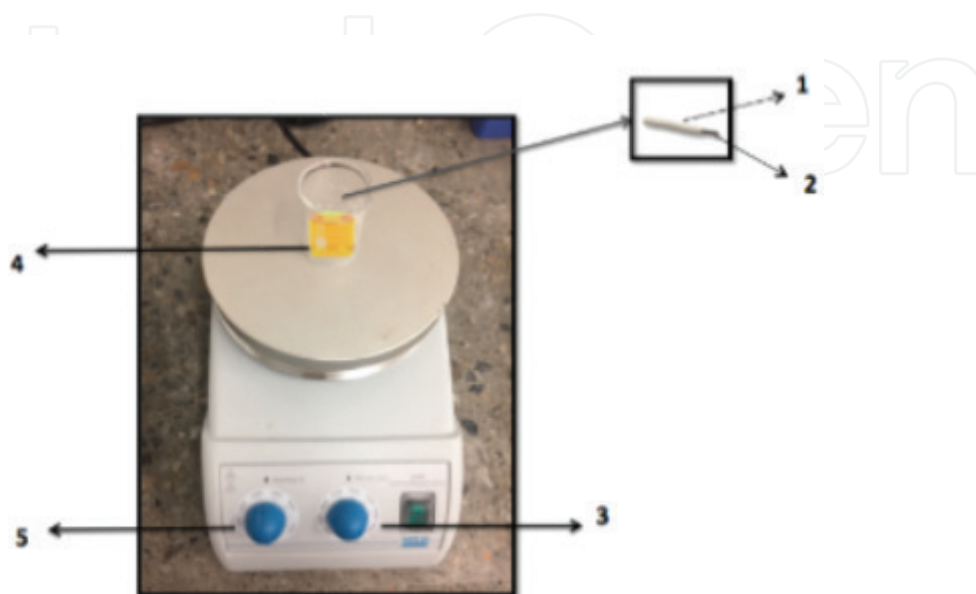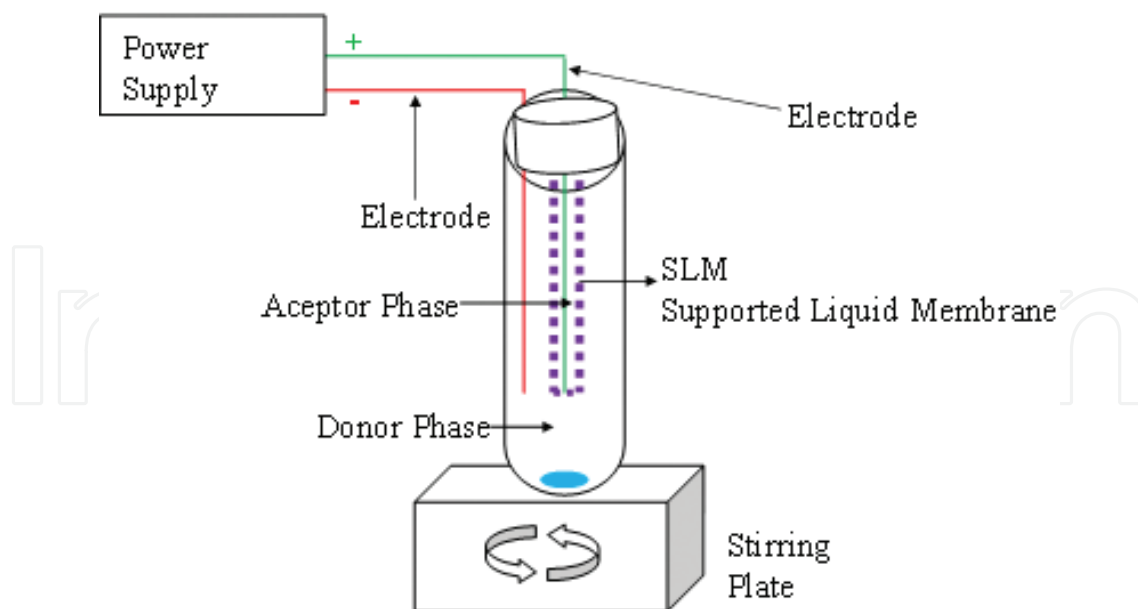

Figure 7. Assembly system of HF-SBME.

