

## Review

## Electronic tongue applications for wastewater and soil analysis

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## SUMMARY

**Assessment of water and soil quality is critical for the health, economy, and sustainability of any community. The release of a range of life-threatening pollutants from agriculture, industries, and the residential communities themselves into the different water resources and soil requires of analytical methods intended for their detection. Given the challenge that represents coping with the monitoring of such a diverse and large number of compounds (with over 100,000 chemicals registered, yet in continuous increase), holistic solutions such as electronic tongues (ETs) are emerging as a promising tool for a sustainable, simple, and green monitoring of soil and water resources. In this direction, this review aims to present and critically provide an overview of the basic concepts of ETs, followed by some relevant applications recently reported in the literature in environmental analysis, more specifically, the monitoring of water and wastewater, their quality and the detection of water pollutants as well as soil analysis.**

## INTRODUCTION

The progress evidenced in Analytical Chemistry over last decades has furnished it a key role in our society (Bergquist and Turner, 2018), covering applications in different fields as environmental monitoring, food control, clinical diagnostics, forensic analysis, or process control. Such progress is tied up with the general trend of a more knowledgeable society demanding a better understanding, monitoring, and control of the composition of daily life products.

This demand translates into novel tools for the identification, classification, or quantification of chemical and/or biological species in complex matrices, not only in the scientific context but also in the industrial and social grounds. More importantly, such methods also need to be economic, fast-responsive, simple, portable, and sustainable, the latter, in line with the emerging green analytical chemistry orientations (del Valle, 2020). In this direction, electrochemical (bio)sensors have arisen as promising tools, offering fast and accurate information in a cost-effective manner. Their high sensitivity, wide linear range, minimal power requirement, potential for miniaturization and portability, and also ease of operation are some of their many advantages (Wang, 2002).

However, there are certain analytical problems not requiring the quantification of a certain analyte, but evaluating an overall effect over a biological system (e.g., toxicity or quality indices, origin, freshness, etc.). Conversely, assuring that even in complex samples without any pre-treatment or pre-concentration step, the developed (bio)sensors will not suffer from interferences or matrix effects compromising the selectivity or sensitivity for a given analyte is always challenging. Such limitations led to the appearance of electronic noses (ENs) and electronic tongues (ETs), a new strategy to tackle these problems (Persaud and Dodd, 1982; Vlasov et al., 2005).

These biomimetic analytical systems are inspired by the sensory physiological principles in mammals, where a set of slightly broad response receptors (rather than highly specific ones) allow discriminating thousands of targets by combinatorial principles. Analogously, ENs and ETs rely on the combination of sensors with cross-response features (low selectivity), with a complex data treatment stage analogous to the brain functioning, which allows the classification of different samples or the quantification of the desired parameter. Thus, unlike the conventional approach, sensors' responses are not necessarily specific toward a particular species, but provide an overall fingerprint of the sample constituents, which with the aid of appropriate chemometric tools, can be related to the desired features.

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Initial studies involving ENs and ETs focused mainly on proving the potential of the approach to distinguish between basic substances (mainly associated to taste), but soon afterward, the identification and classification of beverages and food variants became one of the most explored topics, due to obvious reasons. Nonetheless, ETs have also been applied in other fields, e.g., environmental monitoring, clinical, forensic or pharmaceutical analysis, between others (Ciosek and Wroblewski, 2007; Riul et al., 2010; del Valle, 2012; Cetó et al., 2016). Herein, we will focus on the application of ETs in environmental analysis, more specifically, in the monitoring of water quality, the detection of water pollutants and in the analysis of soils. In this direction, this review aims to present and critically provide an overview of the basic concepts of ETs, followed by some relevant applications recently reported in the literature.

### Electronic tongues

ETs are defined as “an analytical instrument comprising an array of nonspecific, low-selective, chemical sensors with high stability and cross-sensitivity to different species in solution, and an appropriate method of PARC (viz. pattern recognition) and/or multivariate calibration for data processing” (Vlasov et al., 2005). Despite being defined as an instrument, it must be reckoned that the number of commercial devices is still rather low, being mainly used in research laboratories working in its development. Consequently, the term ET is used to refer to the approach that combines the usage of an array of sensors with some chemometric processing, rather than to a physical instrument that performs both tasks. Indeed, such combination is rarely done simultaneously, as the measurements are first taken, and later the recorded data are processed with the chemometric method of choice.

Besides, from the definition, there is no restriction regarding the type of sensors that can be used in ETs. In this manner, initial studies used potentiometric sensors (Vlasov and Legin, 1998); from the very beginning voltammetric sensors were also used (Winqvist et al., 1997); nowadays, this has been expanded to practically all the families of sensors such as impedimetric, optical, piezoelectric, etc. However, despite the concept being equivalent, the choice of the type of sensors used is crucial as the information provided can be entirely different. Therefore, the type of sensors used can be the basis to classify ETs into different categories and included as a qualifier when referring to them, e.g., potentiometric ET, voltammetric ET, etc. The variant hybrid is reserved to the case when sensors of different nature are used simultaneously.

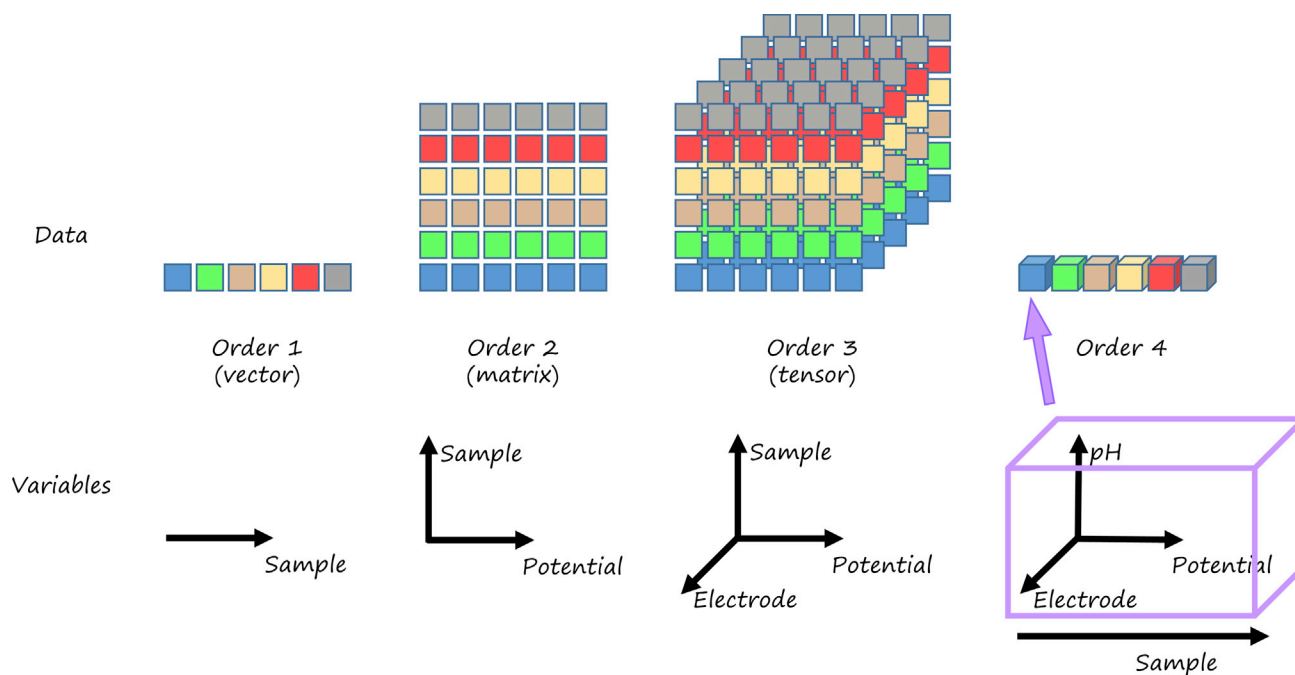
Along with the type of sensors employed, there is another key fact defining any ET application, which is the nature of the extracted information. In this manner, we will distinguish between qualitative applications, in which the identification and classification of sample types is sought, and quantitative applications, in which the determination of the concentration of different compounds or a certain index is called for. Such categorization is very important when defining the application to be developed, as it will affect the choice of the chemometric tool to be used, but also it will impact on the type and number of samples required to build the model.

Based on the aforementioned, over the next sections, we will comment on the particularities arising from the usage of different sensors, while for a more detailed description on the different chemometric approaches to be used, specific research may be consulted (Richards et al., 2002; Cetó et al., 2013; Kumar et al., 2014).

### Classification based on the technique

As already introduced, ETs can be classified based on the sensors used, being potentiometric and voltammetric the more common variants due to the intrinsic advantages of electrochemical methods.

The choice of the sensor array is something that must be considered depending on the actual application being developed, as some types of sensors might be preferable to others. For example, potentiometric sensors provide information mainly about the ionic composition of the samples (either cations or anions; viz. charged species), although sensing of organic neutral molecules might also be feasible if those have acidic or basic groups that can be charged by changing the pH (Jańczyk et al., 2013; del Valle, 2017). On the other side, voltammetric sensors provide information about compounds in the sample that can be oxidized or reduced, even though sensing non-electroactive molecules might also be achieved indirectly upon modification of the sensor with e.g., an enzyme that catalyses the formation of an electroactive product.



