Non-conventional electrochemical and optical sensor systems

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Abstract Electroanalytical methods are a common tool for the assessment of chemical peculiarities of aqueous solutions. Also, the analysis of water based on optical sensors is a mature field of research, which already led to industrial applications and standard laboratory practices. Nevertheless, scientific literature is still offering new sensor techniques and innovative measurement approaches in both fields. In particular, for fast characterisation of liquids and change detection applications in a continuous monitoring context, the technology of taste sensors based on electrochemical techniques is still witnessing a growing interest. Such devices are often defined as “electronic tongues” or “e-tongues”. In addition, emerging inexpensive and portable devices with optical sensing capabilities can be used for monitoring applications with a novel approach. This chapter gives an overview of recent techniques developed in both fields, and presents several potential applications and case studies that deal with the context of water quality assessment. A brief introduction about the basics of each measurement technology, even if not exhaustive, is also provided.

Keywords Drinking water, electrochemistry, optical sensors, electronic tongue, computer screen photoassisted technique

Abbreviations

CSPT	Computer Screen Photoassisted Technique

ISE	Ion Selective Electrode
WE	working electrode
REF	reference electrode
LAPV	Large Amplitude Pulse Voltammetry
PCA	Principal Components Analysis
HPCA	Hierarchical PCA
MLAPS	Multiple Light-Addressable Potentiometric Sensor
ST	Stantlet Transform

1 Introduction

Monitoring technologies take an essential role in the implementation of innovative and integrated techniques for the sustainable management of groundwater resources. As a general idea, the information coming from traditional field instrumentation, typically providing the main physical/chemical parameters of water, is inadequate to fully assess the quality of water destined to human consumption. On the other hand, a complete laboratory analytical measurement is expensive and does not provide continuous control over the resource.

There's an expanding interest in multi-sensor systems for the assessment of general attributes of a process under monitoring, which are applicable to various environmental contexts. Such devices are generally based on the technology of taste sensors developed in the research framework of bio-mimetic systems. Acceleration in the advancement of this field has been done during the last two decades. In fact, there are now fairly mature, low-cost and attractive technologies that can produce overall quality indicators of a natural resource in a non-conventional manner.

This chapter gives an overview of non-conventional electrochemical and optical measurement approaches, which have been proposed in the literature in the framework of multi-sensor systems for wet-chemical applications. Systems based on these principles are often referred to as "electronic tongues" or "e-tongues" (Hauptmann et al., 2000; Lindquist and Wide, 2001; Krantz-Rulcker et al., 2001; Vlasov et al., 2005). As a general idea, the combination of non-specific and even overlapping sensor responses (which are often very informative) can address the issue of extracting aggregate chemical information, useful to characterize the liquid under measurement. Electronic tongues can actually be used as taste sensors but, more generally, they can be applied to a broader context where the human taste is not necessarily involved.

A high number of e-tongues have been described in the literature, based on different measurement techniques, such as potentiometry with Ion Selective Electrodes (ISE), lipid/polymer membranes, SH-SAW (Shear Horizontal Surface Acoustic Wave) devices, spectrophotometry and voltammetry. Among this diversity of measurement techniques, most of the proposed approaches are based on electrochemical methods.

Behind the somewhat misleading terms "electronic tongue" and "taste sensor", one finds some kind of array of sensors. The sensor array in these systems produces signals, which are not necessarily selective to any particular species in the measured sample, but a signal pattern (often a large dataset) is generated, which can be related to some chemical/physical features of the sample. In this particular framework, electrochemical methods are probably among the oldest measurement techniques, and also comprise a very wide range of analytical possibilities, enriched by relatively recent developments in signal processing, sensors manufacturing and front-end electronic systems (Scozzari, 2008a).

For what regards electrochemical techniques, potentiometry is the fundamental principle of e-tongues based on arrays of Ion Selective Electrodes (ISE). The proposed devices are essentially based on the cross-selectivity between electrodes that are made sensitive to different ion species (Krantz-Rulcker et al., 2001; Vlasov et al., 2005). Further explanation about this class of devices is given in section 2 of this chapter.

Another class of electrochemical techniques used in the context of e-tongues is represented by voltammetry. Voltammetry is a group of electroanalytical methods in which information about the analyte is derived from the measurement of a current flowing in a polarised working electrode, as a function of an imposed potential between such electrode and a reference (Krantz-Rulcker et al., 2001; Scozzari, 2008a). Further explanation about this class of devices is given in section 3 of this chapter.

Deep theoretical explanations about the working principles of potentiometry and voltammetry can be found in (Bard and Faulkner, 1980 & 2000; Janata, 1989 & 2009).

Among the relatively wide literature available, applications of these techniques to water classification and change-detection purposes can be found in Di Natale et al. (1997), Winquist et al. (1997), Legin et al. (1999), Paolesse et al. (2003), Ciosek et al. (2004), Lvova (2006), Scozzari et al. (2007a,b). It must be noted that even the combination between potentiometry and voltammetry has been proposed in the literature with promising results. As an example, in (Men et al. 2005) the authors combine a Multiple Light-Addressable Potentiometric Sensor (MLAPS) with stripping voltammetry, in order to improve the detection capability of heavy metals in wastewater or seawater.

Finally, this chapter introduces non-conventional optical sensor systems, having the capability to provide overall information about the quality of water, in the perspective of low-cost monitoring systems easy to deploy and use. Recent findings demonstrated the analytical capabilities of a regular computer screen with a web camera for detecting and recognizing different molecules with an inexpensive (and eventually disposable) optical-sensing interface. This technique can also potentially enable common devices like mobile phones to act as a particular kind of water quality sensors. This class of devices will be discussed in section 4.

2 E-tongue based on potentiometric arrays

In potentiometry, the potential of an electrochemical cell is measured in static conditions. The advantage of this approach is that since no current flows the composition of the solution remains unaltered.

The electrochemical cell is in principle formed by two semi-cells each containing an electrode immersed in a ionic solution. Typically one of the two cells is a reference cell where a standard solution maintains the immersed electrode to a constant potential. The other cell is the working cell where the working electrode is in contact with the solution to be measured. The electrical continuity between the two cells is maintained by a salt bridge containing an inert electrolyte (e.g. KCl) and terminated by porous glasses. A schematic picture of a standard electrochemical cell is shown in Fig. 2.1.

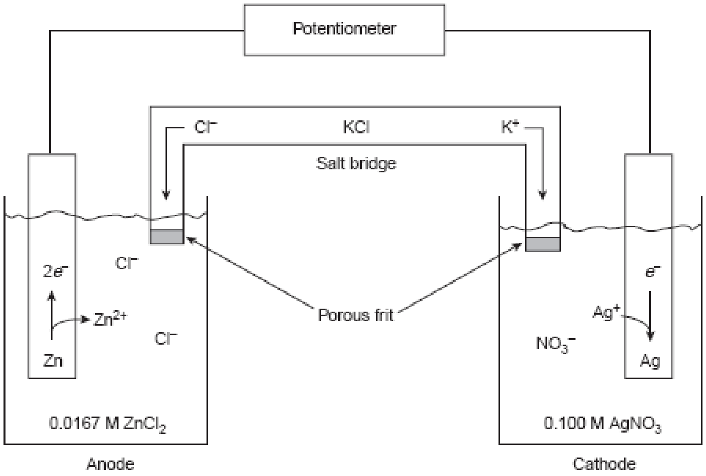


Fig. 2.1 Schematic view of a general electrochemical cell for potentiometric analysis.

The potential of the electrochemical cell is given by:

$$E_{CELL} = E_C - E_{REF}$$

where E_C and E_{REF} are the reduction potentials of the reactions occurring at both electrodes. These potentials are a function of the ionic species in equilibrium with the electrode. The relationship is given by the Nernst equation.

The Nernst equation can be demonstrated in different conditions. For instance in the case of a metal electrode aimed at measuring the concentration of ions of the same metal (the so called electrode of the first kind) the electrode potential can be derived from a simple thermodynamical approach. Let us consider the following reaction occurring at the metal surface where atoms of the metal flows in ionic form into the solution leaving an excess of electrons in the solid and ions from the solution recombines with the electrode electrons.

$$Me \leftrightarrow Me^{n+} + n \cdot e^{-}$$

The free energies of reagent and products are:

$$G_{Me} = G_{0,Me} + RT \cdot \ln\left(a_{Me}\right); \quad G_{Me^{n+}} = G_{0,Me^{n+}} + RT \cdot \ln\left(a_{Me^{n+}}\right)$$

noteworthy, the concentration of the species are replaced by a quantity called activity. The activity takes into account the screening effects of polar and charged molecules in solution. The activity is proportional to the concentration ($a = \gamma \cdot C$), where in many practical applications γ is very close to one.

The change of free energy is equal to the electric work necessary for the reaction:

$$-L = -Q \cdot V = G_{Me^{n+}} - G_{0,Me} = \left(G_{0,Me^{n+}} - G_{0,Me}\right) + RT \cdot \ln \frac{a_{Me^{n+}}}{a_{Me}}$$

$$= \quad G_0 + RT \cdot \ln \frac{a_{Me^{n+}}}{a_{Me}}$$

where Q is the involved charge and V is the electrode potential with respect to the solution. A convenient way to calculate the charge is the Faraday constant, that is defined as the charge of a mole of electrons (1F = 96485 C/mol).

For sensor applications, the ionic species in the solution is the analyte of interest, and $a_{Me^{n+}}$ is the object of the measure. Considering that the activity of a pure solid, such as a metal, is equal to one, the electrode potential is given by:

$$V = -\frac{G_0}{nF} - \frac{RT}{nF} \cdot \ln\left(a_{Me^{n+}}\right)$$

For practical reasons, the natural logarithm is replaced by the logarithm in base 10 and then the Nernst equation is written as:

$$V = V_0 - K \cdot \log\left(a_{Me^{n+}}\right)$$

where K~59 mV/decade is the Nernst constant.

In order to measure the potential V it is necessary a reference electrode whose potential is a stable reference independent on the analyte and the composition of the solution. This is provided by reference electrodes, such as the Ag/AgCl electrode. This is a silver electrode coated by a layer of AgCl and immersed in a solution of KCl. The electrode potential can be modulated by adjusting the KCl solution. Fig. 2.2 shows a standard Ag/AgCl electrode, the KCl solution provides also the saline bridge and the glass enclosure is terminated by a porous frit. A reference electrode based on Ag/AgCl can also be prepared with screen-printed technology giving rise to a miniaturized element that can be conveniently used in small and robust sensor systems (L. Tymeszki et al. 2004).

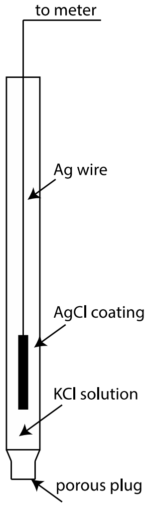


Fig. 2.2: simple drawing of an Ag/AgCl reference electrode. One of the semicells and the salt bridge of Fig. 2.1 are contained in this element.

The potentiometric measurement requires the use of an amplifier with a virtually infinite input resistance. These conditions cannot be met in practice, but for the scope a number of amplifiers with very large input resistance are available. Particularly suitable to the scope is the so called instrumentation amplifier. This is a particular amplifier provided by a differential input, suitable for making differential voltage measurements. The input stages of these devices must exhibit low current losses and high impedance, as it is a typical requirement for electrometric applications. The input current, which is the leakage current flowing into the electrochemical cell, is typically of the order of femtoamperes.

