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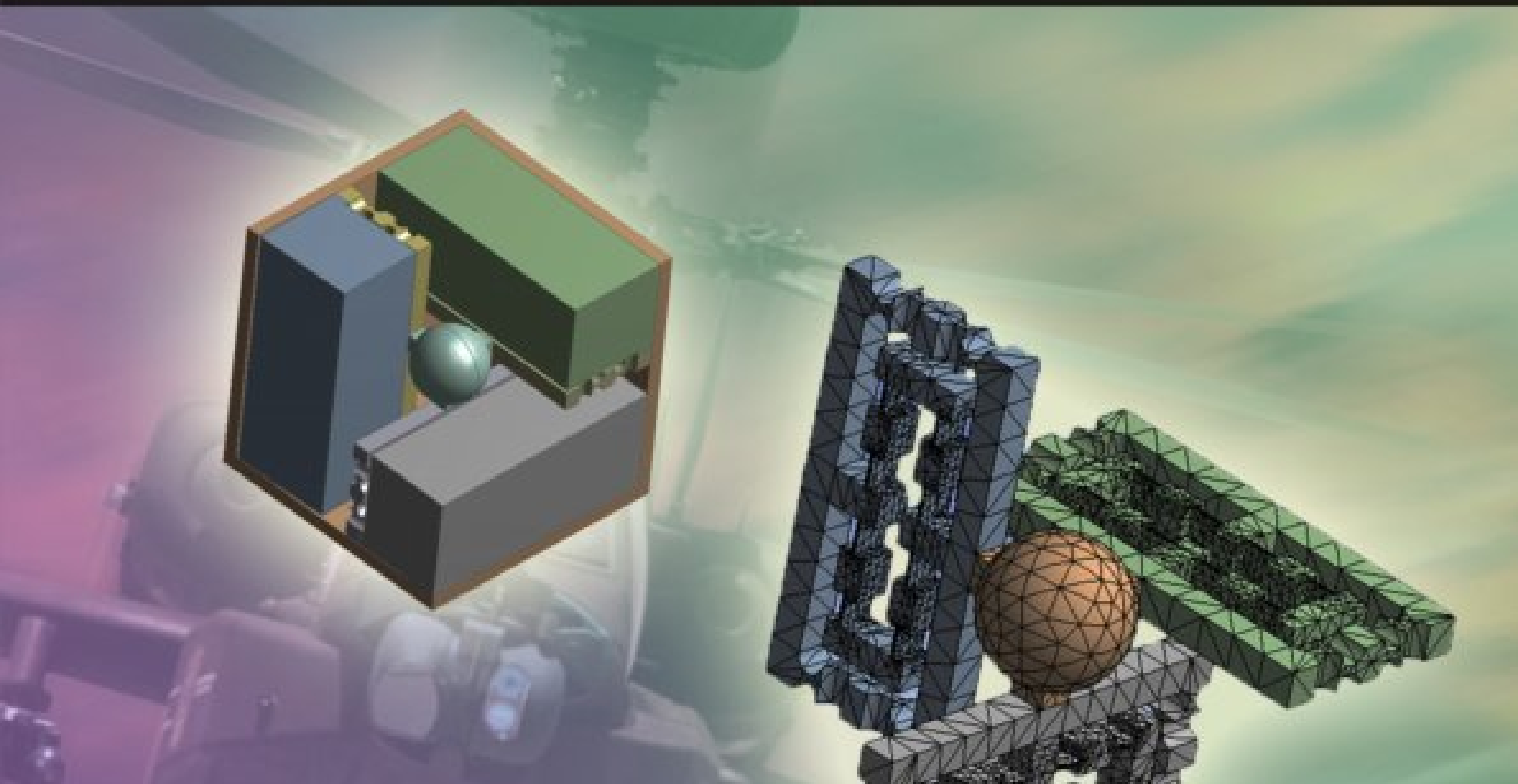

Sensors and Transducers Applications

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Development of a Portable Water Quality Analyzer

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Abstract: A portable water analyzer based on a voltammetric electronic tongue has been developed. The system uses an electrochemical cell with two working electrodes as sensors, a computer controlled potentiostat, and software based on multivariate data analysis for pattern recognition. The system is suitable to differentiate laboratory made and real in-situ river water samples contaminated with different amounts of Escherichia coli. This bacteria is not only one of the main indicators for water quality, but also a main concern for public health, affecting especially people living in high-burden, resource-limiting settings. *Copyright © 2010 IFSA.*

Keywords: Water quality, Electronic tongue, E. Coli, PCA.

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1. Introduction

The water quality is one of the mayor concerns worldwide. In developing countries, like Peru, there are areas, located mainly in cities, where the quality of water accomplishes the international standards. But in suburban and rural locations the quality decreases dramatically, due mainly because of lack in infrastructure. This fact carries health, social and economic problems.