**Figure 1. Representation of generated data dimensionality when employing ETs**

Schematic representation showing the increase of the dimensionality of the registered responses (order of the data) for a voltammetric ET. Each squared symbol represents a single numeric value, while cubic symbols represent already a three-dimensional array of values. Colored symbols represent different samples. One voltammetric sensor alone generates a 2D matrix (currents measured per each sample at different polarization potentials). Oppositely, potentiometric ETs yield a lower dimension of data as generally a single value is registered for each sensor; use of a single potentiometric sensor (left) originates a simple data vector.

In other words, what we want to point out is that each technique has their inherent advantages and disadvantages and that its suitability will ultimately depend on the nature of the target analytes (e.g., are they ionic? Are they oxidizable? Are they fluorescent? Is there a suitable (bio)receptor available? etc.) and the sensing strategy (e.g., direct or indirect determination). That being said, it has to be reminded that ETs are beyond the conventional sensor approach and that regardless of the type of sensors chosen, it might be possible to estimate an unmeasured variable (e.g. a toxicity index) from other measured variables by means of a mathematical model, an approach which is sometimes referred as “software sensor” (James et al., 2002). In this manner, by combining the information extracted from the array of sensors, it may be possible to correlate their responses with a variable difficult to measure, arranging for its estimation.

Besides, the choice of the sensor array is also important from the practical point of view as the instrumentation, the procedure to carry out the measurements and the nature of the responses are significantly different. Again, when taking potentiometric and voltammetric sensors as an example, one of the main differences is the dimensionality of the generated data. With potentiometric sensors, normally a single value corresponding to the thermodynamical electromotive force (emf) is taken for each electrode and sample, and consequently training information can be sorted in a 2D matrix (sensor x sample); with voltammetric sensors, the electrode may be polarized at different potentials, recording a  $n$  points voltammogram for each electrode and sample, generating a 3D response matrix (polarization potential x sensor x sample, see Figure 1). On the one side, this multi-dimensionality is advantageous as richer data are generated since each sensor can provide information about different components of the sample in a more selective way, e.g., two species may show response with a specific voltammetric sensor, but at a different potential. However, on the other side, this may hinder the processing of the data, as its dimensionality is increased, requiring the usage of extra pre-processing steps (Cetó et al., 2013).

Lastly, a recent trend for further improving the performance of ETs is the combination of sensors of different nature to obtain more information about the samples (hybrid ET). Such hybrid systems are also bioinspired in the sensory ability of animals, where the different stimuli perceived by the different senses are combined

to generate a unique response in the brain. However, as could be expected, the combination of measurements from very different nature is not straightforward, requiring the use of certain strategies to make those compatible. Such strategies are known as data fusion, and deal not only on how to make the multisource data compatible but also on how to take advantage of their characteristics to better represent the sample information in a unified picture (Khaleghi et al., 2013). Nevertheless, this topic is out of the scope of the current review due to its complexity, and we suggest consulting the more specific reviews above.

### Advances in the development of ETs

Closely related to the choice of the measuring principle, there is also the choice of the transducer, and more importantly the receptor. Despite one may think of ETs being mainly related to the usage of unselective sensors, the truth is that initial studies were based on arrays of ion-selective electrodes (ISEs) (Vlasov and Legin, 1998). The aim was to exploit the potential of chemometric methods to improve the performance of conventional ISEs for quantitative analysis, that is, to correct the drifts and/or lack of specificity (cross-response) that those might show.

Indeed, it was the works of Toko et al. who attempted to actually reproduce humans' taste, using electrodes equipped with different lipid membranes rather than ISEs (Hayashi et al., 1990). Soon afterward, Legin et al. explored the usage of chalcogenide glasses as non-specific, poorly selective potentiometric sensors for the development of ETs showing cross-sensitivity to multiple components in the sample, and from which the term ET was coined. Nonetheless, improved performance may be attained if both conventional and non-specific sensors are combined (del Valle, 2012).

Similarly, in the case of voltammetric sensors, the usage of an array of bare metallic electrodes was the common approach at the beginning (Winqvist et al., 1997). However, to improve performance and tackle new applications, the usage of chemically modified electrodes was soon adopted. Modification of electrodes surface with different electrocatalysts acting as electron mediators allows a more efficient electron exchange and/or faster reaction rate, which results in, e.g., a lower oxidation/reduction potential and/or increase in the sensitivity, and introduces diversity in the response.

Precisely, to further improve the performance of ETs and to spawn new application fields, the usage of different bioreceptors for the modification of the electrodes (converting these into biosensors) was also explored. Despite the approach relies on the same principles, only diverging on the use of one or several biosensors into the sensor array, the term bioelectronic tongue (bioET) was coined (Tønning et al., 2005).

The idea is to combine the higher selectivity and sensitivity of biosensors, with the modeling performance of chemometrics, intending to compensate biosensors' interferences, drifts, or non-linearities and to achieve the classification of different samples or the multi-determination of several species. Thus, although biosensors are expected to be highly selective, the truth is that those may still show some cross-response (e.g., enzymes showing group specificity) and their kinetics might be altered by other compounds (e.g., activators or inhibitors affecting enzymes). Consequently, using biosensors may be equivalent to using other sensors, all of them fitting perfectly within the ET approach. Among the different applications reported with bioETs, enzymes are preferred, while for the transduction, amperometry and voltammetry are the common choice (Cetó et al., 2016; del Valle, 2017).

Lastly, despite the huge advantages that biosensors offer, it cannot be neglected that those still present some drawbacks such as its higher cost, lower long-term stability, instability out of the physiological conditions, or the limitation toward which analytes a bioreceptor might be available. In this direction, in an effort to overcome such drawbacks, molecularly imprinted polymers (MIPs) have emerged as a promising alternative for the preparation of MIP-based ETs (Huynh and Kutner, 2015; Herrera-Chacón et al., 2021). MIPs are artificially synthesized low-cost polymeric receptors with high selectivity toward a desired analyte that aims to mimic the host-guest chemistry of biological receptors (e.g., substrate-enzyme or antigen-antibody). However, like biosensors or ISEs, MIPs can still show some cross-response toward other molecules, especially with chemically analogous structures.

As a final remark, it must be considered that, as already pointed out when choosing the technique, sensors to be used will depend on the desired application, i.e. whether the quantification of a mixture of

compounds is being targeted or if, oppositely, the correlation with a global index is sought, which therefore will not be attributed to a certain compound.

### Applications

As already mentioned, this review focuses on the application of ETs in environmental analysis. Environmental analysis covers the monitoring of soil, water, and air quality, usually to evaluate and assess the impact of anthropogenic activities in natural systems. Consequently, the monitoring is mainly directed to the detection of toxic compounds and pollutants (either chemical or biological/microbiological), but sometimes also covers proactive activities that allow a more rational use of natural resources (e.g., smart farming). In this direction, to demonstrate the potential of ETs in such field, some relevant applications over different scenarios will be presented. Lastly, per definition, ETs are applied to the analysis of liquid samples, whereas ENs deal with gases. Therefore, herein, we will focus only on water analysis as well as soil extracts.

### Water and wastewater analysis

Water quality is a key issue for the welfare of any community. For its assurance, not only the analysis of drinking water is required, but the release of a range of life-threatening pollutants from agriculture, industries, and homes themselves into the different water resources also requires their monitoring. This represents the monitoring of a practically unattainable set of compounds, because of its number and of its diversity (Agüera et al., 2013; Galindo-Miranda et al., 2019). In this respect, holistic solutions such as ETs emerge as promising tools for the sustainable monitoring of water resources, given they can provide more global and generic final information (Table 1).

### Heavy metals

Heavy metals are key elements in water monitoring (Tchounwou et al., 2012). Although technically they are elements naturally present in the environment, their concentration has increased due to anthropogenic activity, as it has also grown the concern about their potential effects on health and ecosystems. This is because they are systemic toxic compounds that can interfere with different organs functionality, even at very low concentrations. In addition, the half-life of these ions in the organism is on the order of years, due to their slow clearance. Consequently, pollution of natural or potable water by heavy metals means a significant threat, which asks for methods for their determination and monitoring. In practice, heavy metals pollution is primarily attributed to Cd, Cu, Pb, and Hg (Lu et al., 2018).

In this direction, ETs can overcome shortcomings of conventional methods for the detection of heavy metals, by allowing not only their on-field determination but even its real-time continuous monitoring. For example, Mimendia et al. reported the application of a potentiometric ET toward the monitoring of Cd(II), Cu(II), Pb(II), and Zn(II) in open air waste streams and rivers (Mimendia et al., 2010). The ET array was made up of eleven sensors using polymeric membranes, which included two replicate ISEs for Cd(II), two replicate for Cu(II), two for Pb(II) (employing different ionophores), two for Zn(II) (employing different ionophores), one for pH, and two generic ISEs toward cations (employing different ionophores). The inclusion of redundant sensors (either identical or using different ionophores) is an approach used to enrich the data as different ionophores respond differently to possible interferents, while concurrently it improved the accuracy of the measurements (e.g., as a decay or drifts in performance may be detected from the comparison of replicate sensors' response). For the monitoring application, the sensors were deployed into the river, and the data were collected with a laptop communicated by a radio frequency link located 120 m far away, which was also responsible for the data analysis by means of artificial neural networks (ANNs) (Figure 2). The system was successfully applied for over 8 h, demonstrating the viability of the approach.

