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**Chapter**

# Sample Preparation Techniques for Electrochemical Analysis of Pesticides and Heavy Metals in Environmental and Food Samples

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## Abstract

The development of an analytical methodology commonly includes sampling and sample pretreatment-preparation. The sample preparation step should provide the analytes (pesticides, heavy metals, drugs, dyes...etc.) in an adequate medium (typically aqueous or non-aqueous solution) to be detected and/or quantified. It is, therefore, necessary to ensure that the sample is homogeneous and free of interferents, as long as the preparation step is the most significant source of error in the analytical method development and is the most time-consuming step especially when solid samples are analyzed. Given its importance, this preparation step has a fundamental importance in the overall analytical method development, mainly when electroanalytical methods are applied. In this chapter, the steps involved in preparing samples for electrochemical analysis will be described in detail. Specifically, we will be focusing on the sample preparation techniques for the electrochemical analysis of pesticides and heavy metals, in environmental and food samples. For non-electrochemical readers, a brief introduction to the most commonly used electroanalytical methods will be described.

**Keywords:** electrochemistry, pesticides, heavy metals, samples preparation, environment, food

## 1. Introduction

Nowadays, several methods for the analysis of compounds such as chromatography, mass spectrometry, fluorescence, ultra-violet (UV–Vis) spectroscopy, electrophoresis, electrochemistry, etc. have been elaborated and are still used by researchers. The last mentioned has become the most popular since it has been established to be the

discipline at the interface between the branches of chemistry and many other sciences [1]. In a simple word, the relationship between electricity (movement of electrons) and chemistry (transformation) is known as electrochemistry, which is the science of the application of electricity to chemistry [2]. As a science, it is combined with other discipline, showing its high potential in biology (bio-electrochemistry), catalyst (electro-catalyst), kinetic (electro-kinetic), photolysis (photo-electrochemistry), etc. As a technique of analysis, it is coupled to many other classical methods of analysis to form new hybrid methods more performant such UV–Vis/electrochemistry, electrochemistry-liquid chromatography-mass spectrometry (EC-LC–MS) largely used recently [3].

Electrochemistry studies the links between chemistry and electricity. One of the electrochemical techniques is voltammetry, which is very popular for electroanalysis. By applying a potential (or a current), it is possible to measure the resulting current (or potential) [4]. The identify electroanalytical methods generally used from the most sensitive to the less one are anodic stripping voltammetry (ASV) and cathodic stripping voltammetry (CSV), linear sweeping voltammetry (LSV), normal pulse voltammetry (NPV), square-wave voltammetry (SWV), differential pulse voltammetry (DPV), chronoamperometry/chronocoulometry (CA/CC), cyclic voltammetry (CV), and polarography [5]. All of these techniques used a common electroanalytical setup constituted of a cell, a potentiostat, and a computer. The cell contains the supporting electrolyte (SE) with the sample to be investigated, and three conventional electrodes (working electrode WE, reference electrode RE, and auxiliary electrode AE) connected to a potentiostat used to allow the passage of the current between the WE and AE, and to establish the potential between WE and RE. This happens during the transformation/redox mechanism of the analyte, and the responses collected in the potentiostat are transferred to the computer for interpretation [4, 6].

Due to the facility, rapidity, low cost, and performance of electrochemistry to provide information on the electron transfer of the system, several types of analytes can be investigated using electroanalytical method. Pesticides, heavy metals, dyes, food additives, endocrine disruptors, pharmaceutical compounds, etc. are the different family of samples generally analyzed. The sample preparation of the first two listed (pesticides and heavy metals) will be investigated in this work.

Pesticides are substances intended to repel or combat any undesirable plant or animal species, during the production, storage, transport, distribution, or processing of foodstuffs intended for human or animal consumption. They are classified into three main classes which are insecticides, herbicides, and fungicides [7]. The aim of using a pesticide in the agricultural production process is to fight against undesirable plants and to repel fungi, rodents, and insects. Unfortunately, the vast majority end up in the soil, water, and atmosphere, and through the food chain are transferred to humans, affecting their health [8].

Heavy metals are chemical elements characterized by a high atomic mass, with a tendency to be highly toxic to living beings [9]. Heavy metals are pollutants that represent a growing environmental problem that can affect various components of the environment [10]. It has a wide range of applications, including the manufacture of electrical cables and heating pipes, cladding materials for buildings, catalysis, pulp production, batteries, pigments, weights, radiation protection, thermometers, and fluorescent light bulbs [11]. However, at elevated concentrations, it becomes detrimental to the organisms and environment.

As those pesticides and heavy metals have been asses to be carcinogenic, toxic, for human being and the environment through the accumulation processes [12], many

electrochemical researchers are developing devices/sensors able to detect, analyze, and quantify them in aqueous and non-aqueous media [10, 12–18]. Moreover, the method of their preparation which is the first crucial step for electroanalysis has to be investigated properly, and it is one of the objectives of this chapter. Thus, sample preparation is the bottleneck for the effective and accurate analysis of trace pesticide and heavy metal residues.

The sample preparation methods in electrochemistry are purely dependent on the state (liquids or solids) and the type (organic or inorganic) of the sample to be investigated. Methods commonly used for the preparation of samples are dissolution, extraction, reaction with some chemical species, filtering, dilution, and emulsion [19]. Why do we need to prepare a sample? To isolate traces of analyte from a large quantity of complex matrices and eliminate matrix interferences as far as possible. This is achieved by successive sampling/homogenization, extraction, and cleaning.

In the ideal situation for a solid sample, in aqueous media, the sample is first dissolved with water/buffer/acid and diluted with SE before analysis in both cases pesticide and heavy metal, while the liquid sample has to be dissolved only with SE. In non-aqueous media, the solid sample is dissolved and diluted with the same solvent, while the liquid sample has to be diluted with a solvent playing the role of SE.