Figure 8. Outline electromembrane EME isolation technique.

2.9.2.2.1. Dispersive liquid–liquid microextraction DLLME

This method involves the dispersion of micro amounts of water-insoluble extraction solvent, normally organic solvent (e.g., chloroform, ionic liquids). This solvent is mixed with 100–500 μL of dispersive agent (methanol normally), followed by the addition of 5 mL of aqueous sample. The whole system has been shaken and further centrifuged (3000 rpm) for 10 min. After centrifugation, a portion of the extracting solvent is concentrated and redissolved in 100 μL of methanol prior to chromatography analysis [34] (**Figure 9**).

2.9.2.2.2. Single drop microextraction SDME

Herein, the miniaturization is concentrated in a single drop (from 1 to 5 μL) of organic solvent which is suspended in a 10 μL Hamilton syringe in a proper holder to assure a stability and avoid the breakout of the drop (**Figure 10**). The organic solvent should be viscous, thermally stable and affordable with the chromatographic system. Also, this extraction mode is possible to do in two formats: direct immersion and headspace.

2.9.3. Stir bar sorption extraction SBSE

The last two microextraction techniques are seemed with the SPME, but these have the advantage to facilitate the mass transfer to the solid sorbent from aqueous sample due to device agitation that allows decrease the stagnant water layer (Nernst's diffusion layer). In special for SBSE, the device has a lot of possibilities to reach the wide sorbent polarities from nonpolar to polar moieties (**Figure 11**).