Electrodes sensitive to a wide variety of ionic compounds are currently available. However, the selectivity of these sensors is not absolute. Selectivity is a great concern in practical applications, where the exact composition of the sample is not known a-priori, and then the target analyte can be in a mixture with a large number of interfering compounds.

The selectivity of an ion-selective electrode is described by the Nikolskij equation, where the sensitivity to the primary ion is compared with the sensitivity to the interferents:

$$V = V_0 - 2.303 \cdot \frac{RT}{nF} \cdot \log\left[a_A + \sum_i K_{A,i} \cdot a_i^{n_A/n_i} \right]$$

where a_A is the activity of the primary ion, namely the species for which the dominant sensitivity is found. The effect of the i-th interferent is weighted by the coefficient $K_{A,i}$ that is the selectivity coefficient, namely the ratio of sensitivity to the i-th species with respect to the primary ion; a_i is the activity of the i-th interferent and n_A and n_i is the charge numbers of the primary ion and the interferent respectively.

In a multi-ion environment the behaviour of the electrode potential is no longer explained by the Nikolsij equation and the estimation of the concentration of ions becomes uncertain.

In these conditions, it is advantageous to release the concept of selective sensors and to approach the concept of sensor array (Otto, 1985). This is an experimental procedure based on an array of partially-selective sensors coupled with a multivariate analysis algorithm. This procedure stems from the so-called electronic noses, namely arrays of gas sensors mimicking the behaviour of olfaction (Gardner & Bartlett, 1994). In the nineties this concept has been transferred also to sensors operated in solution, giving rise to the so-called electronic tongue. Potentiometric electronic tongues have been developed using different materials such as lypidic membranes (Hayashi et al., 1990), chalcogenide glasses (Di Natale et al., 1996), metals (Lvova et al., 2006), polymers (Riul et al., 2003), and porphyrins (Paolesse et al., 2003) among the others.

2.1 A common application in the context of water quality: characterization of mineral waters

As an example of application we report here the usage of a large array of 29 sensors for the characterization of mineral waters (Legin et al., 1999). Materials of the sensors were chalcogenide glass and PVC membranes, specifically designed in order to have an enhanced cross-selectivity. They were complemented by conventional ion selective electrodes such as pH glass electrode, sodium-, and chloride-selective sensors. All measurements were performed versus a conventional Ag/AgCl reference electrode.

The measurements have been made with 6 Italian bottled mineral waters (Levissima, Fiuggi, Sangemini, Uliveto, San Pellegrino, and Ferrarelle) and the tap water from Rome water supply. All waters were bought over the counter. Some of the waters were sparkling ones. The excess of CO_2 was removed by an intensive long stirring before the measurements. Discrimination of the different kinds of mineral waters using the electronic tongue is shown as a PCA score plot in Fig. 2.3.

All the samples can be easily distinguished with the help of the whole array of 29 sensors, but a smaller sub-array, including 5 sensors appeared to be enough for reliable classification, which is shown in Fig. 2.3a.

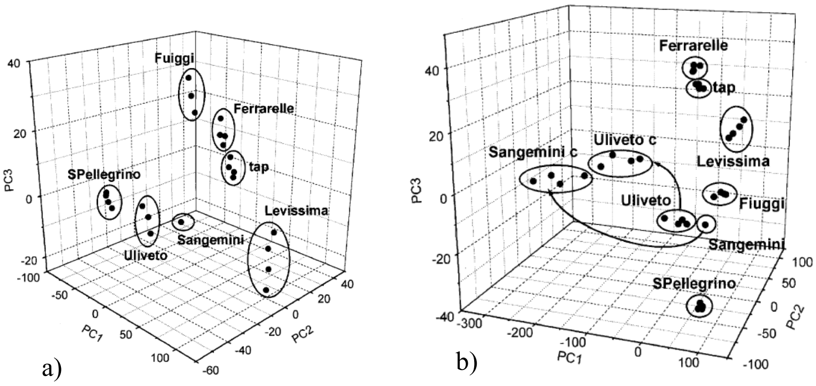
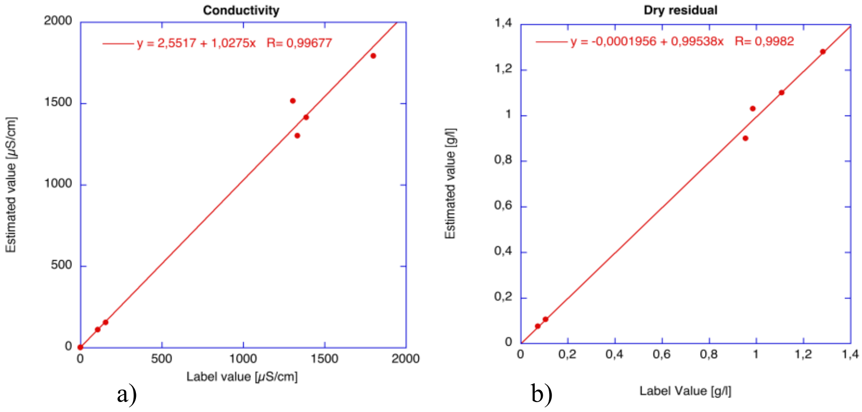


Fig. 2.3 a) PCA scores plot of mineral and tap waters. b) PCA scores plot of the same samples of panel a), but completed with two mineral waters added with an amount of organic material; the deviation, occurring along PC1, suggests the high sensitivity of the whole array to organic compounds dissolved in water (Legin et al., 1999).

At the second stage pieces of strawberry (4 g of fruit per 1 L) were introduced into the bottles of two different mineral waters (Sangemini and Uliveto) and kept for four days. This experiment was carried out as an illustration of the ability of the device to detect some chemical and/or biological disturbance in the analysed sample. Results are shown in Fig. 2.3b. The samples of the mineral water to be contaminated were chosen randomly as well as the pollutant itself, thus, it was possible to conclude that any contaminated water can be distinguished from any pure one belonging to this test set, by using the electronic tongue. This is true at least for the variety of waters studied, but, taking into account that the chosen water samples represent a wide range of possible combinations, the results are likely to be universal.

Besides qualitative recognition of the mineral waters, the quantitative analysis of the content of their components has been experimented by the potentiometric electronic tongue. The concentration of some species, e.g., some ions, can be determined conventionally using ion-selective electrodes, such as pH, fluoride-, chloride-, sodium-, potassium-selective etc. Using the electronic tongue approach all these ions can be measured simultaneously with a multicomponent approach (Di Natale et al., 1997). Moreover, it is also possible to determine the components for which no highly selective electrodes are known, e.g., HCO_3. We have also tried to estimate some characteristics of the mineral waters that usually cannot be measured by ion-selective chemical sensors: conductivity, dry residual and SiO_2 content. The results of quantitative determination of these parameters are summarized in the scatter plots of Fig. 2.4. All the parameters can be measured with reasonable precision. Thus, using the potentiometric electronic tongue, it is possible to determine a set of values necessary for the standard characterization of the drinkable water quality in a single measurement.



a) b)

Fig. 2.4. Scatter plots showing the estimation of conductivity (a) and dry residuals (b) from the electronic tongue data.

3 E-tongue based on voltammetry

During the late -90s, voltammetry has been proposed as a possible tool for the characterization of liquids with a non-conventional chemometric approach (Winquist et al., 1997; Winquist et al., 1999a; Winquist et al., 1999b). Actually, it is a mature sensor technique, which fundamentals come from the early 20th century, and that has been accepted as a standard technique in the mid of the century.

Information about the controlled-potential microelectrode techniques is given here at an introductory level, to allow the reader having an adequate understanding of the methods presented in this chapter. Deep theoretical texts about the fundamentals of electrochemical methods, and specifically about voltammetry, can be found in the cited literature.

The next sub-sections will illustrate the working principles of e-tongues based on voltammetry and their specific methodological approach.

3.1 Fundamentals of voltammetry

Nernst's intuition about the feasibility of some electrochemical analogy of the light spectral analysis methods, found its first tangible embodiment in the conception of the polarographic technique (Heyrovský J., 1924) presented by Jaroslav Heyrovsky at the meeting of the Faraday Society, held in November 1923. Heyrovsky shown that a "polarised drop of a mercury capillary cathode represents a reversible state of equilibrium", in order to achieve a truly reproducible measurement by the current-voltage diagrams obtained in polarisation experiments.

The first textbooks and data about polarographic methods have been produced across the World War II period, being substantially recognized as a standard technique in the mid of the century, when polarographic data where presented as laboratory standard datasets, such as the one presented by Giovanni Semerano and Luciana Griggio (1957).

The first potentiostat presented by Hickling during 1942 was a substantial step forward in the exploitation of the analytical possibilities offered by polarographic methods, and voltammetry in general (A. Hickling, 1942). Hickling already perceived that "a device whereby the potential of a working electrode can be fixed at any desired arbitrary value would seem to have many valuable applications in the exploration of electrolytic processes". It was the beginning of the controlled potential microelectrode techniques.

Technological advances in the '60s – '70s led to the commercial development of laboratory devices based on voltammetry, and a variety of standard methods have been rapidly proposed in the literature, and rated as affordable by the science community.

Nowadays, with the aid of a suitable signal processing methodology, voltammetry represents an interesting option for the continuous monitoring of a process, thanks to its very low analytical limits and to the large amount of data that it is possible to obtain, particularly with "pulse polarography" experiments.

In voltammetry, the information about the analyte is obtained by measuring the current flowing through a polarized working electrode (WE), given an imposed voltage between WE and a reference electrode (REF). That is, the WE potential (calculated with respect to REF) is forced to follow a predetermined program or waveshape, and the current i is measured as a function of the applied potential, or as a function of time. The electronic device that implements such concept is called "potentiostat" (C. Krantz-Rulcker et al., 2001; Scozzari A., 2008; Scozzari et al., 2007a; A. Hickling, 1942).

In the most common 3-electrodes implementations, the potentiostat is a device which injects current into an Auxiliary Electrode (AUX), closing the current loop via a Working Electrode (WE), in order to impose a known difference of potential between WE and a Reference Electrode (REF). Such voltage has to be measured with a high impedance differential amplifier, to make negligible the current going through REF. Figs. 3.1a and 3.1b show a generic cell configuration and a simplified schematic diagram of an experimental system for voltammetry, respectively.

The voltage imposed across WE and REF is supposed to be determined by a function generator placed at the input of the potentiostat. The experimental observable, that is obtained from each measurement session, is the response of the system potentiostat-cell to the excitation signal (voltage) used, that is, the loop current $i(\mathrm{t})$.

Thus, the electrochemical behaviour of a system can be determined by imposing known varying potentials between WE and REF, and recording either the current-voltage curve (voltammogram) or its current-time version (chrono-amperogram), that are obtained in each experiment.

Among the wide literature that is available to probe further into this class of techniques, the fundamentals about electrochemical methods, and specifically about square-wave voltammetry, can be found in Bard A. J. and Faulkner L. R., (1980 and 2000), G. Korthum (1965), Mirceski V. et al. (2007).