In real-life situation, the solid/liquid sample has to be treated to eliminate the effect of organic substances, and the extraction and filtration step will be required. Therefore, different methods of pretreating samples are widely used. In this chapter, the steps involved in preparing samples (pesticides and heavy metals) for electrochemical analysis will be described in detail with the difficulties and issues, prior to a brief discussion on the electrochemical methods of analysis of pesticides and heavy metals.

## 2. Brief review of electrochemical methods of analysis of pesticides and heavy metals

The proper electrochemical analysis of pesticides, heavy metals, dyes, food additives, etc. has all as the first step in the preparation of the sample prior to the sampling. Once this is done, the second task to be performed is to determine the electroactivity domain/potential of the analyte present in the electrochemical cell. This is done by CV, which would also give information about the electron transfer process. After the redox potential of the target identify, the next thing to do depending on the objective to have good sensitivity is to apply a pulse voltammetry technique like DPV, SWV, CA, NPV, LSV, ASV or CSV, etc. Moreover, in contrast to the electroanalysis of pesticides where the two steps are evolved, heavy metals which have known oxidation potential most of the time, during their electroanalysis, the experimenter does not use CV, but directly the pulse method, especially the LSV and ASV [12]. Therefore, for the analysis of pesticides and heavy metals, a brief description of CV and ASV is given below.

### 2.1 Cyclic voltammetry

CV is a very efficient electrochemical technique that enables the reactivity of electroactive substances to be studied quickly, easily, and affordably. It is generally used for the study of a new type of compound [20]. It makes it possible to determine oxidation or reduction potentials, but also to understand the reaction mechanisms

involved in the reaction medium [21]. This technique is based on the change of potential scanned forward and backward between two potential limits (initial $E_i$ and final $E_f$) while the current that circulates through the circuit is recorded in the function of the potential for the oxidation and reduction of the compound [22]. During scanning, the current intensities are measured in the anode ($I_a$) and in the cathode ($I_c$) and the curve obtained represents the variation of the current resulting from the various electrochemical processes as shown by the reversible process given in **Figure 1a**. Moreover, depending on the kinetic of the electrode, electrochemical reactions can be described as reversible (**Figure 1a**), quasi-reversible (**Figure 1b**), and irreversible systems (**Figure 1c**).

For a system to belong to one of the listed systems, apart from the shape difference shown in **Figure 1**, for a transfer of one electron at 25°C, the peak-to-peak separation ($\Delta E_p = E_i - E_f$) must approach 59 mV for a reversible system. A value above 60 mV suggests that the electron transfer is either quasi-irreversible or irreversible. Another difference but not all is based on the peak ratio, that is for reversible and quasi-reversible systems, $Ia/Ic = 1$ while for irreversible systems $I_a/I_c \neq 1$. A practical example in the case of pesticides is shown in **Figure 2**. The multisweep cyclic voltammograms of methyl parathion (MP) pesticide shown in **Figure 2a** shows two redox systems reversible ($E_{a1} = 0.03$ V and $E_{c1} = 0.00$ V, for oxidation and reduction respectively) and irreversible ($E_{c2} = -0.60$ V, for reduction peak) [23], while **Figure 2b** shows the multisweep cyclic voltammograms of diuron pesticide where a single oxidation peak ($E_a = 1.22$ V) for an irreversible process is observed [14].

## 2.2 Stripping methods

Stripping voltammetry is a sensitive electroanalytical technique used for the determination of trace amounts of metals and pesticides in solution. This technique comprises two successive steps. First of all, an accumulation of material (deposit) is carried out on (or in) the electrode by electrolysis at a controlled potential carried out under well-defined conditions (agitation, duration of electrolysis, temperature, etc.). Then, after a short period of rest, re-dissolution is carried out by imposing a suitable potential sweep, while the intensity of the current passing through the electrode is recorded as a function of time. There are several stripping techniques such as ASV, CSV, adsorptive stripping voltammetry (AdSV), and potentiometric stripping analysis (PSA) [24]. Moreover, the one generally used for the electroanalysis of heavy metals
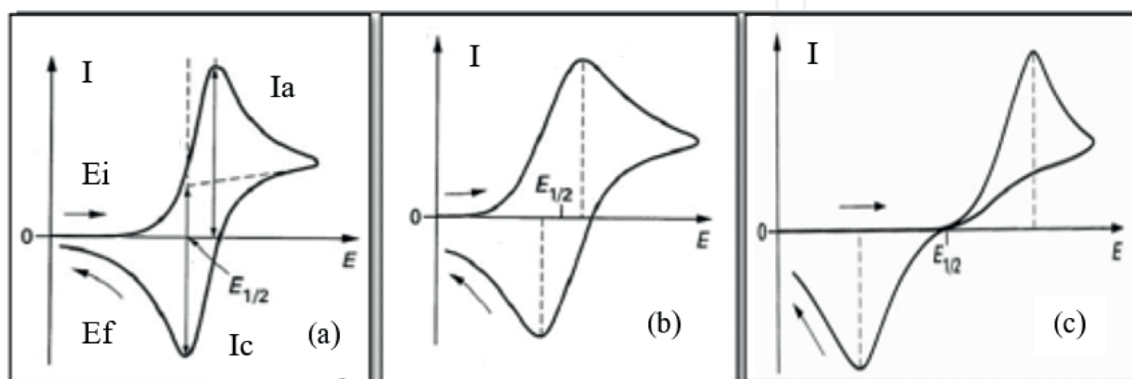