The research group from Lisbon University headed by Nogueira [38] has been developed a miniaturized SBSE coined as BAμE due to smaller size, giving the possibilities the flotation process with the added issue that has a wider range of sorbent's polarities than original SBSE special for polar target compounds inclusively in one same extraction step has been put two
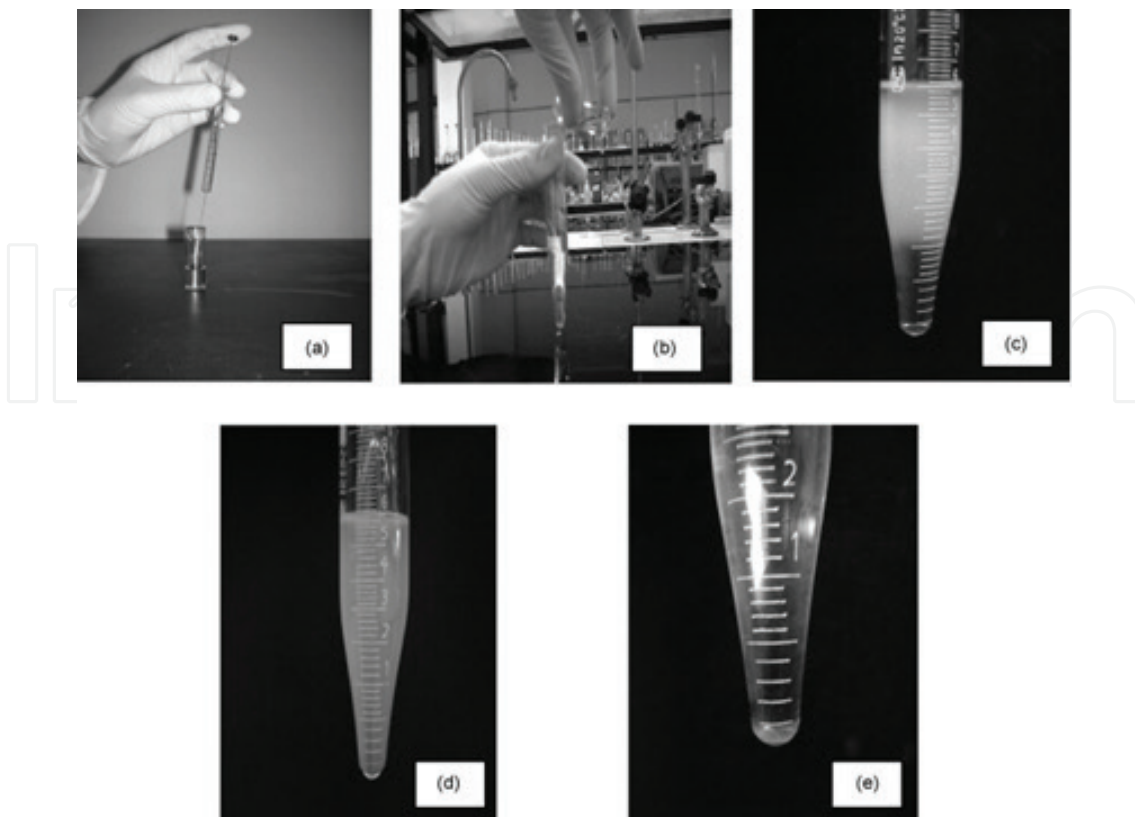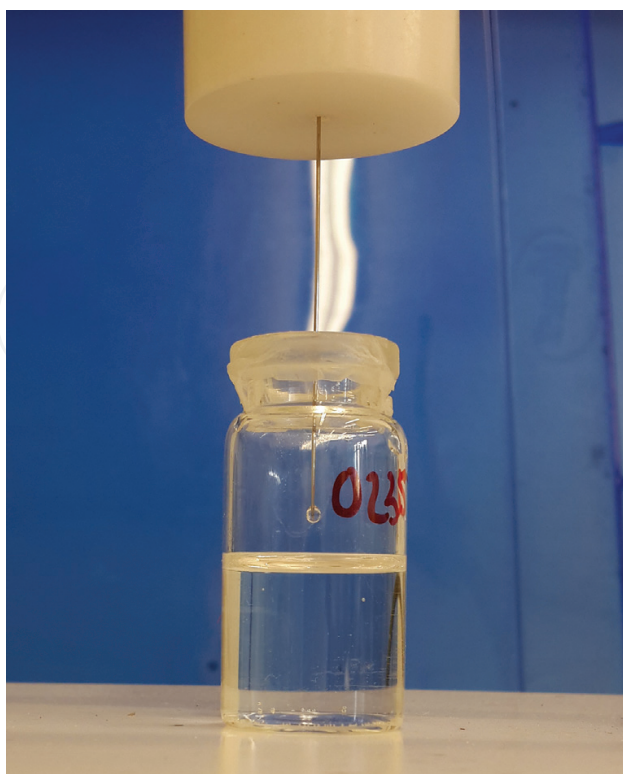
Figure 9. Photography of DLLME. Source: [35].

Figure 10. Assembly for single drop microextraction SDME.

Figure 11. The stir bar sorption extraction (SBSE) representation. Source: [36, 37].

different bars, one of them in flotation and the other one in stirring mode (one bar coated with different sorbent's polarities e.g. PDMS and Carboxen).

2.9.4. Rotating Sorptive disk extraction RDSE

Like that the last microextraction technique, the essential falls in the agitation possibilities, but herein the sorbent phase can be packed or immobilized in the rotating disk made in Teflon with magnet into the body. In both cases, there is no contact between sorbent phase and vial glass of sample, allowing the enlarge shelf life to the extraction sorbent, more tuning abilities respect to the availability of sorbent phases in the market and inclusively faster stirring speed is possible to reach with this device (4000 rpm approx.) and also has the advantage a larger contact surface of the sorbent with the sample allowing satisfactory conditions for extraction and preconcentration of the analytes (**Figure 12**).

