

# **ELECTROCHEMISTRY**

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Edited by **Mohammed A. A. Khalid**

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## **Electrochemistry**

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## Preface

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Galvani concluded from his experiment in the late 18th century, that the brain is considered to be the most important organ for the secretion of the "electric fluid" and that the nerves conduct the fluid to the muscles. He believed that the tissues acted similarly to the outer and inner surfaces of Leyden jars. The flow of this electric fluid provides a stimulus to the muscle fibers. These conclusions deliver the birth of bioelectrochemistry and membrane electrochemistry.

The fundamental membrane processes of living cells, for example, generation of ion gradients, sensory transduction, conduction of impulses, and energy transduction, are electrical in nature. Each process involves charge movement in a specialized protein structure, where part of the protein forms a channel for conduction of ions. The opening of the channel is controlled by changes in physical factors such as the electrical potential across the membrane or the binding of signaling (e.g., neurotransmitter or hormone) molecules and ions to specific receptor or enzyme sites.

Electrochemistry has been undergoing significant transformations in the last few decades. It is now the province of academics interested only in measuring thermodynamic properties of solutions and of industrialists using electrolysis or manufacturing batteries, with a huge gap between them. It has become clear that these, apparently distinct subjects, alongside others, have a common ground and that they have grown towards each other, particularly as a result of research into the rates of electrochemical processes. Such evolution is due to a number of factors, and offers the possibility of carrying out reproducible, dynamic experiments under an ever-increasing variety of conditions with reliable and sensitive instrumentation. This has enabled many studies of a fundamental and applied nature, to be carried out.

The reasons for this book are twofold. First is to show the all-pervasive and interdisciplinary nature of electrochemistry, and particularly of electrode reactions, through a description of modern electrochemistry. Secondly to show the students and the non-specialists that this subject is not separated from the rest of chemistry, and how they can use it.

The book has been organized into three parts, after Chapter 1 as general introduction. We have begun at a non-specialized, undergraduate level and progressed through to a

relatively specialized level in each topic. Our objective is to transmit the essence of electrochemistry and research therein. It is intended that the chapters should be as independent as it is possible. The sections are: Chapters 2-6 on the thermodynamics and kinetics of electrode reactions; Chapters 7-12 on experimental strategy and methods; and Chapters 13-17 on applications. Also, included are several appendices to explain the mathematical basis in more detail. It is no accident that at least 80% of the book deals with current-volt age relations, and not with equilibrium. The essence of any chemical process is change, and reality reflects this. We have not filled the text with lots of details which can be found in the references given, and, where appropriate, we make ample reference to recent research literature. This is designed to kindle the enthusiasm and interest of the reader in recent, often exciting, advances in the topics described. A major preoccupation was with notation, given the traditionally different type of language that electrochemists have used in relation to other branches of chemistry, such as exchange current which measures rate constants, and given differences in usage of symbols between different branches of electrochemistry. Differences in sign conventions are another way of confusing the unwary beginner. We have decided broadly to follow IUPAC recommendations.

Finally some words of thanks to those who have helped and influenced us throughout our life as electrochemists. First to Professor W. J. Albery FRS, who introduced us to the wonders of electrochemistry and to each other. Secondly to our many colleagues and students who, over the years, with their comments and questions, have aided us in deepening our understanding of electrochemistry and seeing it with different eyes. Thirdly to anonymous referees, who made useful comments based on a detailed outline for the book.

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# Chromatographic, Polarographic and Ion-Selective Electrodes Methods for Chemical Analysis of Groundwater Samples in Hydrogeological Studies

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Ricardo Salgado and Manuela Simões