**Figure 1.**
*Typical shape of cyclic voltammograms for different systems: reversible (a), quasi-reversible (b), and irreversible (c) [20]. (From [21]. Copyright (2014), with permission from Dunod.)*
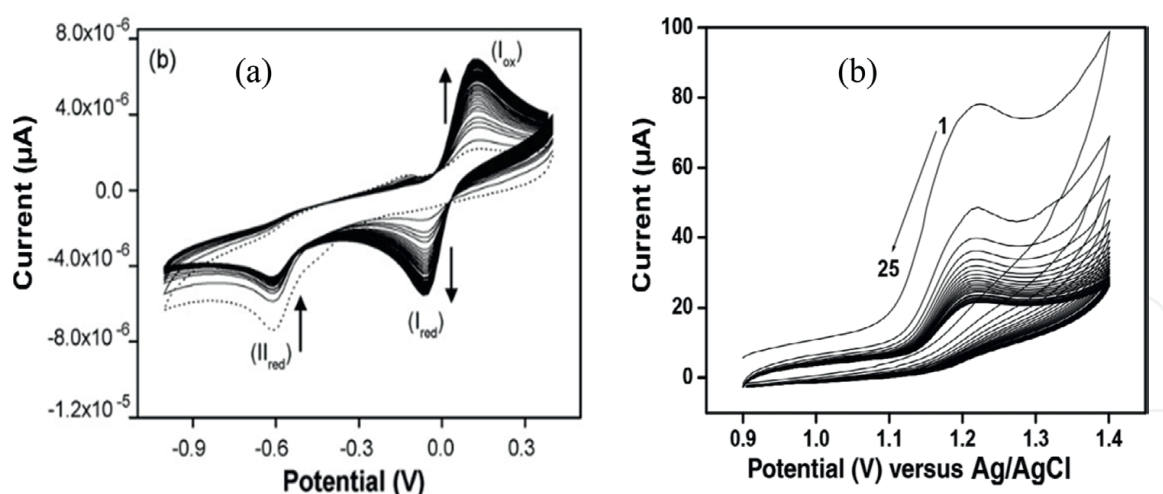
**Figure 2.**
*(a) Multisweep cyclic voltammograms recorded in 41.5 $\mu$M MP in 0.1 mol $l^{-1}$ acetate buffer (pH 5) on the GCE coated by the Ba-DO$_4$ organoclay film. Potential scan rate: 100 mV s$^{-1}$. (b) Multisweep cyclic voltammograms of diuron 5 × 10$^{-4}$ M recorded on GCE/Sa (DODAB)/poly(ARS) in PBS, pH 1, scan rate = 50 mV s$^{-1}$ [14, 23]. (Copyright (2022 and 2010), with permission from Wiley and Elsevier.)*

is the ASV. The principle of ASV is based on electrolysis at a controlled potential. It consists of a reduction, the re-dissolution being carried out by an anodic sweep. By pre-electrolysis, in a stationary convective diffusion regime, at a sufficiently low fixed potential, the cathodic reduction of the metal cation(s) in solution (complexed or not) to metal deposited on the surface of the electrode is produced. This produces the accumulation of a fraction of the element initially diluted in the solution, which becomes "concentrated" in the form of a deposit. After a certain delay intended to return to a regime of pure natural diffusion (without agitation or convection), it is then possible to proceed with a potential sweep of the electrode toward the positive values to cause the re-oxidation of the metallic deposit and thus to cause a current signal corresponding to the pre-concentrated metallic element. The duration of the necessary pre-electrolysis is usually of the order of 2–10 min (1 min is then necessary to ensure that the solution has come to rest). A practical example of the ASV analysis and control of traces of Pb in drinking water is given in **Figure 3**. **Figure 3A** shows the influence of modification of the electrode for the ASV determination of Pb$^{2+}$ [25], while **Figure 3B** shows the influence of the concentration and the calibration curve for the determination of the limit of detection (LOD) of Pb$^{2+}$ using the ASV method [26].