The inherent redox activity of heavy metals in combination with the high sensitivity of stripping methods makes voltammetric methods one of the preferred alternatives for their determination (Lu et al., 2018). Such performance is attained thanks to the combination of a pre-concentration step (stripping) with voltammetric determination which allows the speciation of the different metals. The sensitivity can be further improved upon modification of the working electrodes with e.g., metal oxide films ( $\text{Bi}_2\text{O}_3$  or  $\text{Sb}_2\text{O}_3$ ), carbon allotropes (graphene or carbon nanotubes), and chelating agents (crown ethers, dimethylglyoxime, etc.). However, despite the detection of heavy metals can be achieved down to the ppb level, when complex mixtures of certain metals are analyzed, their determination might be hindered due to the overlapping

**Table 1. Survey of ETs application for the analysis of water and wastewater**

Analyte/Index	Application	Sample <sup>a</sup>		Quali/Quanti <sup>a</sup>	Electrochemical technique <sup>b</sup>	Data processing <sup>c</sup>	Number of sensors	Type of sensors <sup>d</sup>	Ref. <sup>a</sup>
<b>Water &amp; wastewater</b>									
Heavy metals: Cd(II), Cu(II), Pb(II), and Zn(II)	Monitoring of heavy metals in river water	Water	Real	Quanti	Pot	ANNs	11	ISEs	(Mimendia et al., 2010)
Heavy metals: Cd(II), Cu(II), and Pb(II)	Determination of heavy metals	Water	Synthetic	Quanti	SWV	nPLS	1/4	Au-modified with peptides	(Ebrahimi et al., 2008)
Heavy metals: Cd(II), Pb(II), and Zn(II)	Determination of heavy metals	Water	Synthetic	Quanti	AdSV	FFT + ANNs	3	GEC-modified with peptides	(Serrano et al., 2014)
Ammonium and nitrate	Monitoring of water quality at an aeration plant	Wastewater	Real	Quanti/Quali	Pot	PLS/TDA	23	ISEs, metallic, and chalcogenide glass sensors	(Belikova et al., 2019)
Ammonium, chloride and potassium	Determination of alkaline ions	River water and wastewater	Real	Quanti	Pot	ANNs	8	ISEs	(Gallardo et al., 2005)
Nitrogenous species: nitrate, nitrite, and ammonium	Monitoring of nitrogen stable species	Water	Synthetic	Quanti	Pot	ANNs	8	ISEs	(Nuñez et al., 2013)
Perchlorate and Sulfide	Determination of perchlorate and sulfide	Wastewater	Spiked	Quanti	Pot	ANNs	5	ISEs	(Wilson et al., 2011)
BOD, COD, NH <sub>4</sub> -N, PO <sub>4</sub> -P, SO <sub>4</sub> -S	Monitoring of water quality in a bioreactor pilot plant	Water	Synthetic	Quanti	CV/LAPV	PLS	8	Metallic	(Campos et al., 2012)
COD	Monitoring of water quality	Mill water	Real	Quali/Quanti	LAPV	PCA/ANNs	3	Metallic	(Gutés et al., 2006)
–	Discrimination of wastewater based on its quality	Wastewater	Real	Quali	Amp	PCA	8	Enzymatic biosensors	(Tønning et al., 2005)
COD, BOD, TOC, and Microtox® indexes	Evaluation of wastewater quality	Wastewater	Real	Quali/Quanti	Amp	PLS	8	Enzymatic biosensors	(Czolkos et al., 2016)

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**Table 1. Continued**

Analyte/Index	Application	Sample <sup>a</sup>		Quali/Quanti <sup>a</sup>	Electrochemical technique <sup>b</sup>	Data processing <sup>c</sup>	Number of sensors	Type of sensors <sup>d</sup>	Ref. <sup>a</sup>
COD	Monitoring of water quality	Surface water and wastewater	Real	Quali/Quanti	Pot	PCA/PLS	20	ISEs and chalcogenide glass sensors	(Legin et al., 2019)
Daphnia	Monitoring of water quality	Pond water	Real	Quali/Quanti	Pot	PCA/PLS	19	ISEs and chalcogenide glass sensors	Kirsanov et al. (2014)
Microtox® ( <i>Vibrio fischeri</i> )	Monitoring of water quality	Wastewater	Real & spiked	Quanti	Pot	PLS	23	ISEs and chalcogenide glass sensors	(Zadorozhnaya et al., 2015)
Microcystin	Monitoring of water quality	Drinking and surface water	Spiked	Quanti	Pot	PLS	8	ISEs, chalcogenide glass, and polycrystalline sensors	(Lvova et al., 2016)
HAAs	Determination of DBPs	Water	Spiked	Quali/Quanti	CV	FFT + ANNs	1	Au	(Cetó et al., 2017)
Pesticides: carbofuran and dichlorvos	Determination of pesticides	River water	Spiked	Quanti	Amp	ANNs	3	Enzymatic biosensors	(Cortina et al., 2008)
Pesticides: dichlorvos and methylparaoxon	Determination of pesticides	River water	Spiked	Quanti	Amp	ANNs	3	Enzymatic biosensors	(Valdés-Ramírez et al., 2009)
Phenolic compounds: 4-chloro-3-methylphenol, <i>p</i> -chlorophenol and <i>o</i> -cresol	Determination of phenolic compounds	Water	Synthetic	Quanti	LSV	ANNs	1	Graphite	(Gutés et al., 2005)
Phenolic compounds: Catechol, <i>m</i> -cresol and guaiacol	Monitoring of wastewater treatment	Wastewater	Synthetic	Quanti	CV	FFT + ANNs	4	Enzymatic (bio)sensors	(Cetó et al., 2015)
Nitrophenols: nitrobenzene, 2-, 3-, 4-nitrophenol and 2,4-dinitrophenol	Determination of nitrophenols	Water	Real	Quanti	CV	PCR/PLS	1	HDME	(Ni et al., 2001)

(Continued on next page)

**Table 1. Continued**

Analyte/Index	Application	Sample <sup>a</sup>		Quali/Quanti <sup>a</sup>	Electrochemical technique <sup>b</sup>	Data processing <sup>c</sup>	Number of sensors	Type of sensors <sup>d</sup>	Ref. <sup>a</sup>
Nitrophenols	Determination of nitrophenols	Water	Synthetic	Quanti	CV	DWT + ANNs	4	Metallic and graphite	(González-Calabuig et al., 2018)
Triclosan	Monitoring of EOCs treatment	Water	Spiked	Quali	EIS	PCA	5	Au-modified interdigitated	(Magro et al., 2019)
–	Malfunctioning of filtration system from a water treatment plant	Water	Real	Quali	LAPV	PCA	–	Metallic	(Winquist, 2008)
COD	Estimation of COD and difficulty of degradation	Water	Real	Quali	CV	PCA	4	GEC and metallic	(Wang and del Valle, 2021)

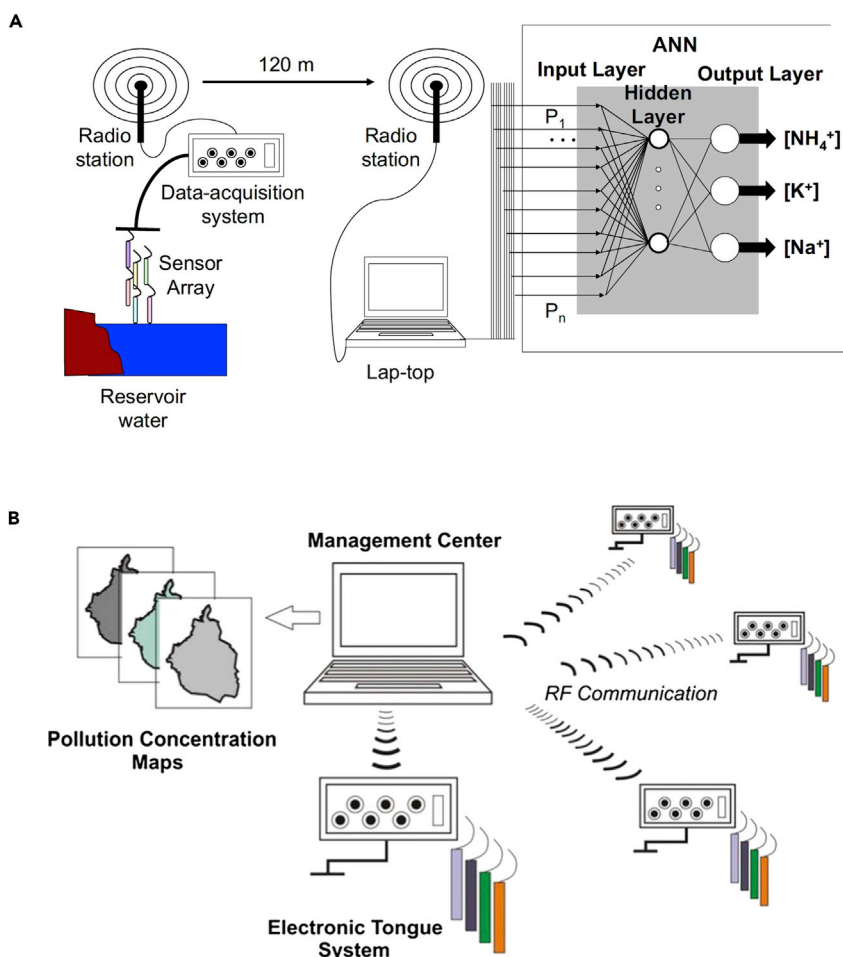
<sup>a</sup>“Synthetic” refers to sensors that have only been tested in buffered media with stock solutions, “Spiked” to sensors that have been tested in spiked real samples, “Real” to sensors which performance has been satisfactorily evaluated in real samples. Quali stands for qualitative application, while Quanti to quantitative.