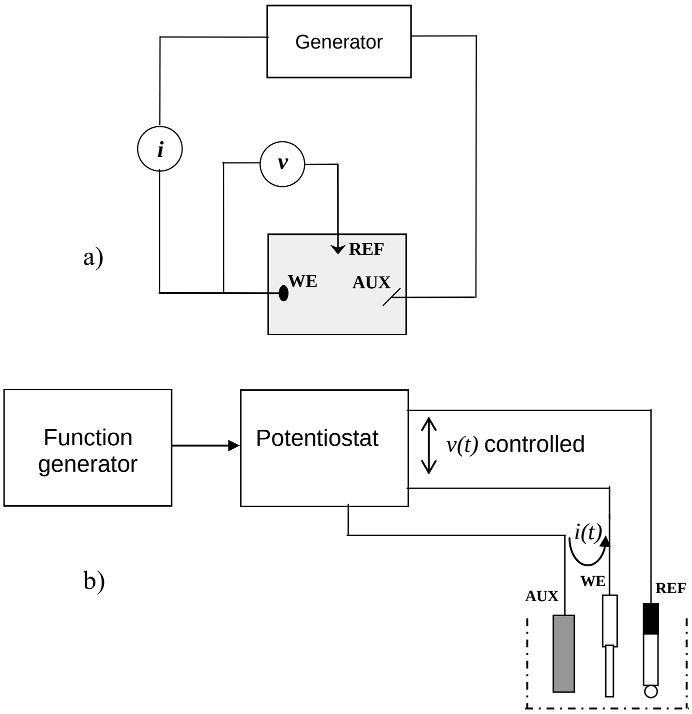


Fig. 3.1 a) Generic three-electrodes cell configuration; b) Simplified schematic diagram of an experimental system.

The different activation overpotential levels, diffusion coefficients and mass-transfer limits that are exhibited by each species in a solution, generate a different contribution to the complex voltammogram obtained; the shape of such contribution depends also on the waveform of the excitation signal.

There’s a wide range of possible implementations of measurement methods based on voltammetry, according to the type and material of the working electrodes (i.e. solid metal microelectrodes, dropping mercury, planar rotating disks, carbon electrodes, etc.), and according to the particular electrochemical experiment, that implies a different program imposed by the generator (i.e. the excitation signal).

It is known that a very informative electrochemical signature of a liquid sample can be obtained by applying a series of square-shaped pulses having different amplitude as *v(t)*, and recording the obtained current vs. time curve, i.e. *i(t)*. More specifically, the usage of pulse voltammetry has been presented in different contexts (F. Winquist et al., 1997; Scozzari et al., 2007; Scozzari & Wide, 2008) as an efficient sensor technique for classification and characterization purposes. In particular, the cited literature proposes excitation signals consisting in a series of rectangular pulses modulated by ramps, both in offset and in amplitude, depending on the peculiarities of the specific methods.

When the applied waveshape is a step signal, such as the one shown in Fig. 3.2a, the obtained response depends on the levels of the applied potential. Under the hypothesis that there's only one dissolved species and that it is electrochemically inactive at potential E_1 but reduced at potential E_2, a typical response of the experimental system would be the one shown in Fig. 3.2b. In fact, the electroactive species eliminated (reduced) at the WE produces a concentration gradient in the proximity of such electrode, such as the one shown in Fig. 3.2c.

Moreover, it is known (Bard A. J. & Faulkner L. R., 1980 and 2000, G. Korthum, 1965) that the flux (thus the current) is proportional to the concentration gradient, thus, the decay of i(t) is basically due to the fact that the flux causes the depletion volume to thicken. The slope of the concentration profile Co(x) from the WE surface declines while the current flows, thus the depletion volume gets higher, producing the described decay of i(t). An example of the concentration profile behaviour vs. time is shown in Fig. 3.2c, where Co* is the bulk concentration of the electroactive species considered.

An example of application is represented by the Large Amplitude Pulse Voltammetry (LAPV) technique (Lindquist & Wide, 2001; Winquist et al., 1997; Scozzari et al., 2007a; Scozzari & Wide, 2008), that applies a series of square pulses modulated by a ramp signal; this approach is equivalent to making a sequence of step experiments involving different species in a progressive manner, according to their excitation overpotential.

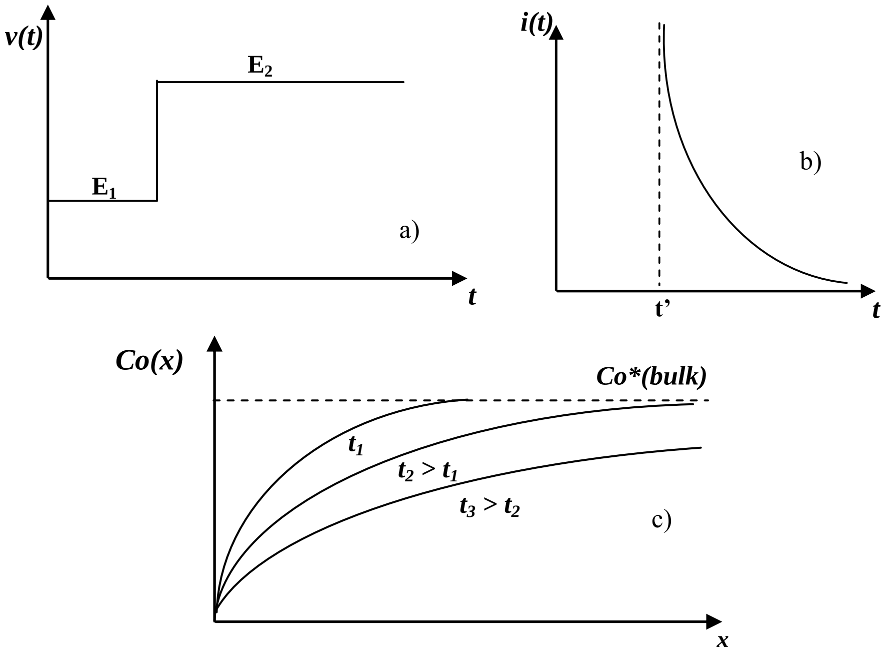


Fig. 3.2 a) Excitation signal waveform for the basic step experiment; b) *i(t)* for the step experiment; c) Concentration profiles at various times.

Both the ability to classify samples and the ability to detect changes in a solution under measurement have been investigated in the recent literature regarding voltammetry for water quality assessment. Some developments during the last decade (Scozzari A. et al., 2007; Scozzari A., Wide P., 2008; Pereira JMD et al., 2007; Iliev B et al., 2006) gave particular attention to the signal processing chain, in the framework of pattern recognition techniques for automatic monitoring systems. In the works cited, emphasis has been given to the assessment of water quality and to food processing applications. The next sections will focus on water quality applications.

3.2 Sensors used for water applications

Most experimental setups described in this class of devices make use a potentiostat (see section 3.1), which drives one or more working electrodes made of solid metal, and are aimed at developing low-cost distributed devices. Such devices are expected to have low maintenance requirements and some capability to withstand harsh environments. Figs. 3.3 and 3.4 show an experimental device mounted on the water tap (Scozzari & Wide, 2008) and a laboratory device with electrodes placed in a measurement cell (Scozzari et al., 2006a), respectively.

In the most common fashion, the presented prototypes rely on multiple working electrodes selected by relay switches, typically with a reference electrode (e.g. Ag/AgCl) and an auxiliary electrode (or counter-electrode) often consisting in a steel plate, having the responsibility to inject the current driven by the potentiostat into the electrochemical cell. An array of working electrodes made by solid metal (e.g. gold, iridium, platinum, palladium, rhenium and rhodium) are generally found in the literature (Krantz-Rulcker et al., 2001; Winquist et al., 1997; Scozzari et al., 2007a; Scozzari & Wide, 2008). Such hardware configuration (with 2 to 6 working electrodes) is commonly combined with the measurement scheme of pulse voltammetry.

Other configurations are reported, e.g. screen printed WE and REF electrodes made by various materials, such as a Pd/Ag alloy and Au as described in Buehler MG et al. (2002). Also, applications based on stripping techniques have been presented, often in combination with specific materials for the wet surfaces of the working electrodes, such as thick-film graphite and screen-printed carbon electrodes, as illustrated in Brainina KZ et al. (2001); such methods basically consist in the preliminary accumulation of the analyte on the WE (by applying an adequate potential) and the successive measurement by sweeping the potentiostat towards opposite potentials.

Fig. 3.5 shows a simplified block diagram of an e-tongue setup based on pulse voltammetry. The experimental observable, which is obtained by each measurement session, is the response of the system potentiostat-cell to the excitation signal $v_e(t)$ imposed, in terms of loop current $i_{WE}(t)$. Under the hypothesis that all the current losses in the system can be neglected, $i_{WE}(t)$ is equal to the output current of the control amplifier (1).

The potential on the WE is tied to the analog ground by the I/V converter (3); the output of the differential electrometer (2) is connected to the negative input of the control amplifier (1) closing the feedback loop, ensuring that the voltage difference between the reference electrode REF and the selected WE is equal to the voltage set by the input signal $v_e(t)$. All of that is true until both the voltage assumed by the auxiliary electrode CE and the current which flows through it, lie in the output swing capability of (1).

Automatic measurements are often performed by controlling the potentiostat with a Personal Computer (PC) and an adequate software. In the example shown in Fig. 3.5, the PC controls the excitation waveform $v_e(t)$, acquires the resulting current $i_{WE}(t)$, and drives the switching sequence of the working electrodes during each measurement session.

As a practical example, Fig. 3.6 shows the shape of a LAPV excitation signal, as firstly described by Winquist et al.(F. Winquist et al., 1997). Fig. 3.7 shows a typical set of recorded chronoamperograms for a system comprising 4 working electrodes.

Fig. 3.3 An experimental device mounted on the water tap

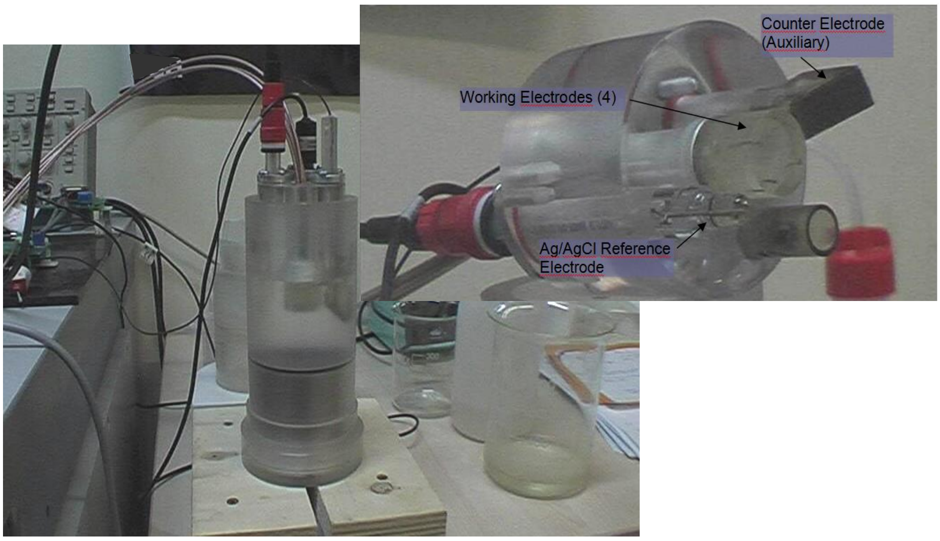


Fig. 3.4 A laboratory device with electrodes mounted in a measurement cell.