2.9.4.1. New sorbent phases and materials

During the last decades, eco-efficiency is acquiring an important position among the typical figures of merit of an analytical methodology [39]. Particularly microextraction techniques have been characterized as a green technology [1] mainly because the use of chemicals is significantly reduced. More recently, the use of eco-sorbents in microextraction techniques have been described such as clays, cork, zeolites, magnetite, biomass, nanotubes, nanoparticules alone or covered with biodegradable material such as agarose, chitosan, polylactic acid PLA, polyhidroxyalcanoate PHA, among others which provides an additional green connotation to this technology [31].

For example, in 2015, we developed a new material by modifying by intercalation way of ionic liquid (IL) based on imidazolium quaternary ammonium salts into the galleries of natural montmorillonite clays (**Figure 13**) has been demonstrated by exhibiting the big possibilities of their use in the extraction and sample preparation field [40]. In this way, the new sorbent MMT-HDMIM-Br developed has been working as a novel solid phase in the rotating disk sorptive extraction with high performance in the PCBs retention, had been exhibited good analytical performance (see **Table 3**).

In 2017, we developed a novel sorptive phase consisting of an ionic liquid intercalated in montmorillonite that has been immobilized onto agarose gel MMT-IL-AF (**Figure 14**). The sorptive phase, a new ecosorbent, has been used in a thin film of 1 mm thickness x 2.5 cm ID
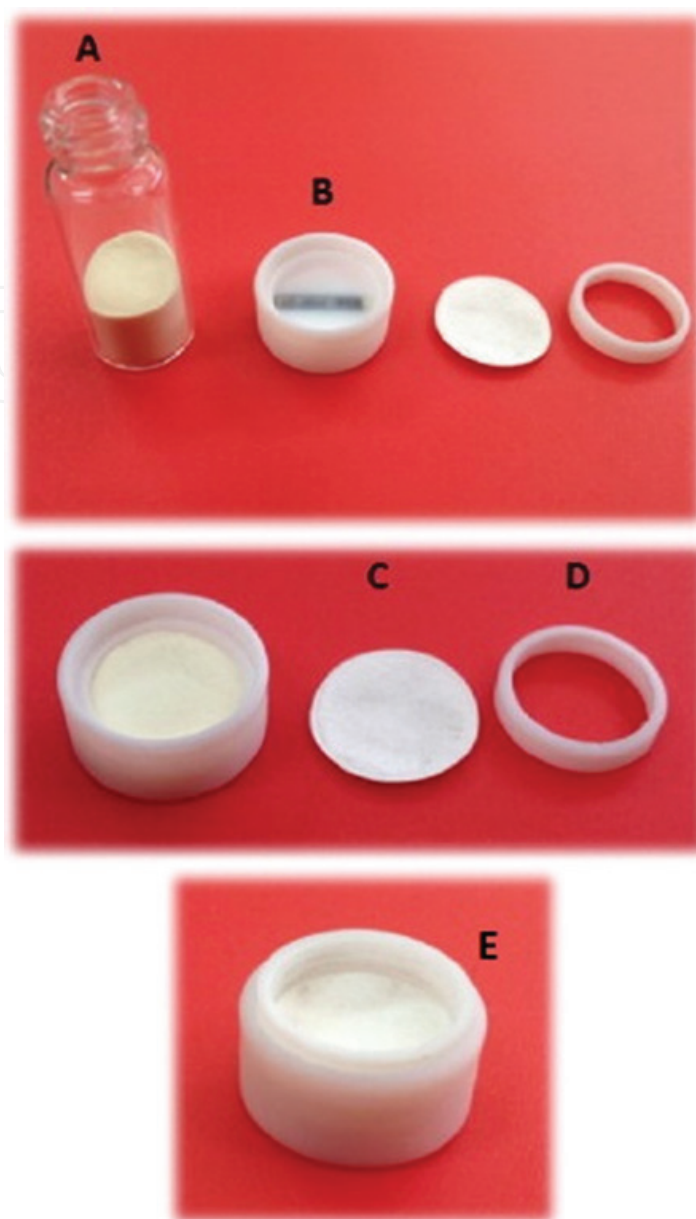
Figure 12. Assembly of rotating sorptive disk extraction (RDSE). Source: [30].
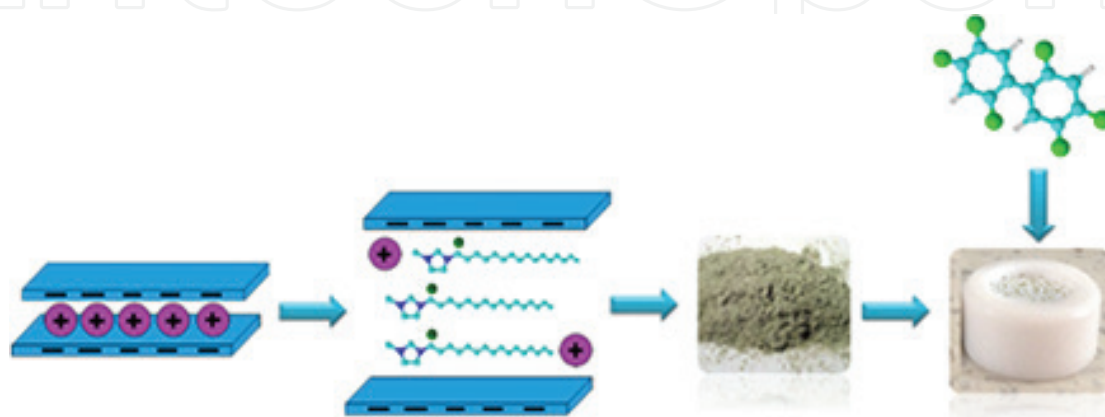