Additional information is available at the end of the chapter

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## 1. Introduction

The chemical and physical characterization of groundwater and surface water is very important to understand the hydrological and geological dynamic that enriched the water in ions and organic compounds. During the water infiltration and movement into the rocks, the water is subject to numerous interactions between the aqueous and the solid phases through physical, chemical and microbial processes such as dissolution, precipitation, oxidation, reduction, complexation, adsorption and desorption, filtration, gas exchange, evaporation, biological metabolism, isotopic redistribution and anthropogenic influences [1]. Groundwater in solution may have a high quantity of inorganic and organic compounds. Its contents are the combined result of the composition of surface water when entering the unsaturated zone of the soil and reactions with minerals in the rock that may modify the water composition. As a result, groundwater contains dissolved solids and gases (CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>S) according to its initial composition, type of the rock, the partial pressure of the gas phase, pH and oxidation potential of the solution. The major ions that can be found in water are chloride, sulphate, bicarbonate, carbonate, sodium, potassium, calcium and magnesium against many others in reduced concentrations (<10 mgL<sup>-1</sup>) such as iron, manganese, fluoride, nitrate, nitrite, cadmium, lead, chromium, strontium, arsenic and boron. Apart from these natural processes, the water also suffers from contamination by human activities. Solutes, such as heavy metals and organic solvents, are chemically introduced in the water systems mostly in the unsaturated zone. When water is in contact with pore gases contaminants there may be transference between the liquid and the gas states. This is an important way of volatile compounds to migrate from the subsurface. After dissolved in

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water, these compounds can persist for a long time as a separate liquid phase which has prejudicial effects for the human life and the ecosystems. One of the aims of the water analysis is to obtain better knowledge concerning the water quality, residence times in the aquifer, age, recharge areas, flow paths, and also a potential or prohibitive use due to human pollution problems.

A high number of analytical analysis with several traditional techniques are no longer adequate for this purpose and the development of more green analytical techniques that can measure different ions and organic compounds with the same technique are more suitable. Over the last few decades there has been an increase growth of equipments capable of measuring very low concentrations and also analytical procedures that could concentrate the compounds and increase the signal detected, allowed the hydrogeologist to get more information about the chemical characterization of the groundwater. Equipments, such as chromatography, sensors and microdevices (e.g. microelectrodes), has undergone extraordinary developments. Most of these new analytical instruments have a lower limit to the range in which the results can be quantified and below that range where a compound can be detected but not quantified or as not detected. The quantification limits can be helpful tool for the decision to select the analytical method and equipment for the determination of a specific parameter for the hydrogeological study.

The chromatographic methods applied for the determination ions and organic compounds can be more appropriated in some cases, however the electrochemical techniques such as polarography and voltametry and the ion-selective methods can also be an alternative. The chromatographic methods can be applied to measure ion concentrations such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{F}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  (ion chromatography) and to measure organic compounds using liquid chromatography (HPLC) with UV detectors (e.g. photodiode array detector (DAD)) and/or coupled with mass spectrometry such as water soluble pesticides and pharmaceuticals or gas chromatography (GC) to measure volatile organic compounds such as polycyclic musk fragrances. The polarographic and voltametric electrochemical techniques can be an option to measure the concentration of organic compounds (e.g. pharmaceuticals) as well as in the same way the ion-selective electrodes for some specific ions in water matrices.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  can be measured by ion-selective electrodes and in some cases this techniques is more advantageous than the chromatographic.

Pharmaceutical active compounds (PhAC), persistent personal care products (PPCPs) and pesticides are commonly occurring as micropollutants with a potentially significant environmental impact. The growing use of pharmaceuticals is becoming a new environmental problem, as both via human and animal urinary or fecal excretion and pharmaceutical manufacturing discharges, increasing concentrations of pharmaceuticals reach sewage treatment plants (STPs). Due to this extensive use, high concentrations of drugs are found in sewage, depending on their half-lives and metabolism. STP is therefore often ineffective in removing these substances, so that varying concentrations of them can be found in surface and groundwater.

The impact in the environment and public health arises not only from wastewater effluents discharged in aquatic media [2, 3], but also from sludge application in agriculture, since they can desorb and contaminate the groundwater [4]. PhAC and PPCPs are becoming increasingly recognised as important micropollutants to be monitored in different matrices, groundwater, surface water drinking water and wastewater. The aquifer recharge with treated wastewater can represent an important point source of ions and organic compounds to natural aquatic systems. Due to the fact that analytical approaches normally used to quantify the abundance of these compounds are labour intensive and require various specific procedures, more simplified analytical methods need to be employed for the quantification of pharmaceutically active compounds (PhACs) and polycyclic musks in liquid and solid samples. Many studies have been carried out in different countries and geographical locations [5], the occurrence of PhAC and PPCPs in wastewater and environmental samples is highly dependent on the local diseases, treatment habits and market profiles, thus, the pollution profile and can vary significantly between different countries [5]. PhACs include many families such as antidepressives, anticonvulsants, non-steroidal anti-inflammatory drugs (NSAID), steroidal anti-inflammatory drug (SAID), drugs for asthma and allergic diseases, antihypertensives,  $\beta$ -blockers, lipid regulators, antibiotics, and estrogens [6]. Due to the high diversity of compounds displaying a wide variance of chemical structures, many previous studies have elected to perform a combination of analytical methods targeting specific families of compounds [7, 8]. While this strategy can be advantageous with respect to the analysis of each target group, the time-consuming and labour-intensive nature of the analytical procedures makes a high number of different methodologies undesirable when the goal of the study is to make an overall assessment of PPCPs present in environmental samples. Most of the PhACs can be analysed through High Performance Liquid Chromatography coupled with mass spectrometry HPLC-DAD-MS with the MS working with electro spray ionization in positive (ESI+) or negative (ESI-) mode with the same set of conditions after solid-phase extraction (SPE) using different adsorbent materials according to the neutral or acidic properties of the compounds. The musks are non-polar and volatile organic compounds and can be analysed by GC-MS after solid-phase microextraction (SPME) with different extraction fibres [9].