## 3. Sample preparation for electrochemical analysis of pesticides

Pesticides are represented as substances or mixtures designated for destroying any group of pests such as insects and plants [27]. Pesticides have led to the improvement of food production, to secure the demands of the increasing human population reason while it is one of the largely used amounts in the world. Moreover, under the degradation process of pesticides which can be biotic or abiotic, and under the accumulation processes, pesticides lead to the formation of residual products that are often even more toxic than the original compounds [3]. Therefore, significant impacts on controlling pests are beneficial to prevent hazardous diseases in agriculture crops and the environment. Electrochemistry is one of the most used techniques for the analysis of pesticides in these decays. For that to be performed, the preparation of pesticides
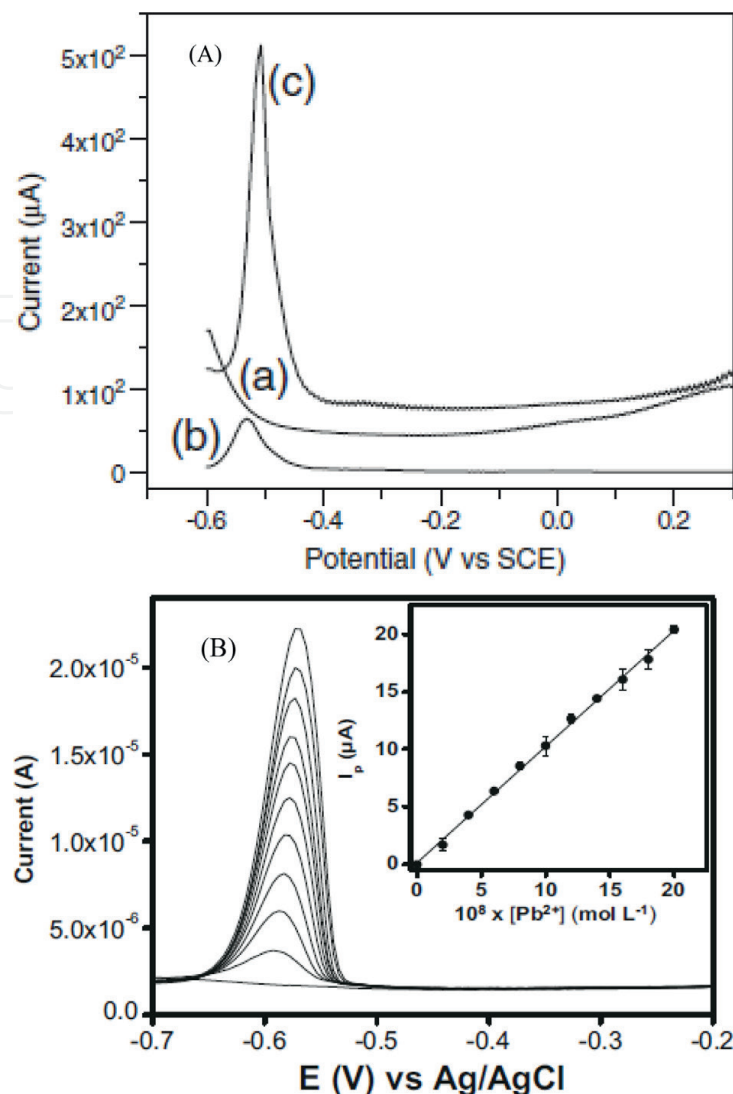
**Figure 3.**
*(A) Influence of the modification of the clay mineral on the electrochemical response: curves recorded in 2 MHNO$_3$ (a) at OP/CPE; (b) at Ba-Na$^+$/CPE; and (c) at OP (40 mM)-Ba/CPE after 2 min accumulation in 1.5 × 10$^{-5}$ M Pb (II) at pH 6. Detection by square wave ASV after 60 s electrolysis at −0.8 V. (B) Differential Pulse ASV signal recorded at GCE/NHAP$_{P0.5}$-CA-β-CD under optimized conditions, after 10 min accumulation in an aqueous medium containing Pb$^{2+}$ in the range from 2 × 10$^{-8}$ to 2 × 10$^{-7}$ M. Other experimental conditions are as follows: 0 s equilibration time, 5 mV potential step and 100 mV amplitude. The inset shows the corresponding calibration curve [25, 26]. (Copyright (2011 and 2021), with permission from Elsevier and Springer.)*

(solid or liquid) has to be done. We illustrate in the following paragraph extraction methods which are the technique for the preparation of pesticides in the environment and foodstuffs.

Traditional sample extraction methods, in particular liquid–liquid extraction (LLE), have been widely used for the analysis of pesticide residues. For the electroanalysis of pesticides in food, new methods have emerged, such as Quick, Easy, Cheap, Efficient, Rugged, and Safe (QuEChERS), solid-phase extraction (SPE), supercritical fluid extraction (SFE), solid-phase micro-extraction (SPME), liquid-phase micro-extraction (LPME), molecularly impregnated polymers (MIP), pressurized liquid extraction (PLE), microwave-assisted extraction (MAE), matrix solid-phase dispersion (MSPD), and ultrasound-assisted extraction (UAE). The most used one for sample preparation in electrochemistry are LLE, SPE, and QuEChERS [8].

### 3.1 Liquid–liquid extraction

LLE is known as the oldest extraction method which is most commonly used up to today. Before the extraction takes place in LLE, solid samples are to be processed into fine, homogeneous particles through mechanical grinding, mixing, rolling, stirring, chopping, crushing, maceration, chopping, pressing, or pulverization, among other methods. Now, whether they are solids or liquids, they are extracted several times with an immiscible organic solvent, followed by centrifugation, concentration and/or purification, and used for the final analysis. A practical situation was described in ref. [28] where they have immobilized the enzyme acetylcholinesterase on a composite of polyaniline/carbon nanotube, to form a biosensor used for the electrochemical analysis of carbamate pesticides in fruit and vegetables. The work reported in ref. [29] highlights the development of an improved method for extracting pesticide residues from food using acetonitrile (MeCN) with magnesium sulfate and chloroform. The method involves homogenizing a mass (10 g) of fruit, vegetable, and meat samples and placing them in a teflon centrifuge tube ($V$ = 50 ml) containing 10 ml of MeCN, and the mixture is shaken vigorously in a vortex mixer for 1 min. Next, 4 g of $MgSO_4$ and 1.0 ml of chloroform were added, and shaken for 1 min. Finally, the extract was centrifuged at 4000 rpm for 10 min to separate the phases. In ref. [30], the authors successively used centrifugation, low-temperature purification at −20°C for 6 h, and dispersive solid phase extraction (d-SPE) with Florisil as cleaning steps to perform the LLE. The efficiency of the extraction of analyte in LLE depends mainly on the distribution/partition coefficient equilibrium between the donor and acceptor phases, which requires the polarities of the extraction solvents and analytes to be matched according to the principle of similarity. The miscibility of MeCN with water has been shown to be effective in extracting polar and/or non-polar pesticide residues with low amounts of matrix co-extracts, as they can be separated from the aqueous phase by the salting-out effect [8]. It is necessary to clean the extracts to reduce interferences after the initial LLE. LLE is a classic method for routine sample preparation due to its simplicity, robustness, and efficiency. However, it remains difficult to implement, with high consumption of solvents and time. It is, therefore, important to choose simple and rapid sample preparation methods for the analysis of pesticide residues in foods.