<sup>b</sup>AdSV: adsorptive stripping voltammetry; Amp: amperometry at fixed potential; CV: cyclic voltammetry; LAPV: large amplitude pulse voltammetry; LSV: linear sweep voltammetry; Pot: potentiometry.

<sup>c</sup>ANNs: artificial neural networks; DWT: discrete wavelet transform; FFT: fast Fourier transform; PCA: principal component analysis; PCR: principal components regression; PLS: partial least squares regression; TDA: topological data analysis.

<sup>d</sup>GEC: graphite epoxy composite; HDME: hanging drop mercury electrode; ISE: ion-selective electrode.





**Figure 2. Remote monitoring of surface water quality using a potentiometric ET**

Schematic representation of (A) the application of an ET for the remote monitoring of different species in a river and (B) how the implementation at different spots would allow building pollution maps. Reproduced with permission from Elsevier (Mimendia et al., 2010).

between peaks, the formation of intermetallic compounds, or the lack of linearity. In this regard, ETs can offer a straightforward solution, specially when combining the usage of modified electrodes with chemometrics.

An interesting application for the determination of Cd(II), Cu(II), and Pb(II) using a voltammetric ET was reported by Ebrahimi et al. (2008). Beyond the reported results, what is significant is the comparison in there. As already known, improvements derived from the usage of chemometrics cannot be neglected (Ni and Kokot, 2008). However, what is demonstrated is that further advantages are obtained when multi-way data are used (sample  $\times$  variable 1  $\times$  variable 2  $\dots \times$  variable  $n$ , see Figure 1). To this aim, a single electrode was simultaneously modified with different peptides, and the obtained results were compared to those from an array of electrodes modified with each of the different peptides. In the case of the sensor array, the simultaneous determination of three metals was possible, while in the case of the single electrode, only Cu(II) could be quantified correctly for mixtures of the three metals.

Similarly, Serrano et al. went a step further and explored the usage of pH as an extra variable to further increase the dimensionality of the data when analyzing mixtures of Cd(II), Pb(II), and Zn(II) (Serrano et al., 2014). Authors compared the performance of a single electrode modified with one peptide at a single and multiple pH values against the performance of an array of peptide-modified electrodes at several pH values (quadrilinear data, Figure 1). Again, a significant improvement was observed when comparing the results from single and multi-pH

values, while only a slight improvement was obtained for the multi-electrode and multi-pH approach. The attempt represents a promising strategy to enrich the departure data, worth to be further explored with more advanced chemometric tools able to cope with such complex datasets (Maggio et al., 2011). Overall, the advantage of multi-way systems is demonstrated, but also the fact that the intrinsic higher dimensionality of voltammetric sensors provides advantages in this regard.

### *Inorganic pollutants*

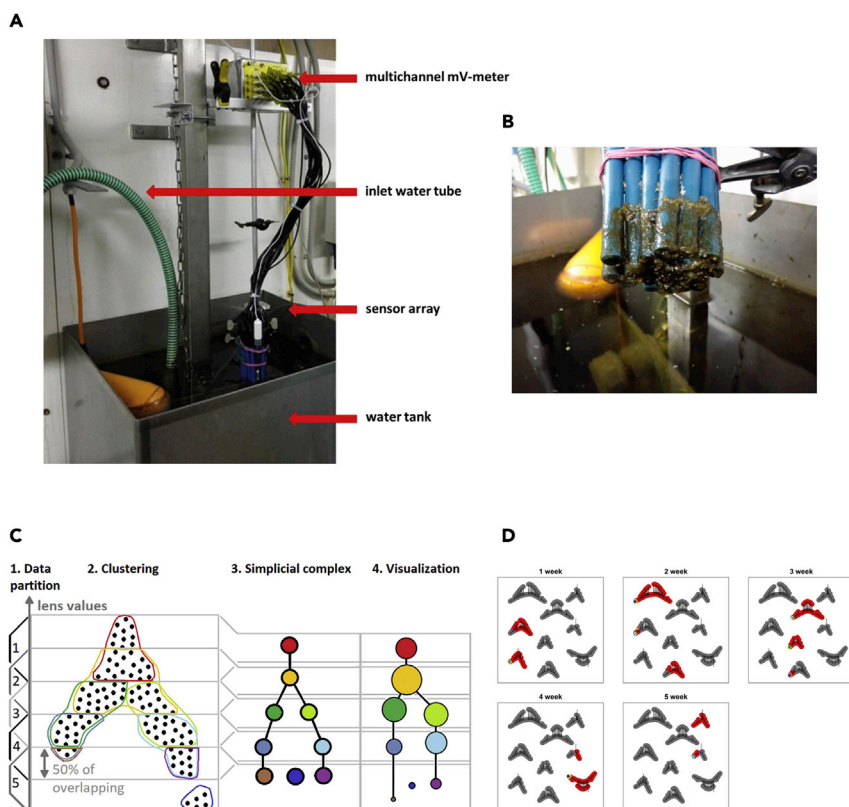
Along with heavy metals, of necessary mention, there are many other inorganic pollutants such as phosphate, sulfate, nitrate, cyanide, perchlorate, etc. or even alkali and alkaline earth metals that are of concern (Ashraf et al., 2014). Such compounds are non-biodegradable and, again, despite most of them are naturally present, their accumulation due to anthropogenic activity threatens not only the public health, but also to the aquatic flora and fauna.

For instance, nitrate is a contaminant in groundwater reservoirs, which levels increase dramatically year after year, mostly as a result of agricultural and farming runoff (Ashraf et al., 2014). In this instance, to better diagnose the status of an ecosystem, not only the quantification of nitrate is required but also the speciation of the different forms of inorganic nitrogen. Unfortunately, as happens with heavy metals, there is a lack of a method that allows the autonomous, simultaneous determination of ammonium, nitrite, and nitrate in real time. Covering this, Nuñez et al. reported the usage of a potentiometric ET formed by 15 ISEs, including membranes sensitive to the three considered nitrogenous species, but also for potential interfering species such as sodium, potassium, or chloride plus some generic ones for cations and anions (Nuñez et al., 2013). From these data, an ANN model was built to achieve the quantification of nitrate, nitrite, and ammonia as well as potassium, sodium, and chloride. Finally, the developed ET was successfully applied to the monitoring of the different species during decontamination of nitrate by photoelectrochemical reduction.

Similarly, quantification of ammonia, potassium, and sodium was reported in river and wastewater samples, without requiring any pre-treatment other than its filtration and dilution in the appropriate buffer (Gallardo et al., 2005). More recently, the continuous on-line monitoring of ammonium and nitrate in processed water at an aeration plant was described (Belikova et al., 2019). The aim was to demonstrate the potential of potentiometric ETs for water quality monitoring over long periods. In this direction, an array of 23 sensors composed of 8 polymeric cation-sensitive, 8 polymeric anion-sensitive, and 7 metallic and chalcogenide glass sensors were installed at the outlet water line of the aeration plant, and their responses read every seven seconds for 26 days (Figure 3A). Given the large amount of organic matter in the plant effluents, sensor surfaces were regenerated by mechanical cleaning every 4–6 days and then re-calibrated to avoid fouling effects. Finally, quantification of both species was achieved with partial least squares regression (PLS). Besides, topological data analysis (TDA) allowed to get a general overview of the sensors' readings as the large dimensionality of the data hindered its processing with other common approaches such as principal component analysis (PCA, see Figures 3B and 3C). Briefly, TDA allows extracting significant information from high-dimensional datasets, even if those are incomplete or noisy, by making them insensitive to the chosen metric and encoding the big amount of information into an understandable and easy-to-represent form.

In another relevant application, Wilson et al. described the application of a potentiometric ET for the determination of perchlorate and sulfide ions in wastewaters (Wilson et al., 2011). The ISEs array was based of different metallophthalocyanines to obtain an anti-Hofmeister response pattern, which allowed generating a richer cross-response from the sensor array in comparison to common quaternary ammonium ion carriers. After the complete characterization of their responses, an ANN model was built which allowed the quantification of both species in wastewater. Finally, to illustrate the benefits derived from the ET approach, quantification of both anions was also attempted by direct interpolation on each individual electrode, showing bigger errors for both species.