The polarographic and voltametric methods have been widely used for the analysis of organic compounds in samples of natural origin. However, the voltametric methods have not been widely explored for the analysis of many PhAC. The voltametric technique most used for PhAC is the direct current polarography (DCP) and differential pulse polarography (DPP) methods for the analysis of PhAC in water samples [10, 11]. The use of glassy carbon electrode has been suggested for linear sweep and cyclic voltammetric studies for some PhAC such as nifedipine [11]. Adsorptive cathodic stripping polarographic determination of trace PhAC has been reported with high sensitivity. The detection limit obtained by these methods can be found lower or comparable to other known methods as well as the linearity range obtained. Precision of the method developed implies very low values of relative mean deviation, standard deviation and coefficient of variation. Recovery experiments showed that these methods can be used for quantitative analysis and errors of  $\pm 0.2\%$  can be expected. The studies have shown that the polarographic and voltametric methods are

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simple, reproducible and accurate and can be used to determine many PhAC in the groundwater. Despite the sophisticated instrumentation of analytical tools, complete noninvasive measurements are still not possible in most cases. More often, one or more pretreatment steps are necessary; whose goal is enrichment, clean-up, and signal enhancement during a process of sample preparation [12].

## 2. Groundwater monitoring plan: Sampling procedure and frequency

The groundwater monitoring plan is determined according to the needs to implement a water quality monitoring program as part of their Source Water Protection Plan. The decision is based, in part, on the high susceptibility of the aquifer and past detections of groundwater contamination and also on the characteristics of the aquifer (confined or unconfined and the soil characteristics (e.g. sand and gravel)). The thin veneer of soil at the ground surface is not a significant confining layer and cannot serve as a barrier to contaminant movement between the ground surface and the aquifer. In addition to the identified aquifer vulnerability, the groundwater contamination by volatile organic compounds (VOC's) can be measured in the source water supply from an unconfirmed spill. Although the detections will show the maximum contaminate levels, and their presence demonstrates the risk of contamination is real. The design of sampling and analysis plan include the top management priorities for developing control strategies in the source water protection plan, such as agricultural chemicals and chemicals associated with auto repair/body shops. Other concerns include underground storage tanks, potential spills along transportation routes, and surface water sources and source of water assessment included in the list of priority contaminants (Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy). In the groundwater monitoring plan, some groups of the compounds that can be included are:

1. Volatile Organic Compounds (VOCs); a group of potential pollutants that includes many solvents, musk fragrances which are the organic chemical constituents that are most commonly found in groundwater effected by domestic, commercial or industrial operations.
2. Synthetic Organic Compounds (SOCs); particularly those constituents which include the most common herbicides and pesticides and pharmaceutical active compounds found in ground water from human activities such as agriculture and domestic activities.
3. Inorganic Compounds: this will include those chemicals found in ground water most associated with agricultural land use or deicing of roadways. Nitrate and chlorine are the primary contaminants of concern.