### 3.2 Solid phase extraction

First introduced in 1970 [31], the principle involves passing extracts through a cartridge. These extracts (analytes) are adsorbed onto solid phase materials (solid sorbents), which have been previously conditioned and activated with water and/or an organic solvent before being used. The choice of an appropriate sorbent is, therefore, very crucial. Interferences are eliminated by pre-washing with organic solvents, while any analytes still retained on the adsorbents can be eluted with other organic solvents so that clean extracts should be obtained. As a trump card, SPE requires small volumes of solvent and standard experimental equipment. It also offers a simple experimental procedure and rapid sample throughput, which is why it is used as an alternative to LLE both for sample preparation and for the clean-up and enrichment of organic compounds in water samples. The work reported in ref. [32] highlights the applications of SPE for sample clean-up in the analysis of pesticide residues in the food matrix. In this work, agricultural samples (chestnut, shallot, ginger, and tea) were first extracted by freeze-drying for approximately

24 h and ground to a homogeneous powder under liquid nitrogen protection. The homogenized samples (0.5 g of tea sample) were placed in a polypropylene centrifuge tube containing 1 ml of water was added and soaked for approximately 30 min. Next, 0.4 ml of D4-labeled imidacloprid and 10 ml of acetonitrile were added in the centrifuge tube and the sample was shaken vigorously for 30 s and then vortexed for 1 min. This extraction procedure was repeated three times with 10 ml acetonitrile and the solvent extracts were then combined. After separation of the organic layer, it was dried under anhydrous sodium sulfate for 30 min, then concentrated to approximately 4 ml under vacuum at 50°C. Activated carbon and Oasis HLB SPE cartridges were used for SPE. The pesticides retained by the activated carbons were eluted with methanol and the eluent was collected in a test tube, then reduced to dryness by rotary evaporation under vacuum on a water bath at 50°C. The residue was reconstituted in 2 ml of mobile phase and the final solution was filtered through a 0.22 m PTFE syringe filter.

The SPE procedure typically involves the selective retention of target analytes on an adsorbent packaged in a disposable mini-extraction column. Adsorbents such as C18, activated carbon, and multiwall carbon nanotubes have been developed for this purpose [33]. SPE is simpler, more practical, less solvent-intensive, and easier to automate than LLE, and it can effectively avoid the emulsion formation often encountered in LLE. However, it is difficult to quickly select suitable adsorbents and elution solvents for the analysis of multi-residue pesticides due to the complexity of their physicochemical properties. Secondly, commercial SPE cartridges are not recyclable, which considerably increases the experimental budget. Recently, a rapid clean-up step based on d-SPE was developed based on the principle of the QuEChERS method [8, 34].

### 3.3 Quick, easy, cheap, efficient, rugged, and safe

QuEChERS, which stands for quick (or fast), easy, cheap, efficient, robust, and safe, is a very flexible approach that can be modified depending on the properties of the target analyte, the composition of the matrix, and the facilities equipment available in the laboratory. The model allows high recoveries to be achieved for many pesticides in many matrices, even if different ratios, types of samples, solvents, salts, and sorbents are used for the modifications. In the analysis of multi-class and multi-residue pesticides, the sample preparation method inherently requires a large analytical scope, making it impossible to achieve a high degree of clean-up without reducing recoveries for some pesticides. Moreover, higher clean-up can be achieved by using different sorbents in d-SPE if the application has a reduced analytical scope [35].

Introduced in 2003 [36], the QuEChERS method is based on microscale extraction using MeCN, water absorption and liquid–liquid separation using $MgSO_4$ and NaCl, and the d-SPE clean-up step using a primary-secondary amine (PSA) adsorbent, as shown in **Figure 4**. By combining conventional extraction, isolation and clean-up procedures into a single step, this method avoids mixing, filtration, high-volume solvent transfer, evaporation, and condensation. It has become very popular in the preparation of samples for the analysis of pesticide residues in the food matrix. In the work reported in ref. [37], detection and quantification of cypermethrin with the enzyme glutathione S-transferase which catalyzed the reaction between glutathione and 1-chloro-2,4-dinitrobenzene in the presence of several solvents such as methanol and ethanol. The QuEChERS method was used to validate their study by fortifying
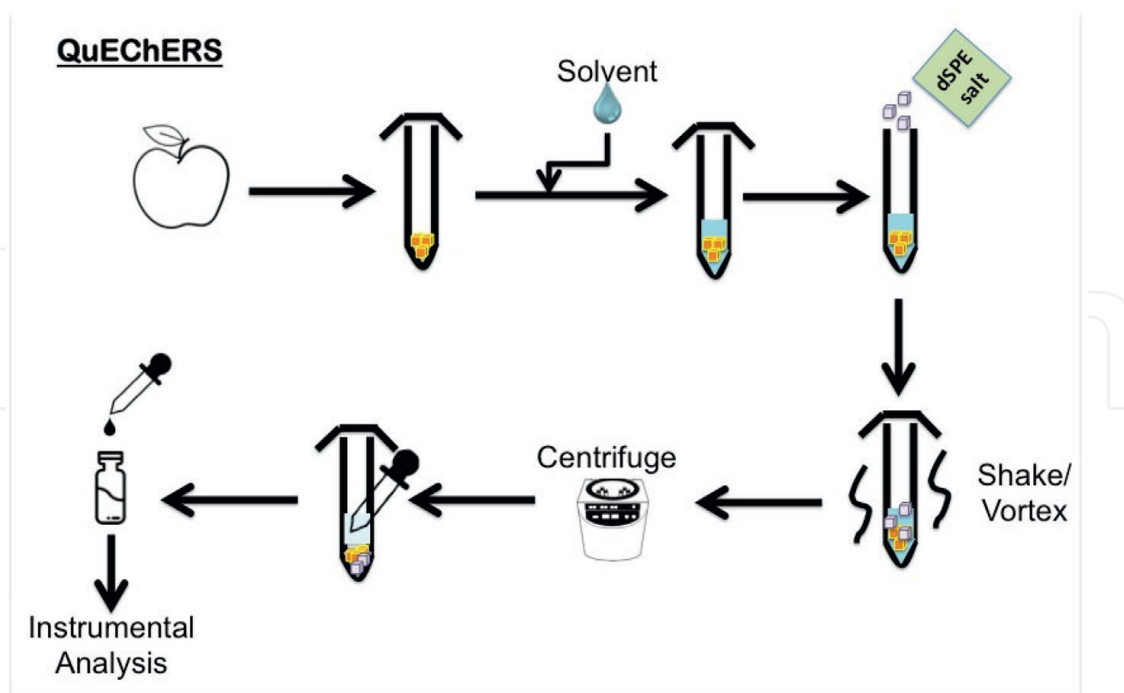
**Figure 4.**
*Schematic diagram of the common procedure of QuEChERS [8]. (Copyright (2012), with permission from Wiley-VCH GmbH.)*