In order to determine the water quality, physical, chemical and biological parameters are measured. In water free of heavy metals, the biological parameters have the better score in water quality characterization. The coliforms, bacteria Escherichia coli and Enterobacter aragene, are good indicators of potable water quality. Their presence indicates bad quality of water.

There are several standard microbiological tests in order to determine the presence of coliforms in water, for example: the most probable number of coliforms (MPN), membrane filtration (MF) and Colilert Test (CT) [1, 2].

In the MF test the water sample passes through a sterile membrane; the coliforms are trapped on the membrane. After that a cultivated media is added to the membrane and after a digestion time of 18 h, the surface of the membrane is observed using a microscope. The presence of colonies indicates the presence of coliforms. In the commercial Colilert® test the Colilert regent is added to 100 mL of the sample, if there are coliforms, the color of the sample becomes yellow, after 24 hours at 350 ^{0}C. These microbiological tests take at least 18 h to be completed, making it impossible to perform an in situ real-time monitoring.

The analysis device called “electronic tongue” or “taste sensor”, try to mimic the human sense of taste. It has a three components structure: a sensor array, the equipment for emitting and receiving signals, and pattern recognition. The sensors of the sensor array are non specific sensors so they can give response for as many different kinds of liquids as possible.

In recent years three types of electronic tongues have been developed, which are based on potential, impedance spectroscopy or voltammetry [3].

The first voltammetric electronic tongue was developed at Linköping University by Fredrik Winquist et. al. [4]. It comprised several metallic electrodes (platinum, gold, palladium, iridium, rhenium and rhodium) as working electrode, a Ag/AgCl as reference electrode and a stainless steel electrode as counter electrode for standard three-electrodes system.

Chronoamperometry is the technique used in this type of electronic tongue. The voltage levels and times are set for each application. The current response for each time and for each working electrode is combined into a vector that characterizes the sample.

Principal Component Analysis (PCA) is used to recognize patrons in the characteristic vectors, in order to link them to a specific sample.

This kind of system has been successfully used to analyze milk [5], tea [6], drinking water [7], detergent in washing machine waste water [8] and also to recognize different microbial species [9].

A system that analyzes water quality based on a voltammetric electronic tongue has been developed. The system was able to differentiate laboratory made water contaminated with E.coli. And also water from a river contaminated with E.coli during a process of decontamination.

2. Experimental

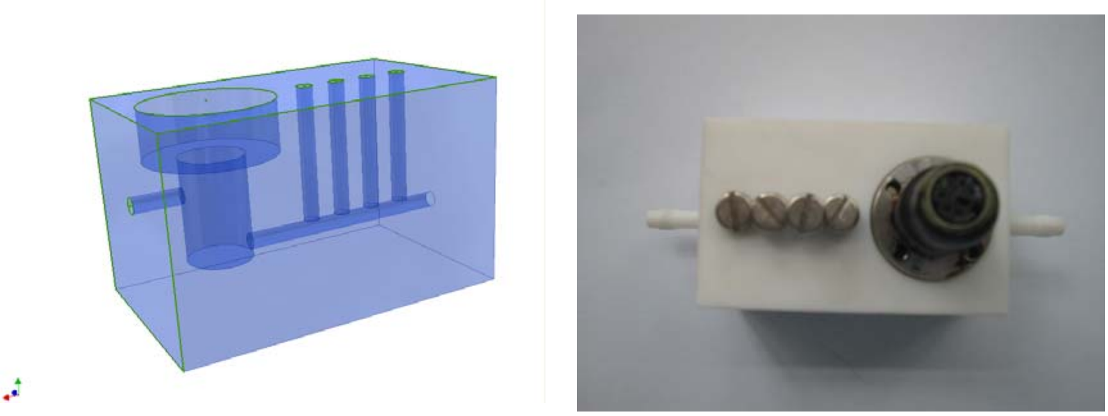
The sensor is a two-electrodes chemical cell. The counter electrode was made in stainless steal, this electrode supports in its inside two working electrodes made of gold wire (Premion®, 1 mm diameter, 99.985 % purity) and platinum wire (World Precision Instruments Inc, 1 mm diameter). In order to fix the gold and platinum wires, a dental acrylic polymer (3M ESPE Valux Plus) has been used. The Fig. 1 shows the details.

Because the current value varies with the working electrode being in contact with the liquid, a flow cell has been used to maintain this area constant (Fig. 2).

The cell was made in Teflon®, it has one inlet which is connected to the samples bicker, an internal cylinder where the counter electrode is mounted on and one outlet where a mini pump (Hargraves LTC series W311-11) is connected (Fig. 2). In this work the vertical inlets where not used.