Prior to purging and sampling a monitoring well during each monitoring event, the depth to water in the well is measured from a reference point at the top of well casing using an electric ullage tape. Using this measurement to calculate the volume of water in the well, three well volumes will be extracted by bailing. After purging, a sample will be collected for field measurement of the selected indicator parameters; pH, specific conductance, redox

potential and water temperature. Results of these measurements will be recorded on the appropriate field sampling form. Next, water samples will be obtained using the dedicated bailer for the required VOC, SOC and inorganic parameters. Upon collection, these samples will be properly labeled and stored in an iced cooler for shipment to the contract laboratory. Finally, one additional sample will be collected from the well and a second field measurement of the indicator parameters will be made. A very large volume of water sample should be collected (e.g 5 L) to analyse organic compounds and it should be collected to plastic (PET) bottles and preserved at 4°C in an isothermal bag during transportation to the laboratory. The purpose of purging – removing water continuously from the well – is to ensure that the water sampled is fresh groundwater and not stagnant casing water, which may differ significantly in quality. The use of bottom loading PVC bailers as the type of sampling equipment to purge their monitoring wells and draw samples is commonly used in the groundwater sampling. This technique is the least expensive to implement and works well with shallow monitoring wells. The purchase of a dedicated bailer for each monitoring well, will eliminating the need for decontamination between sampling events. To insure the removal of casing water and for consistency between sampling events, the technician collecting the water samples will remove three well volumes prior to sample collection. This is a conservative and accepted protocol for groundwater sampling in prolific aquifers. This suggests representative water samples from the monitoring well could be obtained just after one well volume is removed.

The sampling frequency can be defined according to the previous experience of monitoring a specific aquifer. Assuming the results for the first year groundwater monitoring, and near the spring, confirms water quality results in a well within anticipated and acceptable levels, subsequent years monitoring events can be defined as semi-annually. Preferably, sampling of monitoring wells will occur in the spring and fall of each year to better define the water quality of the aquifer at periods of high and low water levels. The collected groundwater samples will be analyzed for the same set of constituents measured during the first year of monitoring.

### **3. Groundwater sampling and field analysis**

In the sampling process of surface or groundwater, it is important to define the purpose of the collecting program, number of samples to be tested, which physical parameters and chemical constituents will be analyzed, as well as where the samples will be collected. It is difficult to obtain samples that accurately reflect the composition of groundwater in the aquifer conditions because the pressure and oxygen concentration change considerably during the sampling process. As a result, the temperature, Eh and pH of the water can change too. Atmospheric oxygen oxidizes components, which are commonly found in anoxic groundwater. Also the degassing of CO<sub>2</sub> will increase the pH causing carbonate precipitation (CaCO<sub>3</sub>) and concomitant loss of alkalinity.

Most of this type of problems can be overcome by carefully sampling and measuring some parameters in the field such as pH, SC, Eh, and temperature, and a pressurized sample for alkalinity determination. Alkalinity can be rapidly quantified in field by the titration

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method using a burette or a field alkalinity kit. In some cases, a down-hole determination of temperature, pH, specific conductance, and redox may be needed in conjunction with down-hole sample collection. Hence, any pressure-dependent reaction that will affect the water will result in different values for samples collected in situ and at the well head.

In addition, conservation of samples is typically done to ensure that they retain their physical and chemical characteristics. In the field, it is important to collect samples in clean sample bottles (500 mL high-density polyethylene bottles with polypropylene screw caps), preserve them by cooling, freezing, or acidification immediately after collecting and then storing in a chilled vacuum container in a dark place before transportation to a laboratory for analysis. It is good field practice to clean the sampling device prior to use providing that no residue remains. For that, bottles and devices should be rinsed with a sample of water being sampled to prevent any contamination. After use, acetone and distilled water can be used to rinse thoroughly.

Frequently, nitric acid is added for metals preservation, since it prevents adsorption or precipitation of cations. At the same time, the acidification limits bacterial growth and, as an oxidant, converts ferrous iron to ferric iron and precipitation as FeOOH. Before being analyzed, the samples can usually be preserved for all inorganic compounds during 28 days, at 4°C.

### 4. Analytical methods for inorganic compounds

The analytical measurement can be either qualitative or quantitative and a very large variety of instruments and techniques can be used for different types of analysis, depending on the cost, information, accuracy, and precision acquired. In most laboratories today, ion chromatography (IC) has replaced older methods of ion analysis because it offers superior sensitivity, accuracy, and dynamic range. Also, it is environment-friendly, extremely fast and versatile. Therefore, this method is particularly advantageous in the analysis of low concentrations as such in high-purity water. IC can also be used for detection and quantification of different ion species in a wide variety of water samples. However, older techniques that do not provide such high results are still in use.