tomato samples with a known quantity of cypermethrin. Among the solvent used in this QuEChERS procedure which are methanol, acetone, and MeCN. MeCN has been chosen as the best solvent not only because it helps to achieve higher recovery rates and less interference than other solvents such as acetone and methanol, but also to offer a slightly better LOD and relative standard deviation (RSD) than acetone. Compared with the classic LLE method, the QuEChERS method offers the advantage of a simpler, less time-consuming procedure and lower consumption of organic solvents. Since it considerably simplifies the extraction and cleaning stage during sample preparation and provides reliable quantitative results, QuEChERS has a bright future in the field of chemical analysis. It has a bright future in the analysis of pesticide residues in foods.

The general steps for the preparation of a sample for the electroanalysis of pesticides are illustrated **Figure 5** [38].

## 4. Sample preparation for electroanalysis of heavy metals

The daily applications of heavy metals in the manufacturing of several varieties of equipment used by human beings with the consequence of releasing some trace particles which can accumulate in the environment and pollute the foods and drinking water has become a serious problem to be solved. Heavy metal pollution has therefore become a priority, as they can affect biological functions or become accumulated in organs, causing illnesses such as cancer. These pollutants are released into soil, water, and the food chain as a result of a number of anthropogenic factors. This section provides a clear overview of the different sample preparation methods developed for electrochemical analysis of samples, which can be classified into liquids and solids, or organic and inorganic.
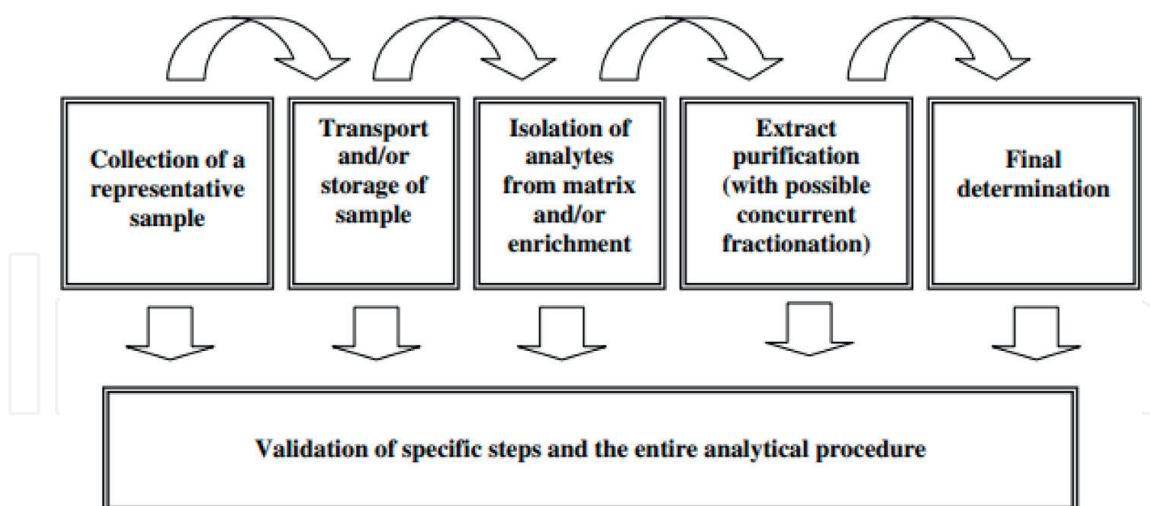
**Figure 5.**
*Main steps of sample preparation for electroanalysis of pesticides [38]. (Copyright (2012), with permission from Elsevier.)*

### 4.1 Types of samples

To analyze heavy metals in the environment and foods, samples can be liquids, solids, or organic and inorganic like in the case of pesticides. Sample preparation still needs to be optimized to meet the same requirements as the analytical procedures needed to determine the analytes [39]. Liquid samples may be in aqueous solution (e.g., natural water, beverages, and biological fluids), but also in organic form (oils and fuels). Solid samples may be predominantly organic in nature (e.g., foods, plants, and biological tissues) or predominantly inorganic (e.g., soils and sediments). Once samples have been collected, they can be analyzed by electroanalytical re-dissolution techniques either directly or after dilution.