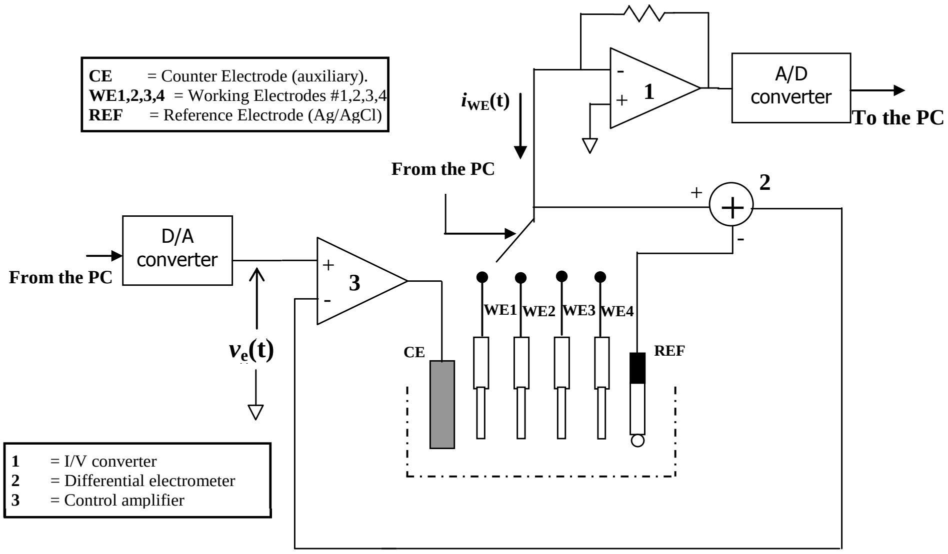


Fig. 3.5 Simplified block diagram of an e-tongue setup based on voltammetry.

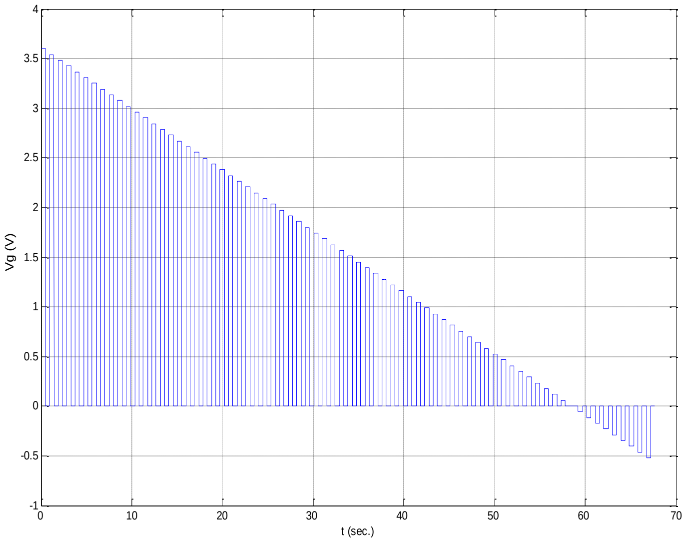


Fig. 3.6 LAPV excitation signal according to Winquist et al., 1997 (F. Winquist et al., 1997)

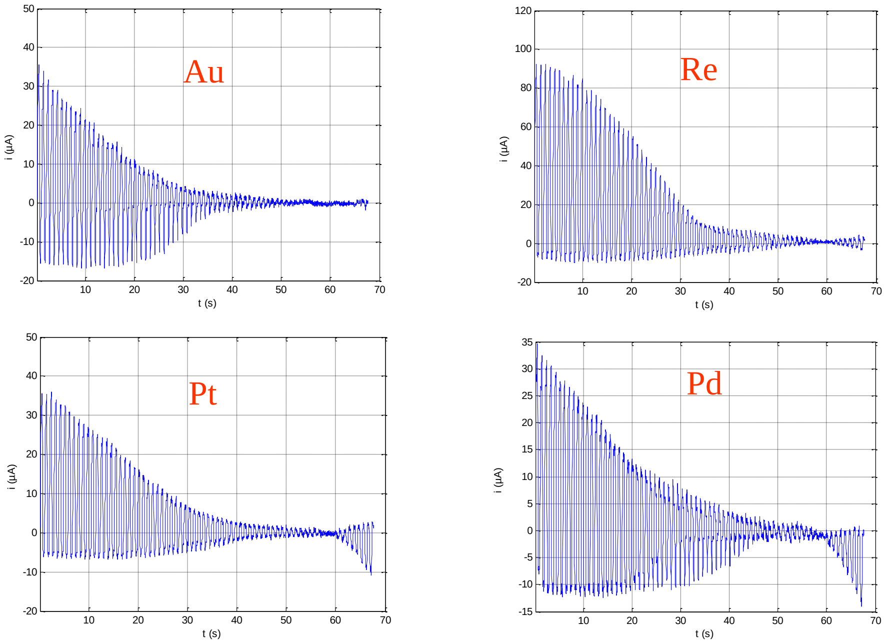


Fig. 3.7 Set of 4 voltammetric measurements, made with distinct working electrodes on the same sample of bottled mineral water. The respective electrode material is specified by the text in red colour.

3.3 Signal processing

In most e-tongues based on voltammetry, samples of the current signal measured by the potentiostat are sequentially collected, making a kind of chronoamperometry rather than a traditional polarography. Each observation may be represented as a vector represented in a multidimensional space, where each component corresponds to a specific instant in the time domain.

For multi-electrode systems (i.e. multiple working electrodes), one session is formed by K sequences of M data points (i.e., time domain samples), each one generated by the voltammetric scan involving each one of the K WEs.

In this class of non-standard chemometric approaches, the large multivariate space generated by the time series of the acquired current signal is used to characterise the fluid under measurement. Various signal processing techniques applied to such datasets have been proposed in the literature, all of them essentially oriented to the projection of the acquired data onto a representation sub-space, by reducing the dimensionality of the measurement space (the one hosting the observation vectors). Such dimensionality reduction is equivalent of saying that only the most relevant features are extracted from the acquired timeseries, leading to a set of vectors having smaller dimensionality than the original data, but still preserving most of the information; this is accomplished by selecting the most informative components in the observation space according to some metric that maximises the performance of the system (i.e., discrimination between classes, change detection capability, etc.) Among the wide literature available for an appropriate understanding of the basic concepts of feature selection, supervised/unsupervised classification and transformed domain operations, good reference books can be found in the context of the analysis of remotely sensed data, where most of these techniques have been developed and applied. Two good reference books are given here as an adequate beginning (Richards JA, 2012; Landgrebe DA, 2003).

Some authors focused their investigations on the data compaction properties of transformed domains like DWT (Discrete Wavelet Transform) and DCT (Discrete Cosine Transform) (Artursson T, Holmberg M, 2002; Scozzari et al., 2005 & 2007a), in order to enhance the discrimination capability in reduced-dimensionality sub-spaces. This is proposed as a pre-processing step, often in combination with PCA applied as a second step, as a feature extraction and visualization tool. PCA alone and PCA-derived tools (e.g. HPCA – Hierarchical PCA) have also been proposed as a feature extractor directly applied to the acquired datasets (Holmin S. et al., 2001). Feature selection by genetic algorithms applied to polarographic and stripping voltammetric datasets has also been successfully experimented (Herrero A., Cruz Ortiz M., 1999). More recently, the combination of the Stantlet Transform (ST) with a neural network classifier has been proposed for the automatic authentication of water samples by using pulse voltammetry as a measurement technique (Kundu, P.K. et al., 2011). All of the cited papers can represent a good starting point to analyse the different strategies that have been studied and proposed in this particular context.

As a general idea, feature selection represents a critical issue in multidimensional data processing, because it has the dual objective of delivering the most accurate information with a minimum amount of data, while keeping the computational efficiency at the maximum; this justifies the effort to design suitable algorithms and optimize their performance. Selected features (i.e. transformed-domain coefficients, time-domain samples and/or their principal components) can be forwarded to three possible processing paths, corresponding to the following three activities:

- automatic classification
- change detection
- data representation, based on a further reduction of dimensionality

All these three processing possibilities are explored in the literature, with particular attention given to supervised classification systems and the individuation of suitable representation sub-spaces, like the ones used to show the data examples presented in the next section.

3.4 A view on commonly presented applications in the context of water quality

The applications presented in most of the literature about voltammetric e-tongues are focused on the experimentation of the following capabilities:

- discrimination between clusters in a supervised classification scheme
- detection of changes in the chemical characteristics of water
- characterization and validation of samples

When dealing with the big amount of data coming from a high sampling rate pulsed voltammetry, the reduction of dimensionality of the acquired dataset is a crucial issue (see section 3.3 and references therein). The extraction of suitable features enhances the discrimination of the observations between different classes, by projecting the observed vector onto a reduced dimensionality space (feature space).

In this framework, three selected implementations are given as an example of the three capabilities cited above. All of them are focusing on water quality applications. The selected examples are given in order to provide an overview of possibilities offered by this measurement approach. In-depth information about the sensor systems used and details about the signal processing techniques used in each application example can be found in the cited literature.

3.4.1 Classification

The classification system proposed in this example is based on a supervised procedure that determines the basis of the feature space (i.e. the basis onto which the observed vectors are projected) by using a training set of suitable measurements. In practice, only part of the collected measurements (training set) are used to determine the combinations of components of the observed vectors that enhance the discrimination between a-priori known classes, in order to adhere to a supervised classification scheme. In this specific case, the a-priori classes are represented by different brands of bottled mineral water, and the feature vectors are extracted from the DCT version of the observed vectors. The system designed by means of such training set is then used in the subsequent measurements, which are thus used as a “test set”.

This example concerns 4 brands (classes) of Italian bottled mineral water, with an overall dataset formed by 40 measurements (10 per each class), allocated in 5 sessions distributed in 10 days (i.e., one session per day, not necessarily consecutive). Each session consisted in 8 measurements (2 per each brand/class) performed in random order, to check repeatability of the system and avoid eventual artifacts due to a repeated measurement sequence.

Data presented here have been obtained by LAPV measurements with 4 working electrodes made by solid metals (Au, Re, Pt, Pd). Fig. 3.8 shows graphical results in terms of projection onto the representation sub-space of each of the measurements.

The discrimination between the four different brands of mineral water appears to be obvious to the human observer, and allows the successful usage of even the simplest threshold classifiers. In order to keep general and do not give as assumed this particularly favourable situation, an automatic classifier based on an MLP-NN (Multi Layer Perceptron – Neural Network) has been experimented on the feature set extracted from the collected data.

As concerns the MLP-NN, a one hidden layer with four neurons architecture has been chosen. The selected transfer function for the hidden layer neurons was a log-sigmoid one, while the output neuron had a linear transfer function. As expected, the network trained by the said 8 examples achieved 100% of classification accuracy on the full dataset, consisting into 40 measurements.

Details about this application example can be found in Scozzari, A. et al. (2006a).

Such automatic classification capability, due to the high discrimination exhibited by this kind of systems, is the gateway to the change detection and sample validation applications that are of direct relevance to the water quality context.