With the purpose of proceeding to the efficient chemical characterization of water and to turn possible the comparison among results, laboratories, hydrogeologists and others have developed sampling protocols. For environmental analysis and determination of inorganic ions in drinking water the EPA (United States Environmental Protection Agency) publishes laboratory analytical methods (most of these methods - 120.1, 130.1, 150.2, 200.7, 206.5, 218.6, 300.1, 365.4, etc. - are published as regulations in the Code of Federal Regulations (CFR) at title *Part 136* and *40 Parts 401-503*), and specifies the type of sample that is needed, the type of sampling container to be used, the method by which the sample container is cleaned and prepared, whether or not the sample is filtered, the type of preservative that is to be added to the sample in the field, and the maximum time that the sample can be held prior to analysis in the laboratory [13].

#### 4.1. Ion chromatographic method

Chromatography is a wide range of physic-chemical separation processes in which the components to be separated are distributed between a stationary and a mobile phase. The name for each of the various types of chromatography depends on the state of aggregation of these two phases. The introduction of high pressure in the separation system and the hardware with software for calculation of the peaks, gas and liquid chromatography have developed into one of the most comprehensive and important methods of modern instrumental analysis. Many ions (anions or cations) in the test sample are separated and quantified quickly and with high precision by an ion chromatographic system containing a guard column, a separator column, with or without suppressor device, and are measured using a conductivity detector. In the technique with chemical suppression, the background conductivity is suppressed both chemically and electronically. In contrast, the direct chromatographic technique employs eluents with salts of organic acids in low concentration on ion exchangers of very low capacity to achieve relatively low background conductivity, which can be suppressed directly by electronic means. This method is applicable to the determination of bromide, chloride, fluoride, nitrate-N, nitrite-N, orthophosphate, sulphate, calcium, potassium, sodium, magnesium and ammonium, in water.

#### 4.2. Potentiometric titration method

The water analysis is not completely done if the carbonate and bicarbonate ions are not determined. Using the alkalinity concept, which is the capability of water to neutralize acids when the presence of calcium and magnesium carbonate ions in it is very high, it is possible to quantify the carbonate and bicarbonate ions. The total alkalinity is the contribution due to all bicarbonates, carbonates, and hydroxides present in the water; and it can be determined by potentiometric titration of an unfiltered sample (100 mL) with a standard solution of strong acid ( $\text{HCl } 0.1 \text{ molL}^{-1}$ ) and phenolphthalein (from pH 8 to pH 10) or methyl orange (from pH 3.1 to pH 4.4) as indicator. The result is expressed as  $\text{meqL}^{-1}$  of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ , i.e., the volume equivalent of acid added to the water until it changes colour. This method is applicable to all types of water in the range 0.5 - 500  $\text{mgL}^{-1}$  alkalinity as  $\text{CaCO}_3$ . The upper range can be extended by dilution of the original sample [14].

#### 4.3. Ion-selective electrode method

Ion-selective electrode methods are regularly used to determine many parameters of water in field and laboratory due to their versatile sensors. They are applicable in many situations for the determination of pH, electrical conductivity (EC), hardness, calcium, sodium, potassium, magnesium and others. The electrodes coupled to a multi-parameter analyzer are designed for the detection and quantify of physical and chemical parameters with calibration for any range of values. For example the potassium ion selective electrode consists of an inert fluorocarbon body with a detachable PVC membrane unit, on the end of which is glued the ion selective membrane. The electrical potential of an ion selective electrode is a function of the activity of certain ions in an aqueous solution. This potential

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can only be measured against a reference electrode, such as a saturated calomel electrode, placed in the same solution. The electrode should be used in the pH range 4-9.

The problem associated with results obtained with ion-selective methods is the uncertainty caused by instable equilibrium depending on the ionic-strength of the solution. When the electrode is placed in a water sample, the response time may go from 1 to 10 minutes or even much more, and the equilibrium point varies in conformity to the type of electrode and the parameter in measure. In the daily life of a laboratory, the main difficulty is associated with inaccurate results related to the sodium electrode because of interfering ions in the sample. Also, the response time increases considerably because of that. Another issue is the short lifetime of the membrane which, in good performance, does not extend to more than a year if it works every day. In order to produce acceptable measurements, it is highly important that the electrode chosen is in conformity with the sample characteristics.