Despite most ET applications for the analysis of inorganic pollutants use potentiometric sensors, as justified because they are ionic species, some reports using voltammetric sensor arrays can also be found. For example, Campos et al. attempted the determination of different species such as ammonia, sulfate, or phosphate employing an array of eight metallic electrodes in influent and effluent samples from a pilot wastewater treatment plant (Campos et al., 2012). To this aim, several samples were collected and each of those was diluted in distilled water at different ratios to make 2–4 additional samples from each, which results in a change of conductivity between the different samples due to the dilution, as shown by the



**Figure 3. Monitoring of wastewater quality using a potentiometric ET**

(A) Photo of the potentiometric ET used for the on-line measurement at an aeration plant, and (B) detail of the sensors after long-term online measurements. (C) Schematic of TDA where the colors in the plot designate different clusters, and (D) results using the number of the measurement as the lens. Reproduced with permission from Elsevier (Belikova et al., 2019; Yaroshenko et al., 2020).

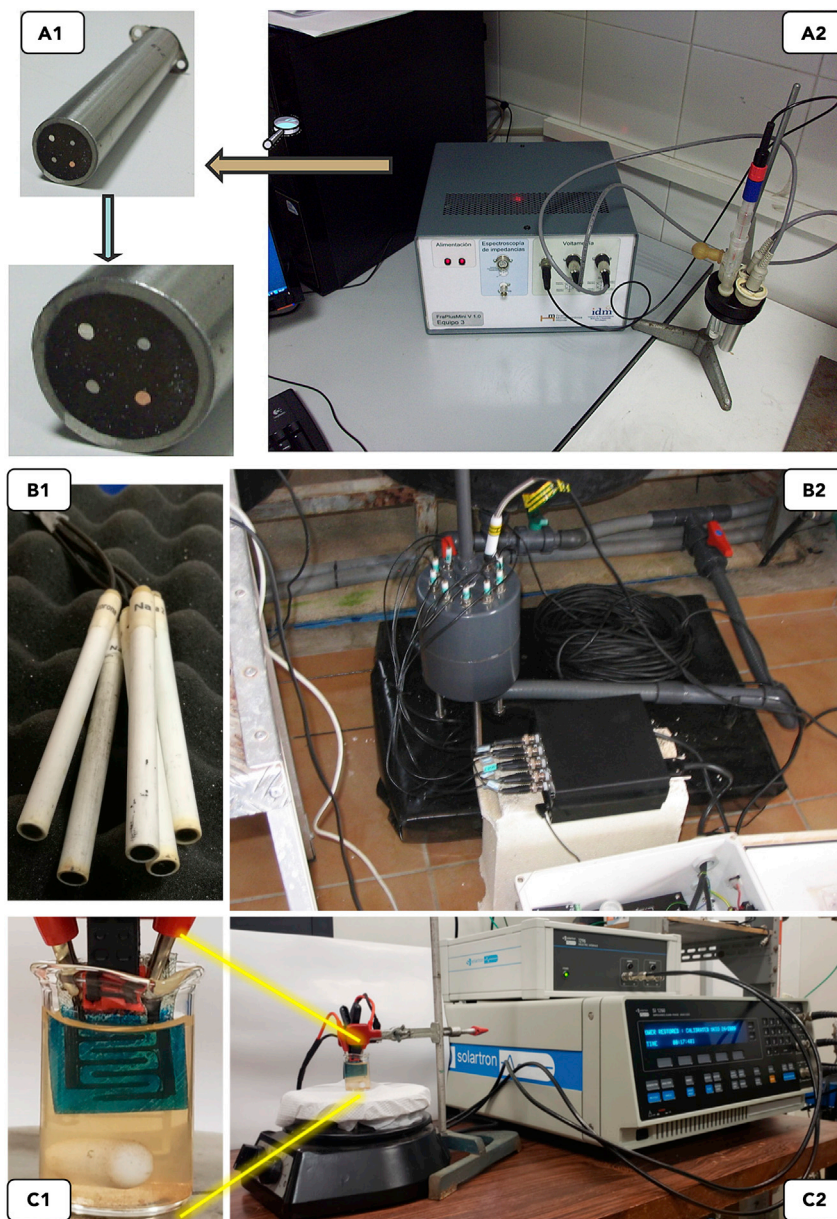
authors. Next, those samples were measured with the proposed voltammetric sensor array (Figure 4A). However, in the absence of Faradaic processes related to the oxidation or the reduction of electroactive species, changes observed in the responses will be related largely to non-Faradaic processes (arising from e.g., changes in the ionic composition or conductivity due to the different dilution of the samples, not the ideal situation to derive a response model). Nevertheless, still being possible to achieve significant correlations for all the considered species, in an application that would be in line to the discussed soft-sensor approach, but far from a realistic scenario without proper validation.

#### Total organic matter in water and water quality indices

According to the IUPAC, chemical oxygen demand (COD) provides “a measure of the amount of oxygen, divided by the volume of the system, required to oxidize the organic (and inorganic) matter in wastewater using a chemically oxidizing agent” (IUPAC, 1997). In other words, it is a parameter that provides a measure of the amount of organic substances present in water, being useful to estimate the effect that an effluent will have in the receiving body.

Similarly, biochemical oxygen demand (BOD) is the amount of oxygen required by aerobic biological microorganisms to break down the organic matter present in a water sample at certain temperature over a specific time. BOD is similar to COD in the sense that it also provides a measure of the load of organic compounds present in the water, with the advantage of being more representative, although at expenses of a longer analysis time. Conversely, COD has the drawback of requiring highly pollutant and hazardous reagents.

Lastly, the use of electrochemical oxygen demand (EOD) has been also proposed. EOD is an alternative parameter defined as the amount of oxygen equivalent to the charge consumed during electrochemical



**Figure 4. Example of different ET set-ups based on different techniques**

(A1 and A2) Photo of the metallic-based voltammetric sensor array and the setup used for the analysis of wastewater samples with a voltammetric ET. Reproduced with permission from Elsevier (Campos et al., 2012). (B1 and B2) Photo of the potentiometric ET based on an array of ISEs used for the in-line monitoring of nutrient solution compositions in closed soil-less systems. Reproduced with permission from ACS (Gutiérrez et al., 2008). (C1 and C2) Photo of the interdigitated 3D-printed graphene electrode and the experimental setup used for the analysis of soils with the impedimetric ET. Reproduced with permission from MDPI (Riul et al., 2010).

oxidation of the sample (Lee et al., 1999). In this respect, ETs provide an advantageous approach as not only the usage of an array of sensors can provide a better estimation of EOD but also a chemometric model can be used to correlate the electrochemical measurements with the classical COD or BOD values, while avoiding their drawbacks.

Several approaches have been reported in the literature tackling the correlation of COD values with ET readings, employing mainly voltammetric measurements for obvious reasons. One of the first attempts

was reported by Gutés et al., where a flow-injection analysis (FIA) system in conjunction with an array of four metallic electrodes was applied to the analysis of paper mill industrial waters (Gutés et al., 2006). In there, large amplitude pulse voltammetry (LAPV) measurements were correlated with COD, conductivity, and pH values. Different materials and techniques were evaluated in the following years to correlate electrochemical measurements and COD values, but one of the most relevant advances was the usage of enzymatic biosensors for such purpose (Czolkos et al., 2016). By replacing metallic-based electrodes with an array of enzyme-modified ones, obtaining more detailed information about environmental pollutants such as phenolic compounds and pesticides was targeted. Concretely, considered enzymes included cellobiose dehydrogenase (CDH), horseradish and soybean peroxidases (HRP and SBP), glucose oxidase (GOx), acetylcholinesterase and butyrylcholinesterase (AChE and BChE), and tyrosinase (Tyr). The bioET was then applied to the analysis of wastewater samples from a chemo-thermo-mechanical pulp (CTMP) mill at different purification stages, achieving a successful correlation with COD, BOD, and TOC values by means of a PLS model. Furthermore, not only the quantification of organic matter was achieved but also the correlation with Microtox® test. Microtox® bioassay measures the disruption that toxic substances cause to the respiratory process of *Vibrio fischeri* bacteria, consequently providing a measure of the sample toxicity.

Such an application is highly relevant as toxicity is a key parameter to be evaluated at any stage (in wastewater as well as in surface or drinking water), but also because no other methods, other than bioassays, may measure toxicity. Difficulties encountered with traditional methods are that toxicity cannot be related to the concentration of a specific compound, as the synergies that different compounds may have exacerbate or mitigate their toxicity. Thus, ETs provide a low-cost, reagentless, and portable alternative for the rapid monitoring of this special aspects of water quality.

Despite COD and BOD are related to the amount of oxidizable organic matter, which *a priori* could seem more suited for amperometric and voltammetric methods, these indexes were also predicted employing potentiometric sensors given the capabilities of ETs to correlate measured variables with other unmeasured parameters (Legin et al., 2019). For instance, different potentiometric ETs based on ca. 20 cross-sensitive sensors including anion-sensitive, cation-sensitive, and chalcogenide glass electrodes with redox sensitivity were successfully applied for the evaluation of toxicity indexes such as Microtox® (Kirsanov et al., 2014) or the one related to the *Daphnia magna* bioassay (Zadorozhnaya et al., 2015).