### 4.2 Sample pre-treatment

Prior to the actual processing step, sample pre-treatment can be carried out depending on the solid or liquid nature of the sample. For solid samples or solutions made directly from wet-washed materials or dry-washed and dissolved materials [40], the amount (size) of material processed can be reduced while maintaining the representativeness of the subsample by mechanical grinding, by abrasion in a cyclone mill or by crushing in a ball mill [40]. In order to eliminate or reduce physical interferences, certain techniques are also used, such as sample dilution, mapping of the template and blank to the sample, using internal standards, chemical separation, and the method of standard addition [41]. Dilution is carried out according to the concentration of the analyte and/or the interference present in the matrix.

### 4.3 Sample preparation

The metals contained in the samples are determined by several analytical methods. Metals such as copper in brass or iron in steel can easily be analyzed by methods such as gravimetric chemical methods. However, many metal determinations involve smaller quantities, or traces, which are determined by various methods like spectroscopic, chromatographic, and electrochemistry. Sample preparation for metal

determination has several objectives, which vary according to the type of sample and the requirements of the analysis. The main objective of sample treatment is to ensure the release of metals from the organic matrix and to remove the sample matrix, which may interfere with electrochemical detection. Sample preparation techniques such as dry ashing, wet digestion, and extraction methods are frequently reported.

### 4.3.1 Dry ashing

Dry ashing was initially used for sample preparation due to its easy operation and effective destruction of organic materials [42]. Organic compounds are ignited and oxidized by air at elevated temperatures (~500°C) and atmospheric pressure. The carbonaceous residues (ashes) are dissolved in diluted acid solutions ($HNO_3$ or HCl solutions). For stripping analysis, a substantial dilution (0.5 g per 100 ml) may be necessary to circumvent the interference from sample ash on the electrochemical detection. For example, in ref. [43] dry ashing was used to prepare vegetable samples for Zn, Cd, and Pb determination. The samples were dry-ashed (in a muffle oven and the temperature was slowly increased up to 500°C) until they yielded white ash, which was then dissolved by a concentrated nitric acid/perchloric acid mixture (4:1), heating gently on a hot plate until almost dry. Despite the simplicity of this process, it cannot be used in some important applications where high temperatures and long decomposition times are used since they can lose in whole or in part [44]. Some of the volatile elements likely to be lost are As, B, Cd, Cr, Cu, Fe, Pb, Hg, Ni, P, V, and Zn [45]. Microwave ovens can incinerate samples in around 20 min, significantly reducing analysis time by 97% compared to normal dry incineration. Reaching temperatures of up to 1200°C, microwave ovens typically digest under high pressure in closed containers heated by microwave energy, breaking down the sample faster while minimizing external contamination and volatile chemical losses [41]. These ovens take more samples than traditional ovens [45]. The advantages of conventional dry incineration are that it is a safe and affordable method that requires fewer samples than other methods, does not require additional acids or other reagents or blank subtractions, has a high sample recovery rate and once ignition has started minimal attention is required [45].

To reduce sample preparation time and to work at lower temperatures, wet digestion processes have been an interesting alternative to dry ashing methods.

### 4.3.2 Wet digestion processes

In wet digestion, primarily for the preparation of mineral analyses, in ref. [45], they have used strong oxidizing acids (mixtures of nitric and perchloric acids ($HNO_3$–$HClO_4$), sulfuric acid ($HNO_3$–$H_2SO_4$), hydrochloric acid ($HNO_3$–HCl), and hydrogen peroxide ($HNO_3$–$H_2O_2$)) that are added to the sample and heated to facilitate the wet digestion procedures by decomposing the organic components of the sample. The maximum temperatures reached are between 122°C and 338°C at ambient pressure and are limited by the acid or acid mixture used [46]. A disadvantage is the contamination that can occur during digestion from reagents, vessel materials, and the environment. However, wet microwave incineration can be carried out safely in an open or closed vessel microwave system. Acids can be heated above their boiling point due to the ability of closed vessels to withstand higher pressures. This technique allows more samples to be processed at one time than conventional techniques, thus increasing throughput. Normal digestions take less than 30 min. Compared

to conventional methods, microwave digestion procedures are preferred since they have short digestion time, low acid usage, and high extraction efficiency [47]. An important parameter to be evaluated when stripping techniques are utilized is the residual organic matter from the digestion process, which may interfere with stripping voltammetric determinations. In the work reported in ref. [48], wet acid digestion was used to destroy organic matter in milk samples and fermented milk products for the determination of cadmium, lead, and copper. The digestion was carried out in quartz Kjeldahl flasks, using a mixture of nitric and perchloric acids (1:1).

### 4.3.3 Extraction methods

The most commonly used extraction methods from solid or immiscible liquid samples are in the aqueous phase containing acids or oxidants, with the main advantage that the operation is simple, does not require drastic pressure and temperature, and does not require sophisticated equipment. For example, cadmium and lead were extracted from the soil sample, just by heating 1 g of the sample in an oven at 80°C for 1 h. The soil sample was then placed in an extraction tube with 40 ml of 0.1 mol l$^{-1}$ acetic acid [49]. Extractions can be improved if external energy is introduced, such as increasing the temperature of the sample-extractor medium. For example, MAE of metals from soils has been reported for the determination of metals by stripping techniques [50]. In addition, ultrasound has also been used for sample preparation, in particular, to facilitate extraction methods. An extraction performance close to 100% has been achieved using hot concentrated HCl (50–90°C) [51] for the determination of metals in petroleum-based oil products. Eight types of retail packaged milk were treated (extraction process) by the ultrasonic-assisted acid digestion method for the electrochemical determination of cadmium and lead [52]. Some extractions are time-consuming and when organic samples are processed, the residual organic matter in the aqueous extractor is not negligible and therefore affects the electrochemical determinations. It is therefore sometimes necessary to use carbon-retaining columns prior to stripping determinations of metals in the aqueous extractor [51]. Removal of these species can also be done by organic solvent extraction [53].