## 5. Analytical methods for organic compounds

### 5.1. Sample preparation for chromatographic and electrochemical methods

The selection and application of the most appropriated analytical technique is related with the proprieties of the organic compound to be identified and quantified in the different samples. Among the proprieties, some of the most important are the acid-base characteristic of the compound, the polarity (polar or non-polar compounds) and the adsorption capacity measured by the octanol-water partition coefficient ( $\log K_{ow}$ ) reported for many of the organic compounds. Values of  $\log K_{ow} < 2.5$  correspond to low adsorption potential,  $2.5 > \log K_{ow} > 4.5$ , to media adsorption potential and  $\log K_{ow} > 4.5$  to high adsorption potential [15]. The adsorption not only depends of the hydrophobicity but also from the electrostatic forces and pKa of the compound [16]. There is a linear relationship between the  $\log K_{ow}$  and the pKa of the most of the organic compounds [17]. Organic compound with high adsorption potential are mostly present adsorbed in the solid matrices and need a previous extraction procedure to a liquid phase before the analysis by chromatographic and electrochemical methods. The polar compounds present in water samples can be analysed taking to account the acidic or basic proprieties and most adequate adsorption media for clean-up and pre-concentration technique. The low concentration ( $\text{ngL}^{-1}$  or  $\text{pgL}^{-1}$ ) mostly frequent of the organic compounds in water samples justifies the previous concentration step by the use of solid-phase extraction (SPE) methods. The non-polar compounds present also in low concentration in water samples need also a previous clean-up and pre-concentration technique by the use of solid-phase micro extraction (SPME) before analysis by chromatographic methods.

#### 5.1.1. Solid phase extraction (SPE)

Solid-phase extraction (SPE) is the most used clean-up technique for pre-concentration of water (surface, groundwater) and wastewater samples prior to analysis of the organic compounds. The samples should be previously filtered by  $0.45 \mu\text{m}$  glass fibre membranes (GF 6,  $<1 \mu\text{m}$ , diameter 47mm from Wathman, England) and stored at  $-20^\circ\text{C}$  before analysis

by SPE. Different sorbents can be used for clean-up the samples: Oasis HLB (hydrophilic lipophilic balance) cartridges and reverse phase Sep-Pak C18 cartridges, which assures good recovery of compounds in a wide range of polarities. For most of the organic compounds, Oasis HLB and reverse phase (RP C18) as SPE cartridges are the most used in literature due to the polar nature of the compounds and the acidic and neutral characteristics e.g PhAC [18,19]. The selection of the SPE media is directly related with the proprieties of the compound (e.g. acidic or neutral characteristics. RP C18 is most appropriate for the neutral and Oasis HLB general it can be more appropriate for the acidic compounds.

SPE was used for the extraction and clean-up of the liquid wastewater samples. OASIS HLB cartridges (60 mg, 30  $\mu\text{m}$ , Waters, Eschborn, Germany) is used for the acidic organic compounds (e.g acidic PhACs) and RP-C<sub>18sec</sub> cartridges (500 mg, 50  $\mu\text{m}$ , Waters, Milfort, U.S.) is used for the neutral organic compounds (e.g. neutral PhACs). Each cartridge was previously conditioned with 1 mL methanol followed by 1 mL of Milli-Q water, then dried in a N<sub>2</sub>-stream. For the acidic PhACs, 200 mL of filtered water and 10  $\mu\text{l}$  of an internal standard were passed through the OASIS HLB cartridges at pH 2-3. For the neutral, 500 mL of filtered water and 50  $\mu\text{l}$  of internal standard (e.g. meclofenamic acid) is passed through the RP-C<sub>18sec</sub> cartridges at pH (7-7.5). Samples passed through the SPE cartridges at a flow rate of 20 mL min<sup>-1</sup> and vacuum pressure of -5 psi, then the cartridges is eluted four times with 1 mL of methanol. The methanol extracts are evaporated to 1 mL by a gentle nitrogen stream. Then, 50  $\mu\text{l}$  of extract are injected into the LC-MS.