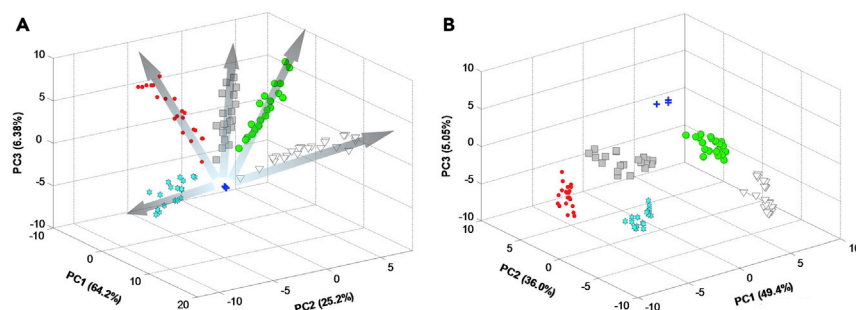
Finally, not only the monitoring of anthropogenic pollutants is important but also the detection of the contamination caused by naturally occurring microorganisms such as cyanobacteria (Lvova et al., 2016). Among cyanotoxins, microcystins (MCs) are the most hazardous and problematic, posing a major threat if present in drinking or irrigation water supplies. In this direction, the application of a potentiometric ET for the qualitative and quantitative detection of MCs contamination was investigated by Lvova et al. An 8-sensor array composed by different potentiometric sensors was used for the measurement of different water samples, and the obtained responses were correlated with the data obtained by both ultra-high-performance liquid chromatography coupled with diode array detection (UHPLC-DAD) and colorimetric enzymatic technique, showing a correct quantification of MCs.

In summary, it cannot be neglected that ETs represent a promising tool for express, reduced instrumental burden, and green water quality monitoring.

### Organic pollutants and emerging contaminants

In order to ensure that water is free from any harmful or unpleasant compounds as well as to control waterborne pathogens, water is submitted to different treatments, being chemical disinfection the most common one (Sadiq and Rodriguez, 2004; Richardson et al., 2007). However, despite the benefits that such treatments offer, they can also lead to the formation of potentially harmful disinfection by-products (DBPs), which arise from the reaction of employed chemical agents with certain organic matter present in water. Research carried out in this topic has boosted the understanding on the formation and control of DBPs as well as their potential health risks, being accepted that potentially harmful products are always generated to some extent regardless of the chosen disinfectant.

Trihalomethanes (THMs) and haloacetic acids (HAAs) are two groups of DBPs found in water when this is chlorinated (Roberts et al., 2002). The usage of alternative disinfection agents has led to the formation of the so-called



**Figure 5. Qualitative analysis of haloacetic acids (HAAs) using a voltammetric ET**

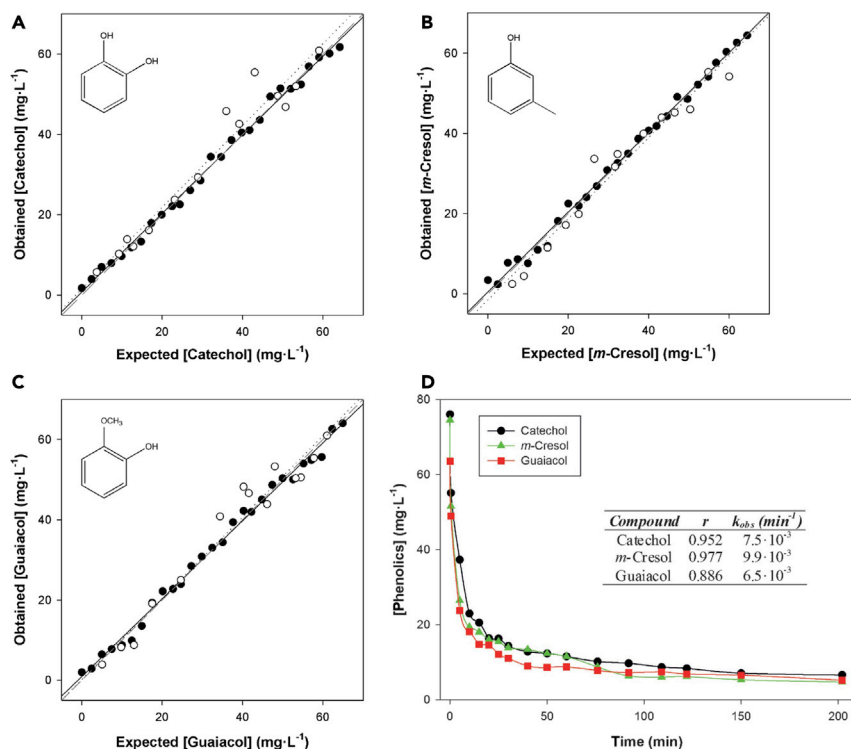
3D score plot obtained from the principal component analysis of the voltammetric responses for different HAAs stock solutions of increasing concentration, (A) without and (B) with the fingerprint extraction algorithm. Concretely, analyzed samples correspond to: (blue +) Buffer, (green ●) BdCA, (gray ■) dBCA, (red ●) tBA, (cyan ✕) mBA, and (white ▼) tCA. Reproduced with permission from Elsevier (Cetó et al., 2017).

“emerging DBPs” (Richardson, 2003; Richardson et al., 2007), which includes several different compounds that have been identified both in laboratory studies and in full-scale water treatment plants.

For instance, the analysis of HAAs in water samples employing ET principles was recently reported (Cetó et al., 2017). Voltammetric fingerprints of the different HAAs were obtained using a gold electrode, which in combination with an ANN model allowed to quantitatively detect and discriminate mixtures of bromodichloroacetic acid, dibromochloroacetic acid, and tribromoacetic acid. From this study, there are two points to be remarked. On the one hand, it must be noted that the fingerprinting approach allowed not only the discrimination of the different HAAs at a certain concentration, but independently of the concentration implied (Figure 5). On the other hand, although the usage of a single sensor would not fit strictly with the ET definition (Electronic tongues), given the larger dimensionality and nature of voltammetric measurements, the same principles are applied as different responses are obtained at different potentials for different compounds.

Apart from DBPs, there are other contaminants of high relevance such as the emerging organic compounds (EOCs), which include newly developed compounds, but also compounds newly found in the environment (Lapworth et al., 2012). EOCs include a wide range of pharmaceutical products (e.g., analgesics such as paracetamol, or antibiotics), lifestyle compounds (e.g., caffeine or cotinine), pesticides, industrial chemicals (e.g., bisphenol A), surfactants, personal care products (PCPs), and food additives (e.g., sweeteners as sucralose or preservatives as parabens), between others. Similarly, another category of compounds receiving much attention is those classified as persistent organic pollutants (POPs), which are toxic organic compounds that persist for long periods of time and end up accumulating in the environment. Lastly, there are other organic pollutants which monitoring is required depending on the industrial activities carried out in the vicinities.

Within this context, the analysis of pesticides in water samples by means of amperometric biosensors has been one interesting topic for bioETs. Developed systems are typically based on the usage of an array of biosensors equipped with different cholinesterases (mainly, acetylcholinesterase, AChE) or other enzymes, for which the enzymatic inhibition is related to the pesticide concentrations. For example, the work reported by Cortina et al., in which an array of screen-printed electrodes modified with three different AChEs was applied to the simultaneous determination of carbofuran and dichlorvos mixtures in water samples taken from a river, before and after a sewage treatment plant (Cortina et al., 2008). As already highlighted with other applications, the authors compared the performance of the chemometric model with the results that would be attained with direct interpolation into the univariate calibration curve for the river samples. The results evidenced the benefits derived from the ET approach, as without the ANN model it was not possible to correctly quantify both compounds (e.g., the recovery yields were in the range 92%–116% for the former, while for the univariate calibration those went up to 566%–962%). Furthermore, the performance of such system was improved by coupling it with an automated FIA system, which improved the reproducibility of operation and reduced greatly the analysis time (Valdés-Ramírez et al., 2009).



**Figure 6. Monitoring of the photodegradation of phenolic compounds using a voltammetric ET**

(A–C) Results provided by the ANN model built for three different phenolic compounds (catechol, *m*-cresol and guaiacol) by means of a voltammetric bioET (filled symbol, training set, empty symbol, external test set) and (D) the predicted concentrations for each of them during the photodegradation process. Reproduced with permission from Wiley (Cetó et al., 2015).

Another group of organic substances, classified as high priority organic pollutants in water, are phenolic compounds. Phenolic compounds are widely used in diverse industrial applications, which in conjunction with the toxicity of some of those make their determination highly relevant. Detection of such compounds may be done employing biosensors that use tyrosinase (Tyr) or laccase (Lac) enzymes; however, given its antioxidant nature, most of them can also be directly oxidized.

A relevant example was reported by Gutés et al. in which a single graphite electrode in conjunction with a sequential-injection analysis (SIA) system was used for the development of an automated voltammetric ET applied to the analysis of phenolic compounds (Gutés et al., 2005). Concretely, mixtures of *o*-cresol, *p*-chlorophenol, and 4-chloro-3-methylphenol were determined to demonstrate the potential of the approach.