## 4.4 Choice of sample preparation methods

Many environmental sample preparation procedures focusing on the determination of metals by stripping techniques have been highlighted in the literature [19]. **Figure 6** summarizes the sample preparation methods for the determination of metals in environmental, biological, and food samples by electrochemistry. Acid digestion methods have been favored when analyzing crude oil and petroleum-based products due to their extremely high organic content. However, the complete decomposition of these matrices requires extreme conditions (high temperature and pressure in the presence of concentrated acids and oxidants) that can be avoided by using ultrasonic and room-temperature extraction methods. Extraction methods are the predominant option for solid environmental samples.

## 5. Conclusion

The methods described in this perspective chapter concern the determination of pesticides and heavy metals. However, heavy metals are present in different forms in
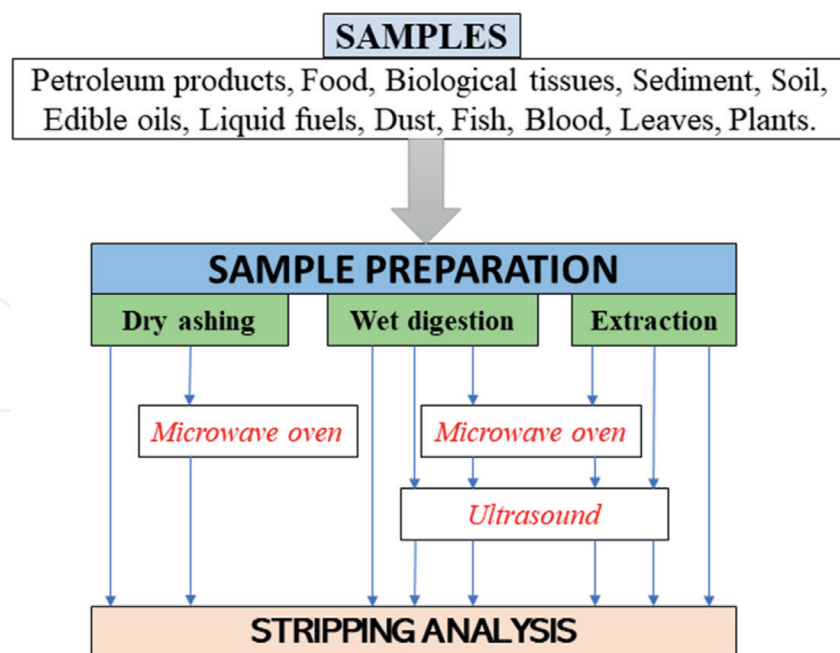
**Figure 6.**
*Summary of sample preparation techniques for the re-dissolution determination of metals in environmental and food samples.*

environmental and food samples. As a result, the use of highly sensitive electrochemical techniques for the determination of pesticides and heavy metals in environmental and food samples is highly dependent on the sample preparation step, especially when analyzing solid-organic material. Technical developments have made it possible to achieve efficient, fast, and inexpensive sample preparation procedures. For the determination of heavy metals, the combination of microwaves and ultrasound with acid digestion or extraction provides important advantages such as the reduction of reagents and samples (environmental, biological, and food) and the reduction of analysis time. The introduction of an ultrasonic horn into the electroanalytical system is a promising methodology to perform the analysis of complex samples in one step (sample preparation, electrode cleaning, and stripping analysis occurring simultaneously in the electrochemical cell). In the case of the analysis of pesticides, the most used technics for sample preparation in electrochemistry are LLE, SPE, and QuEChERS. Among them, QuEChERS was found to be a very versatile approach and serves as a model for modification according to the properties of the analyte, the composition of matrix, and the facilities technique on hand in the laboratory. The toxicity and the bioavailability of pesticides and heavy metals depend on their form. The main challenges in their determination are sample preparation, the presence of interferences, detection limits, and matrix effects. To date, pesticides and heavy metals have been determined in various types of samples, including environmental and food samples. Quality control measures such as blanking, addition of a standard, spike recovery, repeated analysis, and the use of reference materials remain crucial to ensure accurate results. In addition to pesticides and heavy metals, other xenobiotics such as drugs, dyes, and flame retardants can also be analyzed by electrochemical methods, with sample preparation almost identical to those described above. However, there are other, fairly sophisticated and robust analytical methods that allow these analytes to be analyzed efficiently. These include mass spectrometry (for organic compounds and pesticides) and inductively coupled plasma (for heavy metals).

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## Conflict of interest

The authors declare no conflict of interest.

## Abbreviations

| | |
|---|---|
| Ia | anodic current |
| ASV | anodic stripping voltammetry |
| AE | auxiliary electrode |
| Ic | cathodic current |
| CSV | cathodic stripping voltammetry |
| CA | chronoamperometry |
| CV | cyclic voltammetry |
| DPV | differential pulse voltammetry |
| EC | electrochemistry |
| LSV | linear sweeping voltammetry |
| LC | liquid chromatography |
| LPME | liquid phase micro-extraction |
| LLE | liquid–liquid extraction |
| MS | mass spectrometry |
| MSPD | matrix solid-phase dispersion |
| MP | methyl parathion |
| MAE | microwave-assisted extraction |
| MIPs | molecularly imprinted polymers |
| NPV | normal pulse voltammetry |
| PSA | potentiometric stripping analysis |
| PLE | pressurized-liquid extraction |
| RE | reference electrode |
| SPE | solid-phase extraction |
| SPME | solid-phase micro-extraction |
| SWV | square-wave voltammetry |
| SFE | supercritical-fluid extraction |
| SE | supporting electrolyte |
| UAE | ultrasound-assisted extraction |
| UV-Vis | ultra-violet |
| WE | working electrode |

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