For the extraction of the organic compounds (e.g PhAC) adsorbed to the soil, sludges and solid samples, the procedure consists of ultrasonic solvent extraction (USE) using solvents (e.g. methanol/acetone) or pressurized liquid extraction (PLE) using 100% methanol. After this extraction step, non-selective, an additional clean-up can be performed with SPE [19]. The method most commonly used for extraction from solid phase is the ultrasonic solvent extraction (USE) prior to SPE. In this method, the solid sample is centrifuged for 5 min at 10 000 rpm. 2 g of the centrifuged solid sample is for extraction of the organic compounds adsorbed. The concentrated sample is mixed with 4 mL methanol in an ultrasonic bath for 5 min. The slurry is then centrifuged for 1 min at 10 000 rpm. The supernatant is collected in a separate vial and 2 mL of methanol is again added to the solid sample. Centrifugation and supernatant collection is then repeated. To ensure the extraction is complete, 2 mL of acetone is then added to the solid sample and the same procedure (i.e. ultrasonic bath, centrifugation, supernatant collection) is repeated. Then, the 4 extracts (2x2 mL of methanol and 2x2 mL of acetone) are combined and evaporated to a volume of ca. 1 mL. The concentrated extract is diluted in 150 mL of Milli-Q water prior to SPE.

#### 5.1.2. Solid phase micro extraction (SPME)

The most used technique for the determination of the non-polar (e.g polycyclic musk fragrances (PMF)) in water, wastewater, soil and sludge samples of the WWTP is the headspace solid-phase micro extraction (SPME), followed by GC-MS analysis [19]. SPME is also a pre-concentration and clean-up technique previous to analyze by GC-MS. Due to their elevated lipophilicity ( $\log K_{ow} = 5.90-6.35$ ), most of non-polar organic compounds are,

therefore, sorbed onto soil or sludge and suspended matter. In literature, analytical methods are reported for analyzing polycyclic musk fragrances (PMF) in soil, sediments and sludge using soxhlet or pressurized liquid extraction (PLE) with dichloromethane, silica gel, alumina columns and gel permeation chromatography (GPC) as clean-up methodology previous to GC-MS analysis [18]. In all the cases, several clean-up steps must be applied to the extracts before chromatographic analysis. The SPME is a solventless technique that simplifies the long and tedious processes of sample preparation and analyte extraction in a single step. The SPME technique is a very sensitive technique that can be applied to adsorb the volatile and non-polar compounds released from the aqueous or solid phase to the headspace completely isolated where a fiber of an adsorbable material or can be immersed in the liquid sample to extract selectively the target compounds [20]. The fibers can be of polyacrilate (PA), polydimethylsiloxane (PDMS), divinylbenzene (DVB), PDMS/DVB and carboxen-PDMS (CAR-PDMS) and carbowax-DVB (CW-DVB), carboxen-PDMS-DVB (PDMS-DVB-CAR) and they are selected according to the characteristics of the compound that need to be extracted. The head space technique is more used than the immersed fiber in the liquid phase due to the matrix characteristic of some samples that are inappropriate for the submerged fiber.

The extraction of non-polar organic compounds (e.g. musks) from the water, wastewater, soil, sediment and sludge samples was carried out by solid phase micro extraction (SPME) with fibres previously described. The fibres are pre-conditioned prior to use for 30 min at 250 °C. 2 g of sample is added to a vial with 0.5 g NaCl and 10 µL of an internal standard. The fibre was exposed to the sample headspace in a sealed vial with a Teflon lid for 15 min at 90°C. The fibre was thermally desorbed and analysed by GC-MS.

Sludge is a very complex sample and the extraction of the organic pollutants from the matrix usually implies solvent extraction of the dried soil or sludge samples assisted by accelerated solvent extraction, sonication, microwave heating, solid phase extraction (SPE), simple agitation or solid phase micro extraction (SPME). The determination of non-polar organic compounds in solid samples samples by SPME with different fibers can be influenced by the extraction temperature, fiber coating, agitation, pH and salting out on the efficiency of the extraction. An extraction temperature of 100 °C and sampling the headspace over the stirred sludge sample using PDMS/DVB as fiber coating lead to best effective extraction of the musks in general. The method proposed is very simple and yields high sensitivity, good linearity and repeatability for all the analytes with limits of detection at the ngg<sup>-1</sup> level. The total analysis time, including extraction and GC analysis, in only 40 min, and no manipulation of the sample is required. The GC-MS with MS in electronic impact (EI) in positive mode analytical technique is the most appropriate for the identification and quantification of the polycyclic musk fragrances (PMF) [9].

### 5.1.3. Chromatographic analysis of organic compounds

The liquid chromatography coupled with mass spectrometry (LC-MS), liquid chromatography tandem mass spectrometry (LC-MS/MS) and liquid chromatography with diode array detector and coupled with mass spectrometry (LC-DAD-MS) with MS in