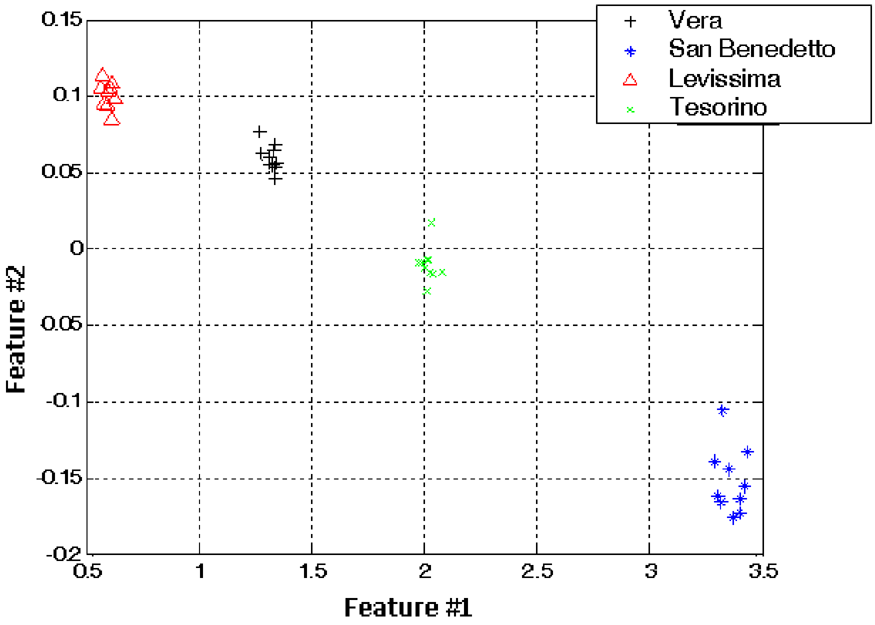


Fig. 3.8 Graphical representation of the measurements in the "classification" experiment, after projection onto a bi-dimensional representation space.

3.4.2 Change detection

The demonstration of the change detection capability of such systems relies on a field experiment, in which water samples are taken at the input and the output of a carbon filter pack, in order to detect how treated water is separated from raw water in the representation domain. This peculiarity gives the possibility to observe eventual changes in the behaviour of the filter, in terms of projections of the input/output samples onto the representation domain. In this case study, four wells in the proximity of two different industrial areas have been considered, all exhibiting a slight pollution due to trichloroethylene and tetrachloroethylene from an unidentified source, probably a dismissed activity of industrial oil treatment (Scozzari et al., 2006b).

Even though the pollution level was inside legal limits for drinkable water, a carbon filter pack has been installed. Water samples have been taken from one of the wells, at both the input and the output of the filter. The measurement procedure has been repeated twice for each sample and in reverse order, with the aim to exclude any artifacts linked with the measurement sequence. The separation between raw and filtered water is again apparent (Fig. 3.9), confirming the perspective capability to detect eventual changes in the performance of the water filter, in terms of positioning the projected clusters (both in relative and absolute position).

The first 4 observations (2 OUTs and 2 INs) are used as a training set. The second 4 observations (2 INs and 2 OUTs) are used as a test set, i.e., they are projected onto the bi-dimensional feature space determined by using the first training set of vectors.

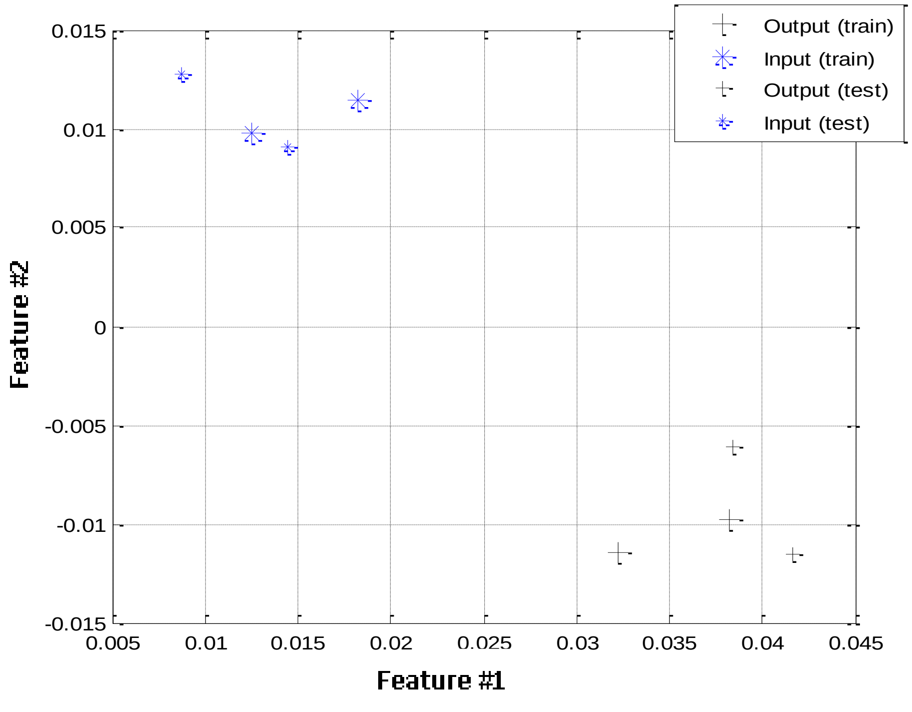


Fig. 3.9 Graphical representation of the measurements in the “change detection” experiment, after projection onto a bi-dimensional representation space.

3.4.3 Sample characterisation

One effective way to assess the characterization capability of non-specific sensor systems is to perform traditional chemical analytical measurements over a wide range of water samples, comparing the results with the output of the multi-electrode device, i.e. the e-tongue. The example shown here comprises 11 classes of groundwater and surface water, all of them taken in the Campi Flegrei area of Naples, southern Italy (Scozzari, 2007b).

The interesting aspect that makes this case study a kind of natural benchmark, lies in the fact that different kinds of water with different chemical characteristics can be found in a small area of a few sq. Km. Their different peculiarities well suit the concept of making a general characterisation of the water by giving an aggregate chemical information, as it is one of the major strength of an e-tongue system. According to the representation metric, similarity between samples is expected to be reflected by their distribution in the representation domain. A test of such characterisation capability is shown by comparing the e-tongue results with classical classification/clustering based on traditional chemical analytical measurements.

Fig. 3.10 shows a tri-dimensional representation of the distribution of the 11 classes according to the e-tongue (three measurements each class, in order to check the repeatability of the system). Fig. 3.11 shows the Principal Components Analysis (PCA) applied to the analytical chemical measurements, where 15 parameters were taken into consideration. The projection of the 15 measured parameters onto the first 3 principal components is shown in Fig. 3.11.

It must be remarked that e-tongue measurements were not made on site, thus a loss of information about redox potentials, due to sample transportation and its interfacing with free air, is expected. Samples destined to the analytical chemical measurements have been collected and treated in the same way. As a consequence, the main discriminating factor for the e-tongue measurements comes to be the chemical composition of each sample, making the comparison with the principal components of the analytical measurements particularly interesting.

It appears immediately clear how the two thermal water samples (“Terme Puteolane” and “Agnano”, numbers 8 and 11) are strongly discriminated from the others in both the representations. In addition, the water samples grouped in the PCA representation (numbers 1…7) are also close to each other according to the e-tongue results, even with the sample number 2 exhibiting a slight separation from the remaining six. It is finally interesting to see that the “Averno” and “Castello di Baia” samples (9 and 10) are discriminated in both domains, staying in the middle between the two groups (1…7 and 8…11).

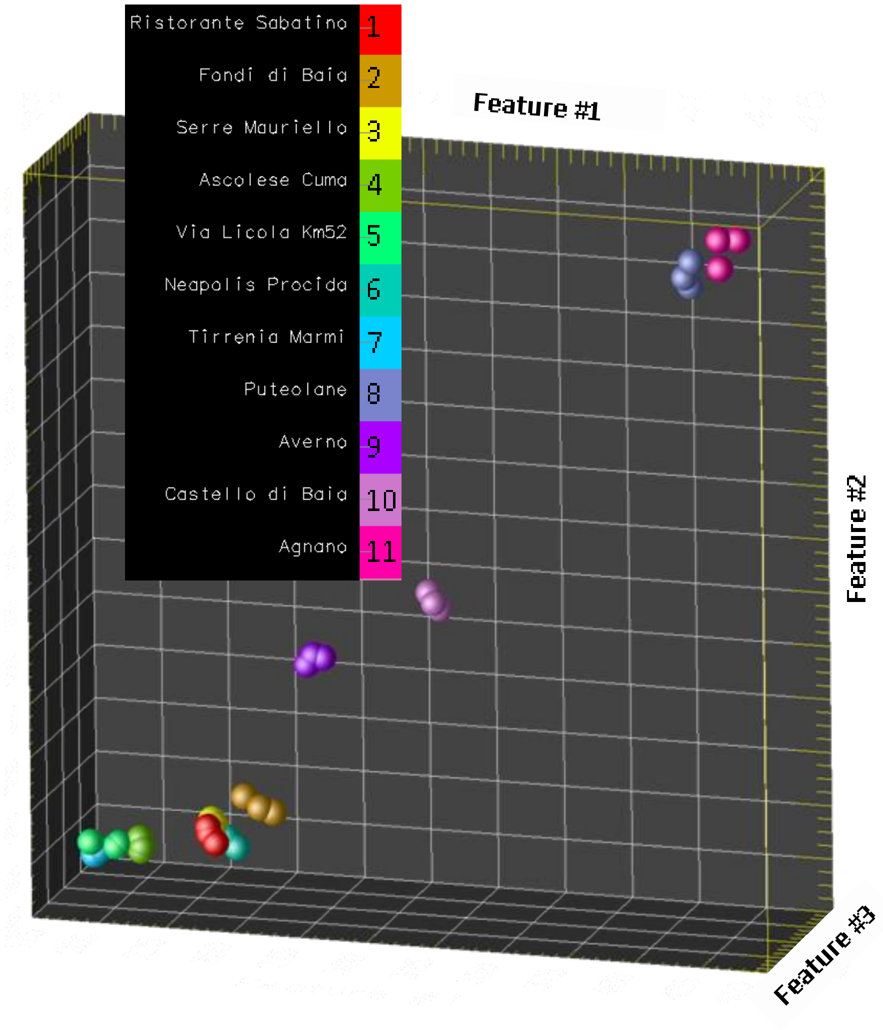


Fig. 3.10 Representation of 11 water classes in the e-tongue feature space for the “sample characterisation” experiment (three measurements per each class).

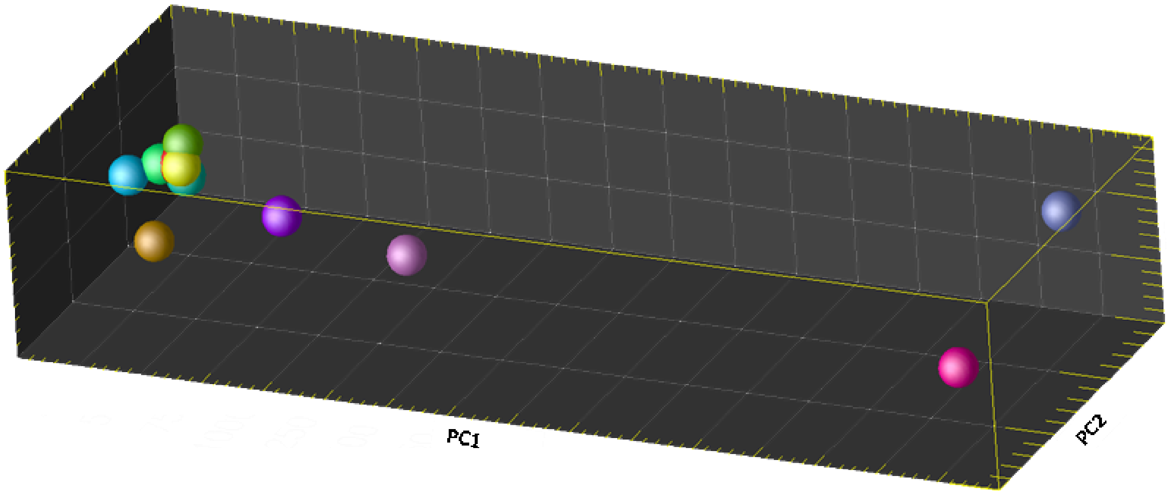


Fig. 3.11 Representation of the same 11 water classes shown in Fig. 3.10 in the domain spanned by the first three principal components of the analytical measurements. The two pictures share the same legend.