Figure 13. Schematic preparation of new sorbent phase on basis of montmorillonite intercalated with ionic liquids.

Analyte	Matrix	Microextraction technique	Chromatographic system	LoD ng mL⁻¹	LDR ng mL⁻¹	Recovery %	RSD %	Reference
THMs	Drinking water	HF-SBME	GC-μECD	0.017-0.037	10-900	74-91	5.7-10.3	[33]
THMs	Drinking water	HS-SPME	GC-μECD	0.057-0.319	5-200.	74.7-120.9	1.8-11.0	[41]
THMs	Drinking water	HF-LPME	GC-ECD	0.018-0.049	0.88-337.5	80.3-104.2	1.8-3.7	[23]
		HS	GC-MS	0.023-0.102	1.04-230.8	86.3-90.0	6.8-7.8	
HAA	Waste water	EME	HPLC-UV	0.72-40.3 (pg mL⁻¹)	5-200	87-106	2.9-6.7	[42]
HAN	Drinking water	DLLME	GC-MS			79-105		[19]
HAA	River and tap water	SDME	GC-MS			82-98		[19]
THMs	Water	SBSE	GC-HRMS	N.R		N.R		[19]
THMs	Tap and recycled waters	HS	GC-μECD	0.09-0.14	0.1-100		2.4-4.3	[43]
HAN,HK	Drinking water	SPME	GC-MS	2-180	0.01-20	N.R.	4-7	[44]
HAA	Drinking water	SBME	GC-μECD		1-100			[45]
THMs	Drinking water	ITEX	GC-MS	1-10 (pg mL⁻¹)		90-103	< 10	[25]
THMs	Drinking water	SPME with MMT-IL-AF under liquid desorption	GC-μECD	0.020	2-500	> 75	< 12	This work
PCBs	Drinking water	RDSE	GC-ECD	3-43 (pg mL⁻¹)	500-3000	80-86	2-24	[40]
TCS	Drinking water	RDSE	GC-MS	1.8	1000-5000	70		[45]
Parabens	River and Tap waters	RDSE-cork	LC-MS/MS	0.27	0.80-75	80.1-123.9	< 17	[46]
		RDSE-clay		2.0	6-50	82.4-119.9	< 13	
		RDSE-C18		4.2	12.5-100			

LoD: Limit of detection; LDR: Linear dynamic range; RSD: Relative standard deviation.