Similarly, the application of a bioET for the monitoring of the photodegradation of catechol, *m*-cresol, and guaiacol mixtures in wastewater was reported (Cetó et al., 2015). The three considered phenols were selected as they are common phenolic compounds present in various industrial effluents, but of difficult removal by conventional wastewater treatment processes. Samples were analyzed with an array of four voltammetric (bio)sensors employing the above-mentioned enzymes, which in combination with ANNs permitted the individual quantification of each of the compounds (Figure 6).

Nitrophenols are also another group of high-toxicity chemicals, the entry of which to the aquatic environment is of special concern. Despite electrochemical methods have been demonstrated advantageous when limited to a single chemical component or the total amount of nitro-compounds, the serious overlapping of individual compounds in the voltammogram hinders their analysis when mixtures of those are to be assessed (unless a pre-separation step is performed). In this direction, Ni et al. achieved the simultaneous determination of five nitro-aromatic compounds in water samples based on their reduction at a hanging

mercury drop electrode (HMDE) (Ni et al., 2001). When classic least squares regression was used, the relative prediction error was as high as 38%, while the usage of PLS allowed a reduction of the latter down to ca. 10%. The developed method was next applied to the analysis of those in field water samples with recoveries ca. 90%–110%. Although an important drawback of this approach is the use of mercury electrodes, highly questioned worldwide, similar performance has been demonstrated later with metallic and graphite electrodes in an ET scheme (González-Calabuig et al., 2018).

Recently, the usage of an impedimetric ET was explored for the real-time degradation and quantification of triclosan and its derivative by-products in an electrochemical flow reactor (EFR) (Magro et al., 2019). Triclosan is categorized as an EOC, which degradation can lead to the formation of polychlorinated dibenzo-p-dioxins, one of the 12 initial POPs recognized under the Stockholm Convention. The proposed ET was based on an array of five thin films prepared with polyelectrolytes by layer-by-layer (LbL) nano-assemblies onto gold interdigitated electrodes, which were coupled to the EFR that operated as the secondary clarifier of a wastewater treatment plant. Registered data were processed by means of PCA, which provided information regarding the degradation of triclosan. However, despite the authors claim that a semi-quantitative determination could be achieved, the usage of PCR or PLS would be more suited for such purpose.

### Classification of water samples

Finally, one of the most straightforward applications of ETs focuses in the classification of water samples based on different criteria. Obtained responses from the sensor array might be submitted to PCA as it provides a better visualization of samples (dis)similarities, allowing to identify patterns in the data. In this sense, some of the already presented works proceeded in this way. For example, for the discrimination of wastewater according to its origin (Gutés et al., 2006) or according to the expected toxicity (Czolkos et al., 2016).

Similarly, an interesting application was proposed by Winquist, in which a voltammetric ET was used to estimate the water quality of samples collected from sand filters in a drinking water production plant (Winquist, 2008). Voltammetric responses from the array of metallic electrodes were submitted to PCA, which allowed detecting the malfunctioning of the filters if a drift was observed in the scores plot.

Qing et al. proposed the usage of a voltammetric ET for the evaluation of the organic load of water samples (Wang and del Valle, 2021). The usage of ETs to predict COD or BOD values has already been discussed in *Inorganic pollutants*, but such index only provides a measure of the total organic load, failing to provide information on how easily that organic matter can be oxidized. To overcome such limitation, the authors propose the usage of PCA. Polluted water samples were analyzed with the sensor array and those compared to some reference substances of increasing difficulty of degradation. In this manner, the joint information provided by the sensor array shows the ability to estimate both the organic load and its difficulty of degradation.

### Soil analysis

The number of manuscripts describing the application of ETs for soil analysis is much smaller than those related to the analysis of water samples (Table 2). Nonetheless, there are still a few relevant applications that demonstrate the potential and advantages that the approach can offer, beyond those of sensors alone (Nadporozhskaya et al., 2022). In this direction, most relevant applications are related to the monitoring of nutrients in farming (either in soil-less cultivations or in soil extracts), the quantification of different pollutants in soil extracts (e.g., heavy metals), or even the discrimination and classification of soils. Moreover, as particularities of different cases have already been presented, plus the fact that some applications are analogous to some already discussed (being the main difference that a soil extraction step must be performed before carrying out the measurement), a briefer discussion focusing only on the applications will be provided.

### Nutrients

As many other fields, agricultural practices are affected by information technologies. Their integration is referred to as *smart farming* or *digital agriculture* and is aimed to improve efficiency and/or quality of the products. In this regard, tailored application of water, fertilizers, pesticides, etc. can minimize the inputs required to achieve a given yield, which in turn reduces the negative effects for the environment. Besides,



**Table 2. Survey of ETs application for the analysis of soils**

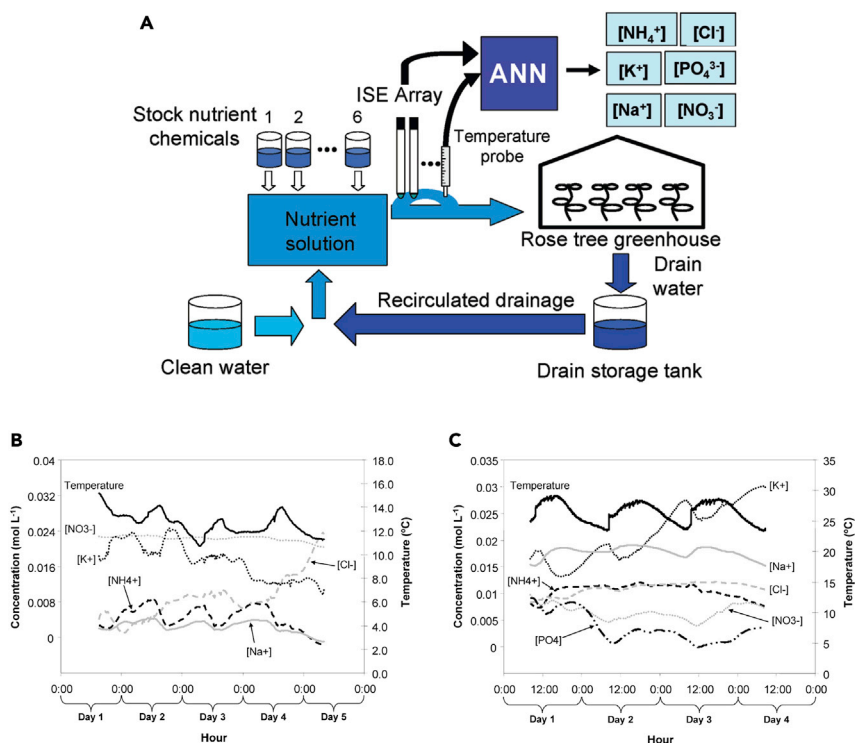
Analyte/Index	Application	Sample <sup>a</sup>		Quali/Quanti <sup>a</sup>	Electrochemical technique <sup>b</sup>	Data processing <sup>c</sup>	Number of sensors	Type of sensors <sup>d</sup>	Ref. <sup>a</sup>
–	Discrimination of soils and assessment of its fertility	Soil	Real	Quali/Quanti	Pot	PCA-ANN	20	ISEs	(Mimendia et al., 2014)
Heavy metals: Cd(II), Cu(II), Pb(II), and Zn(II)	Determination of heavy metals in soils	Soil	Real	Quanti	Pot	ANNs	9	ISEs	(Wilson et al., 2012)
Heavy metals: Cd	Determination of heavy metals in soils	Soil	Spiked	Quanti/Quali	LAPV	PCA/PLS	3/1	Metallic	(Winqvist et al., 2009)
NPK	Evaluation of NPK in soils	Soil	Real	Quanti	Pot	PLS	26	ISEs and metallic sensors	(Khaydukova et al., 2021)
NPK	Evaluation of NPK in soils	Soil	Spiked	Quali	EIS	PCA	4	3D-printed interdigitated graphene electrodes	(Americo da Silva et al., 2019)
Ammonium	Determination of ammonium in fertilizers	Fertilizer	Real	Quanti	Pot	ANNs	8	ISEs	(Gallardo et al., 2005)
Ammonium, potassium, sodium, chloride, nitrate, and phosphate	Monitoring of nutrient solution in greenhouse	Soil-less	Real	Quanti	Pot	ANNs	8/11	ISEs	(Gutiérrez et al., 2008)

<sup>a</sup>“Spiked” refers to sensors that have been tested in spiked real samples, “Real” to sensors which performance has been satisfactorily evaluated in real samples. Quali stands for qualitative application, while Quanti to quantitative.

<sup>b</sup>LAPV: large amplitude pulse voltammetry; EIS: electrochemical impedance spectroscopy; Pot: potentiometry.

<sup>c</sup>ANNs: artificial neural networks; PCA: principal component analysis; PLS: partial least squares regression.

<sup>d</sup>ISE: ion-selective electrode.