4 Optical detection

4.1 Principles of chemical detection in Optics

In the most conventional arrangement of optical detection systems for liquid phase samples, the sample is irradiated with a monochromatic radiation and the extent of the interaction is evaluated from the attenuation of the original radiation or by observing the secondary radiation emitted by the sample.

The classical way to observe emission or absorption spectra is to disperse the radiation, which means separate the different wavelengths from each other. A triangular prism of transparent material or diffraction gratings can be used to this purpose. Absorbance is usually measured with spectrophotometers. In spectrophotometers, the light is dispersed and collimated into a beam of nearly parallel rays, so that only a narrow band of wavelengths passes through the sample at one time. A detector determines the intensity of the transmitted radiation.

A quantity that is commonly plotted to represent an absorption spectrum is the transmittance, $T(\lambda)$, defined as follows:

$$T(\lambda) = \frac{I(\lambda)}{I_0(\lambda)}$$

where $I(\lambda)$ is the spectral intensity after the light beam passes through the cell and $I_0(\lambda)$ is the incident spectral intensity. Complementarily, the absorbance is defined as follows:

$$A(\lambda) = -\log\left[T(\lambda)\right] = \log\frac{I_0(\lambda)}{I(\lambda)}$$

Absorption spectroscopy can be used to measure the concentration of a chemical species dispersed in the optical path between source and detector. Fig. 4.1 shows the drawing of a cell containing an absorbing substance with concentration c, with a beam of light passing through it in the x direction. Considering a thin slab of unit area within the cell, lying between a generic abscissa x_0 and x_0+dx, the volume of the slab is dx times the unit area, so the amount of absorbing substance in this portion of the cell equals $C \cdot dx$ times the unit area

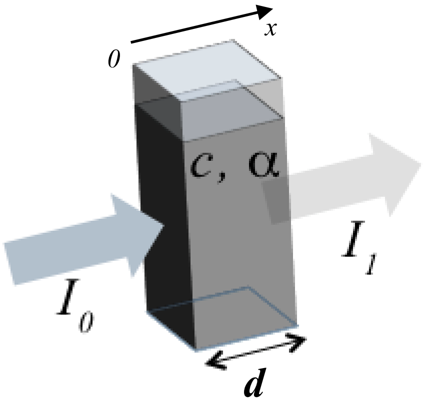


Fig. 4.1 Simplified sketch for the explanation of the light transmission measurement concept.

Let the intensity of light in the small range of wavelengths *dλ* be denoted by *I(λ, x) dλ*. This intensity depends on *x* because of absorption phenomena that make the light extinguish while travelling through the cell. The amount of light absorbed in the slab per unit of time is proportional to the initial intensity of light and to the amount of absorbing substance, so that the change in *I* from one side of the thin slab to the other is given by:

$$-dI = k(\lambda)\cdot I\cdot C\cdot dx$$

The proportionality factor *k* is a function of wavelength that does not depend on concentration. Roughly, spectrometric applications rely on the fact that *k(λ)* is different from zero only for wavelengths where the photon energy equals the energy difference between a significantly occupied molecular energy level and a higher level, giving rise to a kind of spectral signature of the involved substances.

Previous equation is a differential equation that can be solved for the intensity of light as a function of position. It is solved by a definite integration, letting $x = 0$ be the front of the cell and $x = d$ be the back of the cell. Assuming that the concentration is uniform, it yields:

$$A(\lambda) = \varepsilon(\lambda)\cdot C\cdot d$$

This equation is known as Beer-Lambert law, where *ε(λ)* is the absorptivity (also called the extinction coefficient). The absorptivity depends on the wavelength of light as well as on the absorbing substance and on the solvent. This relationship is well obeyed by many substances at low concentrations. Deviations occur at higher concentrations, corresponding to an extinction coefficient that is dependent on concentration. These deviations can be caused by specific chemical effects such as association of the molecules of the substance, which provides one way to study molecular association.

When an analyte does not exhibit a convenient spectroscopic optical response such as absorption or luminescence, sensing can be achieved by monitoring the optical response of an intermediate species or reagent whose response is modulated by the presence of the analyte. In fact, in a classical sensing scheme of optical sensors for liquid phase applications, a reagent has a specific reaction towards certain analytes by changing optical properties of the solution, such as absorbance, reflectance or fluorescence.

This indirect sensing technique requires the reagent to be immobilized, either in the liquid or in the solid phase, to facilitate interactions with the analyte. Reagent-based optical sensing is based mainly on solid-phase immobilization matrices, where the reagent dye can be adsorbed, covalently or ionically attached, or simply encapsulated in a solid matrix that is permeable to the analyte. If the immobilization matrix has the capability of being coated on a substrate in liquid form, as is the case for sol-gel glasses or polymer coatings, a wide range of sensor configurations is enabled including, for example, fibre optic, planar waveguide and array-based sensors. Indirect optical sensors are very well developed for pH sensing, that is based on the change in optical absorption of organic pH indicators. They also allow for colorimetric detection of CO_2 by measuring the pH change in response to carbonic acid generated by the acidic CO_2 gas (Segawa et al., 2003). On the other hand, many analytes, are detected with luminescent probes with the advantage that luminescence is intrinsically more sensitive than absorption as a sensing technique (R. Paolesse et al., 2011).

In those applications that need to study the distribution of the concentration of non-luminescent species over larger areas, the system to be analysed is exposed to a *paint* that responds to the respective parameter of interest. The term paint refers to a material that consists of a solvent, a polymeric support (sometimes referred to as a binder), and an indicator dye. This mixture can be painted or sprayed onto the surface of the object of interest or can be manufactured as a thin film that, after solvent evaporation, is placed on the system to be studied. The indicator dye in the paint undergoes diffusional equilibration with its environment, and the analyte of interest thereby modulates either the fluorescence or the absorption features of the paint, which is then photographed or imaged.

4.2 The Computer Screen Photoassisted Technique

The Computer Screen Photo-Assisted Technique (CSPT) is an optical-sensing interface firstly reported by Lundström and Filippini in 2003, which allows for the analytical investigation of visible absorption features of several kinds of samples

(Filippini et al., 2003). It consists of easily available, cheap and widespread diffuse computer peripherals. The basic hardware is a standard computer screen that is used as a programmable polychromatic light source and a web camera used as a three bands detector.

Computer screens are capable of displaying confined areas of arbitrary shape, colour, and intensity that can be two-dimensionally scanned on the screen with resolutions down to 200 μm resolution defined by the pixel pitch (distance between two contiguous cells of the same colour) (Filippini et al., 2006). In CRT monitors an electron beam scans the inner surface of the screen, exciting a spot of phosphorescent coating emitting a burst of visible light that decays until it is reached again by the beam in the next scanning cycle. Colour CRT screens use three electron beams exciting blobs of three different screen coatings. In this case the phosphors are band limited emitters of visible light corresponding to the perception of red, green and blue. The frequency at which the beams reach the same spot is about 85 Hz, and since it is faster than the eye's response it induces the perception of a steady intensity. On the contrary, in LCD screens each cell contains a liquid crystal between two crossed linear polarisers. If a voltage is applied to the cell, the liquid crystals rotate the direction of polarization of the light allowing to regulate the intensity escaping from the second polarizer. A large area white lamp illuminates the rear of the screen. Colour screens are produced by the repetition of groups of cells with red, green and blue filters. LCD screens produce a steady intensity and can refresh images at relatively low frequencies, typically 60 Hz. As far as CSPT measurements are concerned, the main differences between these two types of screens is the pulsed nature of the CRT displays and the linearly polarized light emitted from LCD screens (Schubert & Kyu Kim, 2005).

The light emitted from a computer screen is not monochromatic but it is the combination of three polychromatic primary sources. The spectral radiance of these primaries excites the human perception of red, green and blue colours. Any other colour can be generated by the linear combination of these primaries according to (Jackson et al., 1994):

$$v_i(\lambda) = r_i \times R(\lambda) + g_i \times G(\lambda) + b_i \times B(\lambda)$$

where $R(\lambda)$, $G(\lambda)$ and $B(\lambda)$, are the spectral radiances of the primary colours, r_i, g_i and b_i are numbers within [0 1] that represent the particular modulation of the primaries for a given desired colour, and λ, the wavelength, is limited to the visible range (390-800 nm). Conventional true colour systems have a resolution of 8 bits (0–255 values) for each colour channel, for a total of 2^{24} colours that can be displayed on the screen.

Digital colour cameras capture colour images of the real world by transmitting the image through a number of colour filters having different spectral transmittances and sampling the resulting coloured images by using electronic sensors.

4.3 CSPT measurements

During a CSPT measurement, a colour sequence is displayed in a portion of the screen to illuminate the sample. The light emerging from the assay is simultaneously acquired by the camera operating at a capture rate usually of 1 frame/s. The result of such a measurement is a digital video file (AVI format) of the array under different illuminating colours. The video stream is then decomposed into individual frames and the information from selected regions of interest (ROIs) in the image is extracted. ROIs are marked with white circles in Fig. 4.2, and they are located both on the sensing spots and on background areas.

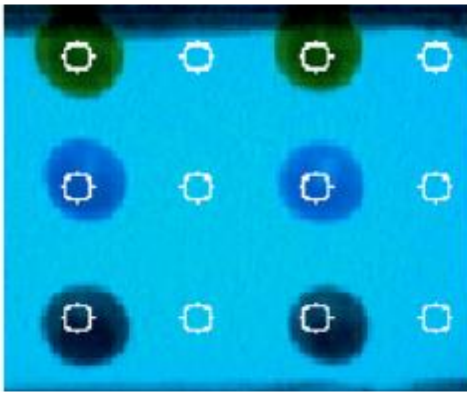
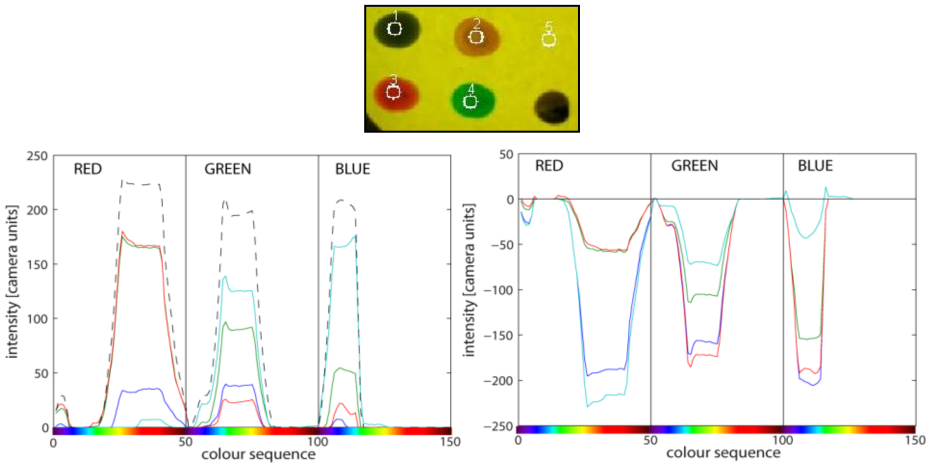


Fig. 4.2 Camera image of sensing layers under a bluish illumination. The regions of interest (ROIs) for each sensitive layer and the corresponding background are also shown.