Table 3. Developed methods for analyzing DBPs (and other halogenated compounds) by using microextraction techniques as sample preparation and greener sorbents.

that was supported onto the top of a rotating disk or as a novel SPME configuration for head space extraction of volatile DBPs (**Figure 14**).

For other side, in 2016, we used the bio sorbents cork and clay for the development of the method for analyzing of four parabens: methyl 4-hydroxybenzoate, ethyl 4-hydroxybenzoate, propyl 4-hydroxybenzoate and isobutyl 4-hydroxybenzoate as the targets compounds because they are widely used as preservatives in daily hygiene products and are associated with the

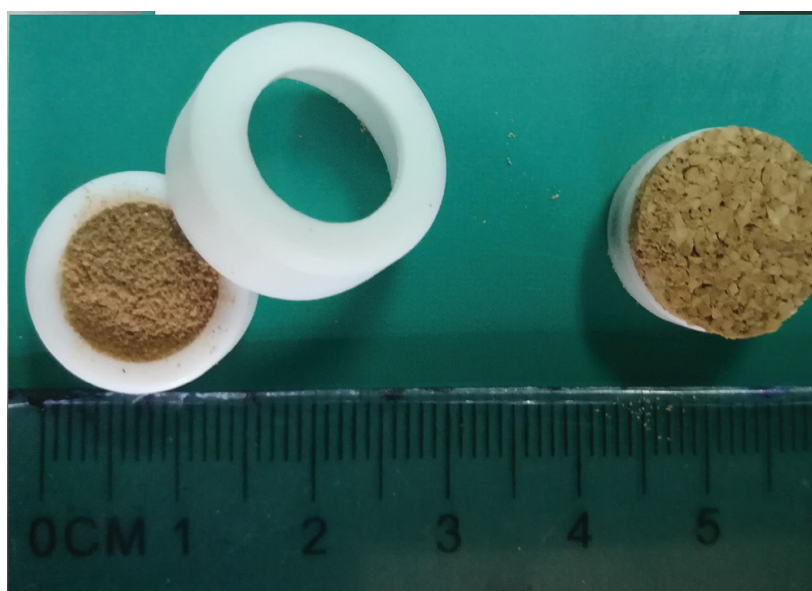**Figure 14.** Preparation of the new eco-material and extraction assembly.

Figure 15. Device used in RDSE.

incidence of cancer. The rotating-disk sorptive extraction (RDSE) was used as supported device for the above mentioned biomaterials (**Figure 15**).

2.10. Sampling and monitoring of aqueous matrices for DBPs analysis

Once reviewed the new microextraction techniques and the possibilities for using greener sorbents, let us present in **Table 3** the different arrangements for the analysis of DPBs by using these new procedure for sample preparation.

3. Conclusions

The existence nowadays over 500 by-products disinfection in low concentrations, by requesting for more sensible and more selectiveness methods of analysis in water samples and all matrices of its whole water's production cycle (wastewater, sludge and surrounded wells

samples) and their big direct implications in the public health, is leading to develop new methodologies for their extraction, signal magnification and validate analysis but inspired in the green chemistry ideology. In this sense, the microextraction techniques, a very interesting role until now have been complied, because in the one whole step, they can isolate, preconcentrate and cleanup the target analytes from proved matrix's interferences using less amounts of toxic organic solvents invocating the necessity of automation and with obviously enhancing of its performance and its analytical figures. Some researchers have been pointed that the new trends in the analysis are requesting for developing greener and more selectiveness sorbents/ solvents by attaching the high performance of the revised miniaturized methods in this chapter with the advantages of these new eco-materials that are biodegradable materials, has been generated less production of waste, and these composites have a wide natural distribution by assuring the equilibrium of the relationships between the man and its environment.

Acknowledgements

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