**Figure 7. Monitoring of nutrients in soil-less cultivation using a potentiometric ET**

(A) Schematic representation of the set-up used for the in-line monitoring of nutrient solution compositions in closed soil-less systems. (B and C) Monitoring of the different considered cations and anions with the proposed potentiometric ET. Reproduced with permission from the American Chemical Society (Gutiérrez et al., 2008).

such systems are not only interesting for traditional terrestrial settings (e.g., greenhouse production), but could also be applied to nominal on-orbit water and soil quality monitoring, an important issue for interplanetary travels someday (Bamsey et al., 2012).

Fertilizer analysis is an area with enormous potential for the application of ETs as has been demonstrated, either in hydroponic systems or actual soils. In this regard, although strictly hydroponic or soil-less systems might not be considered as soil analysis, it obviously represents a scenario in between water and soil analysis.

In an approach similar to the systems described for the monitoring of heavy metals, Gutiérrez et al. reported the usage of a potentiometric ET for the monitoring of nutrient solution compositions in closed soil-less systems (Figure 4B) (Gutiérrez et al., 2008). Curiously, one of the inconveniences found was the interferences of certain PVC membrane sensors due to the high levels of other ions and/or its dependence with pH or temperature. To counterbalance such effects, some PVC membrane sensors were replaced with second-kind electrodes, a pH sensor was incorporated, and a temperature probe was also included to compensate any possible effect of temperature changes on sensors response. Thus, when building the ANN response model, the stock solutions were measured at different temperatures to consider such effect. Finally, the system was successfully applied for the continuous monitoring of ammonium, potassium, sodium, chloride, nitrate, and phosphate ions for 13 days (Figure 7). In order to further demonstrate the potential and advantages of the ET approach, the performance of the model was compared to that obtained from the interpolation of each specific sensor into the Nernstian calibration curve, showing much higher errors in general (e.g., 14.0%–58.5% for sodium or 15.3%–26.9% for nitrate). Additionally, the ET was purposely used under an incorrect configuration of the system that controls the recomposition of the nutrient solution to evaluate the ability of the ET to detect such malfunctioning, overall, confirming the suitability of a potentiometric ET for this application.

Moving to the analysis of fertilizers in actual soil samples, Khaydukova et al. described the application of a potentiometric ET for the simultaneous determination of N, P, and K content in water extracts of soils (Khaydukova et al., 2021). Those three correspond to the main soil macronutrients, being NPK fertilizers one of the common choices for farming, where a three number convention is used to refer to the actual amount of each of the nutrients in the fertilizer. Thus, by determining their actual amount in soil, a smart introduction of elements into the soil can be achieved, which in turn allows to decrease the negative impact derived from over-fertilizing without reducing crop yield. Because the authors aimed for the simplest sample extraction method, distilled water was used as an extracting agent, optimizing only the amount of soil and time required. Upon extraction, samples were filtered and measured directly with an array of 26 potentiometric sensors. Lastly, a PLS model was built allowing to relate sensors readings with NPK content as well as its pH, electrical conductivity, and organic carbon.

### Pollutants

Common pollutants found in soil include petroleum products, organic solvents, pesticides, and heavy metals (Ashraf et al., 2014). Those derive typically from industrial and agricultural activities, although warfare and military activities are also a significant source of pollutants.

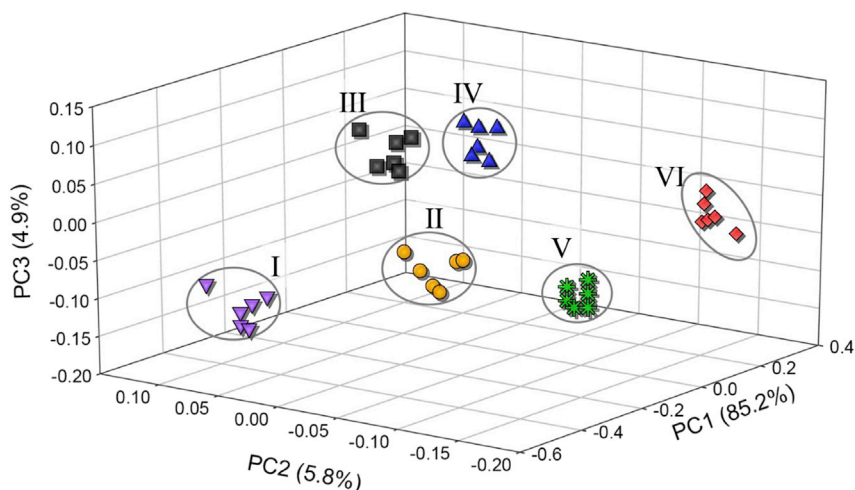
Within this context, Winquist et al. described two systems based on voltammetric ETs for the analysis of cadmium in soil samples (Winquist et al., 2009). Soil samples were extracted using two different methods, with an AL-solution or with nitric acid solution. The first system employed an array of Pt, Au, and Rh electrodes, while the second relied only on a Au electrode. Upon its extraction, samples were analyzed by anodic stripping voltammetry employing the two proposed systems. Interestingly, both systems incorporated a polishing unit which regenerated the electrodes prior to each measurement. Quantification of Cd(II) in the range 0.2–10 µg/L was possible by means of PLS. To enhance the sensitivity of the method and to automate its operation, a flow through system was developed. The final system was described as virtually maintenance free due to the incorporated polishing unit, and the lifetime estimations were of one year with a 6-hour daily use.

Similarly, the application of a potentiometric ET for the analysis of Cd(II), Cu(II), Pb(II), and Zn(II) in soil samples has been reported (Wilson et al., 2012). Extraction of the heavy metals from the soil was done with aqua regia; and the extracts were subsequently diluted in buffer for the potentiometric measurements. Quantification of the different metals was achieved by means of an ANN model, and the results obtained were compared with those of atomic absorption spectroscopy (as the reference method). Overall, good precision and accuracy were achieved for Cu(II), Pb(II), and Zn(II), while in the case of Cd(II), the content in the samples was too low for its adequate determination.

### Classification of soil samples

Lastly, as pointed out with the analysis of water samples, one of the applications in which ETs clearly can stand out is in the classification of soils. In this regard, a very illustrative application was reported by Mimendia et al. in which a potentiometric ET was applied for the discrimination of soil types (Mimendia et al., 2014). Three different extractants were compared in the study (viz. MilliQ water, acetic acid, and barium chloride), which were mixed for 1 h with the soil. Afterward, the samples were allowed to rest for 30 min for the soil to sediment and the resulting solution was measured without any filtering. Obtained responses were examined by PCA, from which clear clusters for the different types of soils could be observed (Figure 8). Additionally, different physicochemical parameters related to soil fertility such as the nitrate, chloride, or organic carbon content were also successfully estimated.

More recently, an innovative application was reported by Americo da Silva et al. employing an array of four electrodes formed by LbL films deposited onto 3D-printed graphene-based interdigitated electrodes (Americo da Silva et al., 2019). To demonstrate the potential of the proposed device for soil analysis, soil samples of different textures were spiked with different amounts of nitrogen, phosphorus, and potassium (NPK). Soil samples were then extracted by sonication using MilliQ water as extractant and measured under non-turbulent stirring to avoid soil decantation (Figure 4C). Capacitive responses were examined by PCA, which showed a good discrimination of soils, with PC1 corroborating soil fertility. In this sense, some of the main advantages of such a device include its fast and simple prototyping, the use of biodegradable materials, and its low-cost; all of them interesting properties for the development of commercial sensors.



**Figure 8. Qualitative analysis of soils using a potentiometric ET**

3D score plot obtained from the principal component analysis of the potentiometric responses of the ET for different soils using acetic acid as the extractant. The samples correspond to soils from different regions of Catalonia: (I) Vallgorguina, (II) Bellmunt, (III) Montesqui, (IV) Taradell, (V) Bellaterra, and (VI) Delta de l'Ebre. Reproduced with permission from Wiley (Mimendia et al., 2014).

## CONCLUSIONS

The potential of ETs as early alert screening tools in environmental analysis has been demonstrated over very different scenarios. Using this approach, the quantitative multi-determination of several species, the correlation with different quality indexes, or the classification of different samples could be attained by shifting the complexity from the sensor development to the software side.

In comparison to standard analytical methods for certain pollutants, which usually are time consuming, involve expensive laboratory equipment and/or reagents, and are not suitable for on-site monitoring, ETs' main advantages include its portability and ease of miniaturization, facilitating field-detection in a rapid, reliable, and inexpensive way, which should thus foster decentralized screening applications.

Furthermore, ETs have been already identified as one of the clear examples of green analytical systems, where the manipulation is reduced to a minimum (just the immersion of the sensors into the sample under analysis), consumption of reagents or generation of residues can be minimal, and instrument complexity is translated to the software component, where the response model and the effort in its generation is now the toughest task. In contrast, applications developed can be of high complexity, which, on the one side, supplied performances can be close to heavy instrumentation (AAS, HPLC, etc.), and on the other, it can be possible to evaluate complex information situations, e.g., toxicity, normally related to high manipulative and wait efforts.

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## AUTHOR CONTRIBUTIONS

All authors have read and agreed to the published version of the manuscript. Xavier Cetó: Conceptualization, Writing - Original Draft. Manel del Valle: Conceptualization, Writing—review and editing, Funding Acquisition.

## DECLARATION OF INTERESTS

The authors declare no competing interests.

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