The digital values of each colour level (red, green and blue components) of the pixels contained in the ROI are averaged, yielding the intensity per colour channel of each screen colour. As a result, a distinctive spectral signature of the sample is obtained. Usually it is in the form of intensity versus illuminating colours curves and it is often referred to as CSPT fingerprint (Fig. 4.3a). The CSPT measurement of the transmittance $T(\lambda)$ of any substance transforms this illuminating space into a measured space distinctive of the substance. The measured space contains both the spectral signature of the substances and that of the particular CSPT assembly where the measurement is performed. In order to highlight the substance signature, the measured space is subtracted by the measured space without substance, corresponding to the intensities measured in the background areas as shown in Fig. 4.3b.



(a) (b)

Fig. 4.3 a) CSPT fingerprints of sensing layers reported in the inset, obtained by concatenating the intensity in the three camera channels for an illumination sequence made of 50 colour combinations. The black dashed line represents the reference light source or background (circle number 5 in the inset). b) Difference between the same fingerprints and the background intensity. It allows to evaluate the absorption exhibited by each spot.

Different substances transform the illuminating space in different measured spaces, and emerging light colours become aligned with the respective camera channels. In CSPT measurements, depending on the transmittance of the evaluated substance, the response to some illuminating colour combinations becomes clustered in the measured space, thus reducing the discrimination capability in terms of spectral diversity of the collected fingerprints. Under this point of view, longer colour sequences (i.e., enriched by a higher number of colour combinations) have better chances to always incorporate well performing patterns.

Illuminating sequences homogeneously representing the illuminating space produce diverse distributions of measured values, suggesting the possibility to optimise such sequences for the spectral properties of any particular compound. However, it is also evident that certain substances will always be represented by a larger volume of the colour space. The larger the volume they occupy in the measured space, the better the chances to find an illuminating sequence that separates all the pertaining features, thus creating a distinctive fingerprint. In summary, for substance transmittances with their minima at the centre of the visible spectrum, CSPT is able to retain more spectral features than for substances absorbing at the borders of the spectrum. These better conditions for substances that affect green, yellow, and orange light than for blue or red light can be intuitively associated to the restricted contribution of the later substances on the signals of various channels. So, substances absorbing light in the far red (or blue) only affect the red (or blue) signal of the camera, whereas a green, yellow or orange absorbing substance gathers distinctive contributions from all the channels, thus enriching the information contained in the fingerprint and improving the discrimination capability (Filippini & Lundström, 2006).

Usually, most applications are well accomplished with a sequence of 50 colours that gradually change from blue to red. However, for selected indicators, a shorter and more targeted sequence can be defined, that allows for a continuous imaging of spectral features of the substance.

4.4 Case study: the detection of natural Cr(VI) with a CSPT setup

The potentiality of CSPT is illustrated in an application aimed at evaluating the concentration of Cr(VI) in natural springs (Santonico et al., 2009). Here the CSPT is used as a method to measure the colour changes in a colorimetric assay for Cr(VI). CSPT results are compared with those obtained by a standard UV-VIS spectrophotometer. Results show that CSPT is a valid alternative for colorimetric assay read-out. It is particularly important to consider that CSPT equipment used for different applications (such as computers and cameras) are temporarily turned into analytical devices without altering their primary function. On this basis, this result demonstrates the possibility to enable analytical capabilities to a personal level.

Hexavalent chromium is a toxic compound with teratogenic and carcinogenic effects on humans. Its presence in the environment is typically due to anthropogenic activities (Nriagu & Niebner, 1988). Nonetheless, recently natural occurring concentrations of Cr(VI) largely exceeding the limits for groundwater quality have been found worldwide (Oze et al., 2007; Fantoni et al., 2002). These anomalies originate from oxidative dissolution, probably driven by mixed-valence Mn oxides, of Cr(III)-bearing minerals contained in particular kinds of rocks called serpentinites and ultramafites, which constitute 1% approximately of the terrestrial landscape and are also found within densely inhabited areas of the Circum-Pacific and Mediterranean regions. As a consequence, the control of Cr(VI) becomes important even in the absence of human activities, displacing the monitoring of this substance from the output of relevant industrial plants to the common water distribution network, by the observation of water bodies prone to the pollution from Cr(VI) of natural origin. Besides more sophisticated techniques, an efficient detection of Cr(VI) is obtained by an analytical procedure based on the absorbance change, around 540 nm, consequent to the reaction of a sample of water with a specific reagent (diphenylcarbazide) under acid conditions.

Fig. 4.4 shows the CSPT measurement arrangement. Fig. 4.5 shows the fingerprints collected during the measurement campaign described in (Santonico et al. 2009). The largest changes of differential intensities collected by the camera are observed in the green channel under green colour illumination. Nonetheless, PLS modelling was applied to whole fingerprints exploiting the PLS property of variable selection. The PLS model was built by using the calibration solutions.

The Cr(VI) concentrations in these solutions were considered as not affected by errors. PLS model was optimized by a leave-one-out cross-validation procedure, and the number of latent variables was chosen by minimizing the root mean square error of validation. As a result, a model with four latent variables was defined, the root means square of calibration (RMSEC) was 0.01 ppb and the root means square of validation (RMSECV) was 2.9 ppb. The error of ±2.9 ppb was then applied to the Cr(VI) estimations. Validated PLS model was applied to the fingerprints of spring waters, results were compared with those provided by commercially available instruments, such as a Cary spectrophotometer and a Hanna portable instrument. For these instruments the estimated errors mentioned in the previous section were applied. .4.5 shows the collected fingerprints related to the calibration samples and the spring waters. Fig. 4.6 shows the Cr(VI) in natural spring water estimated by the CSPT plotted versus the values measured with a Cary spectrophotometer; the calibration data are also plotted.

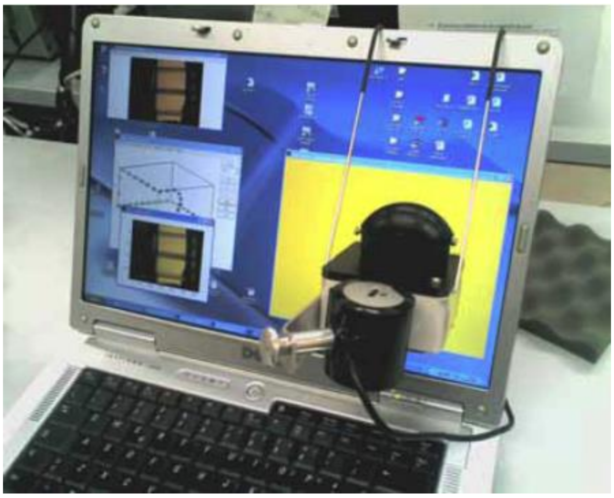


Fig. 4.4 CSPT arrangement. The camera and the sample holder are fixed to the screen of a notebook where a window displays the illumination sequence. In the picture also the image captured by the camera is visible in another window. The software routine runs in MATLAB.

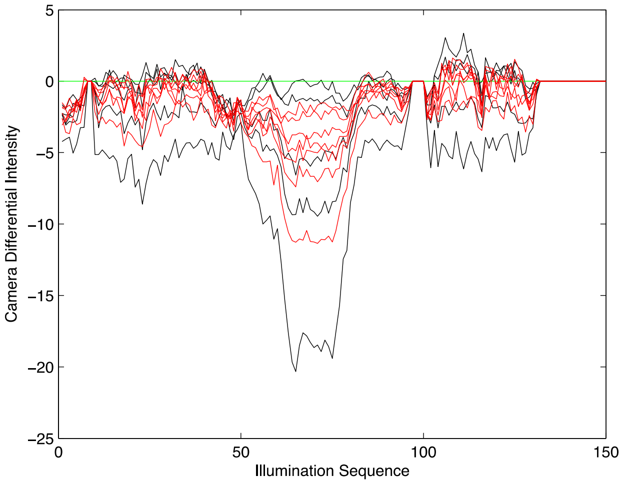


Fig. 4.5 Collected fingerprints related to calibration samples (black lines) and spring waters (red lines). Largest changes occur in the green camera channel under green light illumination.

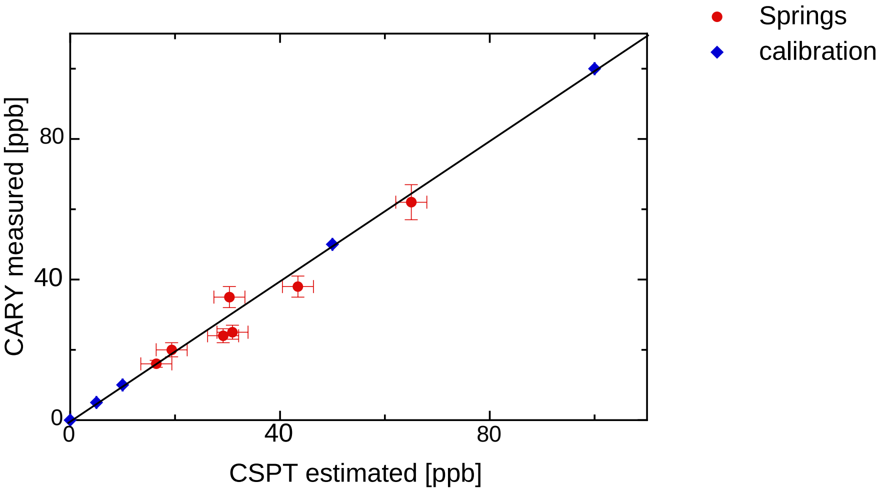


Fig. 4.6 Comparison of spectrophotometry and CSPT estimation of Cr(VI) concentration in spring water samples.

5 Conclusions

This chapter gives an overview of new technologies for the assessment and control of the quality of water resources, as an alternative to the classical chemical-analytical approaches. In particular, non-conventional electroanalytical devices such as e-tongues (or taste sensors) can be applied to the continuous monitoring of natural resources, with advantages in terms of availability, wide analytical coverage, and low cost of the method.

Possible applications for this class of devices may include the usage of expert systems to trigger automatic samplers, alert human operators or perform other automatic actions when the observed data exhibit a significant change with respect to a given reference, e.g. moving outside known boundaries, which may represent an anomalous condition. Being non specific to particular chemical species, e-tongue systems are good candidates to monitoring applications where the mere detection of an overall quality change (e.g. the presence of an unexpected pollutant) is the most required characteristic.

Another fairly mature, inexpensive, and very attractive technology described in this chapter is the Computer Screen Photo-Assisted Technique (CSPT), taken as a promising example of non conventional approach to water quality measurements based on optical sensor systems. In fact, the combined usage of a display (e.g., a computer screen) and a generic camera (e.g., a webcam) has been demonstrated as an effective platform for measuring optical properties of liquid samples. Such an approach is a natural candidate for ubiquitous analyses in the context of water quality monitoring, and is complementary to the electrochemical e-tongues, enriching the analytical possibilities offered by these non-conventional techniques.

References

1. Artursson T, Holmberg M (2002) Wavelet transform of electronic tongue data, Sensors and Actuators B, vol. 87 pp. 379–391
2. Bard A. J. and Faulkner L. R., 1980 (1st ed.), 2000 (2nd ed.), Electrochemical methods, fundamentals and applications, John Wiley & Sons.
3. Brainina KZ, Kubysheva IV, Miroshnikova EG, Parshakov SI, Maksimov YG, Volkonsky AE (2001) Small-Size Sensors for the In-Field Stripping Voltammetric Analysis of Water, vol. 5 pp. 260-271
4. Buehler MG, Kuhlman GM, Keymeulen D, Kounaves SP (2002) Advanced Electronic Tongue concept, 2002 IEEE Aerospace Conference Proceedings, pp. 407-416

5. Ciosek P., Brzózka Z. and Wróblewski W. (2004) Classification of beverages using a reduced sensor array, Sensors and Actuators B, 103, pp. 76-83.

6. Di Natale C., F. Davide, J. Brunink, A. D'Amico, Yu. Vlasov, A. Legin, A.Rudnitskaya. (1996) Multicomponent analysis of heavy metal cations and inorganic anions in liquids by a non-selective chalcogenide glass sensor array Sensors and Actuators, B 34, pp. 539-542

7. Di Natale C, Macagnano A, Davide F, D'Amico A, Legin A, Vlasov Y, Rudnitskaya A, Selezenev B (1997) Multicomponent analysis on polluted waters by means of an electronic tongue, Sensors and Actuators B-Chemical 44, pp. 423-428

8. Fantoni D., G. Brozzo, M. Canepa, F. Cipolli, L. Marini, G. Ottonello, M. Vetuschi Zoccolino (2002) Natural hexavalent chromium in groundwaters interacting with opholitic rocks, Environmental Geology, 42, pp. 871-882

9. Filippini D, Alimelli A, Di Natale C, Paolesse R, D'Amico A, Lundstrom I (2006) Chemical sensing with familiar devices. Angewandte Chemie-International Edition 45:3800-3803 DOI: 10.1002/anie.200600050

10. Filippini D., A. Alimelli, C. Di Natale, R. Paolesse, A. D’Amico, I. Lundström (2006) Chemical Sensing with Familiar Devices, Angew. Chemie 118, pp. 3884-3887

11. Filippini D., I. Lundström, Preferential color substances and optimized illuminations for computer screen photo-assisted classification (2006) Analytica Chimica Acta 557, pp. 393–398

12. Filippini D., S. P. S. Svensson, I. Lundström (2003) Computer screen as a programmable light source for visible absorption characterization of (bio)chemical assays, Chem. Commun. 2, pp. 240–241

13. Gardner J.W., P.N. Bartlett (1994) A brief history of electronic noses, Sens. Actuators B 18–19, pp. 211–220.

14. Hauptmann P., R. Borngraeber, J. Schroeder, and J. Auge (2000) Artificial electronic tongue in comparison to the electronic nose - State of the art and trends, in Proc. IEEE/EIA Int. Freq. Control Symp. Exhib., pp. 22–29.

15. Hayashi H., M. Yamanaka, K. Toko, K. Yamafiji (1990) Multichannel taste sensor using lipid membrane. Sensors and Actuators B 2, pp. 205-213

16. Herrero A., Cruz Ortiz M. (1999) Qualitative and quantitative aspects of the application of genetic algorithm-based variable selection in polarog-

raphy and stripping voltammetry. Analytica Chimica Acta, 378 (1-3), pp. 245-259 DOI: 10.1016/S0003-2670(98)00619-9

17. Heyrovský J. (1924) The processes at the mercury dropping cathode. Part I. The deposition of metals, Trans. Faraday Soc., vol. 19, pp. 692-702 DOI: 10.1039/TF9241900692
18. Heyrovský J. (1924) The processes at the mercury dropping cathode. Part II. The hydrogen overpotential, Trans. Faraday Soc., vol. 19, pp. 785-788 DOI: 10.1039/TF9241900785
19. Hickling A. (1942) Studies in electrode polarisation. Part IV.—The automatic control of the potential of a working electrode Trans. Faraday Soc., 38, pp. 27-33 DOI: 10.1039/TF9423800027
20. Holmin S., Spångeus P., Krantz-Rülcker C., Winquist F. (2001) Compression of electronic tongue data based on voltammetry - A comparative study. Sensors and Actuators, B: Chemical, 76 (1-3), pp. 455-464 DOI: 10.1016/S0925-4005(01)00585-8
21. Iliev B, Lindquist M, Robertsson L, Wide, P (2006) A fuzzy technique for food and water quality assessment with an electronic tongue, Fuzzy sets and systems, vol. 157 issue 9, pp. 1155-1168
22. Jackson R., L. Mac Donald, K. Freeman (1994) Computer generated color, Wiley
23. Janata J. 1989 (1st ed.), 2009 (2nd ed.), Principles of Chemical Sensors, pp. 340, Springer
24. Korthum G. (1965) Treatise on electrochemistry. University of Tubingen, Germany. 2nd ed. by American Elsevier Publishing, New York
25. Krantz-Rulcker C., M. Stenberg, F. Winquist, and I. Lundstrom (2001) "Electronic tongues for environmental monitoring based on sensor arrays and pattern recognition: A review," Anal. Chim. Acta, vol. 426, no. 2, pp. 217–226
26. Kundu P.K., Chatterjee, A., Panchariya, P.C. (2011) Electronic tongue system for water sample authentication: A slantlet-transform-based approach. IEEE Transactions on Instrumentation and Measurement, 60 (6), pp. 1959-1966 DOI: 10.1109/TIM.2011.2115410
27. Landgrebe DA (2003) Signal Theory Methods in Multispectral Remote Sensing. John Wiley & Sons, Hoboken New Jersey
28. Legin A., A. Rudnitskaya, Yu. Vlasov, C. Di Natale, E. Mazzone, A. D'Amico (1999) Application of electronic tongue for quantitative analysis of mineral water and wine. Electroanalysis, 11, pp. 814-820

29. Lindquist M. and P. Wide (2001) Virtual water quality tests with an electronic tongue, in Proc. IEEE IMTC, Budapest, Hungary, May 21–23, pp. 1320–1324

30. Lvova L., E. Martinelli, E. Mazzone, A. Pede, R. Paolesse, C. Di Natale, A. D'Amico (2006), Electronic tongue based on an array of metallic potentiometric sensors, Talanta, 70, pp. 833-839

31. Men H., Zou, S., Li, Y., Wang, Y., Ye, X., Wang, P. (2005) A novel electronic tongue combined MLAPS with stripping voltammetry for environmental detection. Sensors and Actuators, B: Chemical, 110 (2), pp. 350-357 DOI: 10.1016/j.snb.2005.02.032

32. Mirceski V., Komorsky-Lovric S., Lovric M. (2007) Square-Wave Voltammetry, ISBN 978-3-540-73739-1, Springer

33. Nriagu J., E. Niebner (eds.) Chromium in the natural and human environments (1988), J. Wiley, New York USA

34. Otto M., Thomas J. (1985) Model studies on multiple channle analysis for free magnesium, calcium, sodium and potassium at phyisological concentration levels with ion-selective electrode. Anal. Chem. 57, 2647

35. Oze C., D. Bird, S. Fendorf (2007) Genesis of hexavalent chromium from natural sources in soil and groundwater, P Natl Acad Sci USA 104, 6544-6549.

36. Paolesse R., C. Di Natale, M. Burgio, E. Martinelli, E. Mazzone, G. Palleschi, A. D'Amico (2003), Porphyrin-based array of cross-selective electrodes for analysis of liquid samples, Sensors and Actuators, B 95, pp. 400-405

37. Paolesse R., D. Monti, F. Dini, C. Di Natale (2011) Fluorescence based sensor arrays, Topics in Current Chemistry, 300, pp. 139-174

38. Pereira JMD, Postolache O, Girao PS (2007) A smart and portable solution for heavy metals concentration measurements. Proceedings of the IEEE Instrumentation & Measurement Technology Conference. pp: 2427-2430

39. Richards JA (2012) Remote Sensing Digital Image Analysis: An Introduction. Springer, Berlin Heidelberg

40. Riul A., R.R. Malmegrim, F.J. Fonseca, L.H.C. Mattoso (2003) An artificial taste sensor based on conducting polymers, Biosens. Bioelectron. 18, pp. 1365–1369.

41. Santonico M., A. Scozzari, G. Brozzo, L. Marini, A. D’Amico, D. Filippini, I. Lundstrom, C. Di Natale (2009) Detection of natural Xr(VI) with

computer screen photo-assisted technology. Procedia Chemistry 1, pp. 317-320

42. Schubert E.F., J. Kyu Kim (2005), Solid-state light sources getting smart, Science 308, pp. 1274-1278

43. Scozzari A. (2005) Signal analysis of voltammetric data series for water quality tests and classification, Proceedings of the IEEE Instrumentation & Measurement Technology Conference. pp. 89-92

44. Scozzari A., Acito N., Corsini, G. (2006a) A Supervised Algorithm for Water Classification by Voltammetric Measurements. Proceedings of the IEEE Instrumentation & Measurement Technology Conference. pp. 725-728

45. Scozzari A., P. Peruzzi, R. Cioni, M. Guidi (2006b), An innovative approach to urban water management based on taste sensors, EGU General Assembly, Wien (Austria)

46. Scozzari A., Acito N. and Corsini G. (2007a), A novel method based on voltammetry for the qualitative analysis of water, IEEE Transactions on Instrumentation and Measurement, 56(6) DOI:10.1109/TIM.2007.903600

47. Scozzari A. (2007b) Application of an e-tongue to groundwater monitoring: a measurement perspective, 12th Symposium on Water-Rock Interaction, Bullen & Wang (eds), Taylor & Francis group, Kunming (China), vol 2, pp. 1115-1118

48. Scozzari A. (2008a) Electrochemical sensing methods: a brief review. In: Evangelista V et al. (eds.) Algal toxins: nature, occurrence, effect and detection, NATO Science for Peace and Security Series A: Chemistry and Biology, pp. 335-351, Springer Science + Business Media B.V. DOI: 10.1007/978-1-4020-8480-5_16

49. Scozzari A., Wide P. (2008b) The Process from a Redundant and General Sensor Concept - Towards an Optimal Sensor Strategy for the Assessment of Drinking Water Quality, IEEE Instrumentation & Measurement Technology Conference, Proceedings, pp: 836-841 DOI: 10.1109/IMTC.2008.4547153

50. Segawa H., E. Ohnishi, Y. Arai, K. Yoshida (2003) Sensitivity of fiber-optic carbon dioxide sensors utilizing indicator dye, Sensors and Actuators B 94 276-281

51. Semerano G., Griggio L. (1957) Selected values of polarographic data, pp. 286, Arti grafiche Panetto & Petrelli

52. Tymeszki L., W. Zwierkowska, R. Koncki (2004) Screen printed electrode for potentiometric measurements, Anal Chim Acta 526, pp. 3-11

53. Vlasov Yu., A. Legin, A. Rudnitskaya, C. Di Natale, A. D'Amico (2005) Nonspecific sensor arrays ("electronic tongue") for chemical analysis of liquids: (IUPAC technical report), Pure and Applied Chemistry 77, pp. 1965-1983

54. Winquist F., P. Wide, and I. Lundstrom (1997) An electronic tongue based on voltammetry, Anal. Chim. Acta, vol. 357, no. 1/2, pp. 21-31

55. Winquist F, Krantz-Rulcker C, Wide P, Lundstrom I (1999a) Monitoring of freshness of milk by an electronic tongue on the basis of voltammetry, Measurement Science & Technology, vol. 9 issue 12 pp. 1937-1946 DOI: 10.1088/0957-0233/9/12/002

56. Winquist F, Lundstrom I, Wide P (1999b) The combination of an electronic tongue and an electronic nose, Sensors and Actuators B: Chemical, 12th European Conference on Solid-State Transducers - 9th UK Conference on Sensors and Their Applications, Southampton, UK, vol. 58 issue 1-3 pp. 512-517 DOI: 10.1016/S0925-4005(99)00155-0