(a) (b)

Fig. 1. Top view of the sensor showing the electrodes supported by the dental acrylic (a); sensor with cable and connector (b).



(a) (b)

Fig. 2. 3D plot of the flow cell (a); flow cell with sensor attached (b).

The potentiostat (UNISCAN PG580) has been used to perform the electrochemical tests, this potentiostat has a computer RS232 interface. A laptop computer (HP pavilion ze5600 with Trendnet SU-9 RS232 adapter) was used to control and acquire data from the potentiostat.

A LabVIEW® program that controls the potentiostat and save the data has been developed.

The potentiostat has its own OCX library, besides its controlling software. The LabVIEW ActiveX connectivity was used to make the program thus it sets the chronoamperometry mode, voltage wave form, sampling rate, current range, number of experiments to be performed and the file name. In the file, the current data are formatted in columns and time in rows. This matrix has as many columns as measurements have been performed.

In order to analyze the data and find correlation between quality water and shape of the current plot, a pattern recognition analysis based on Principal Component Analysis (PCA) has been used [5, 13].

The software for PCA analysis has been developed in MatLab®, the matrix containing the current data is the input of this program, and mathematical standardization to the matrix was done prior to PCA analysis. The current pattern is composed by discrete current values in time so each time value was used as a variable and each measurement of water, containing several current values, as object in the PCA analysis.

The software gives the 2D score plot, and the variance value for the Principal Component 1 (PC1) and Principal Component 2 (PC2). So if in the score plot a point that represents a sample is close to a cluster formed by the points that represent good quality water, it is possible to infer the sample has good quality.

Fig. 3. View of the portable water quality analyzer.

2.1. Determination of the Voltage Steps for E.coli Analysis

The test to evaluate the electrochemical behavior of E.coli was cyclic voltammetry; this test served us to estimate the voltage steps to be used in chronoamperometry.

E.coli bacteria (ATCC10536) were seed on a Petri dish and incubated for 18 hours at 370 C. After that 3 ml of clean water was added, and mixed with the bacteria, 100 µL of this mixture was added to 160 mL of clean water. And finally this 160 mL of contaminated water was added to 5L of clean water.

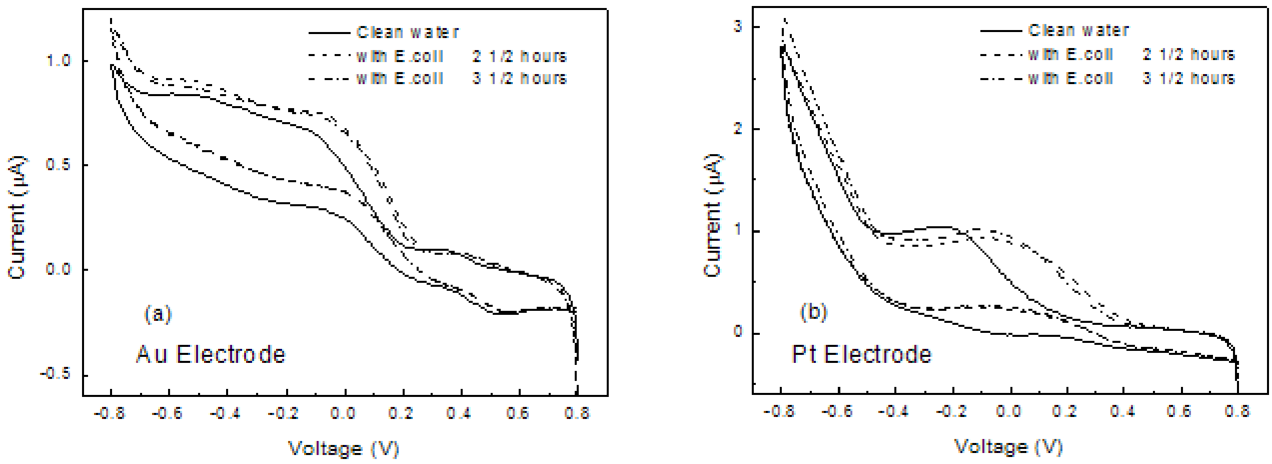
The water was analyzed 2.5 hours later the preparation using MF test. The number of Colony Forming Units (CFU) was more than 800 CFU/10 mL, which is usually referred as uncountable CFU/10 mL.

Cyclic voltammetry test has been performed for both clean and contaminated water for each working electrode. The water quality analyzer setup was used.

The working voltage range was from -0.8 V to 0.8 V, with a sweep rate of 20 mV/s. It is possible to see at the Figs. 4a and 4b, that for voltages between -0.1 V and -0.4 V, a notorious current difference between pure and contaminated water is achieved.

Two tests were performed 2.5 h and 3.5 h after the sample preparation, showing reproducibility in the current-voltage curves for both electrodes. (Figs. 4 a-b).

The voltage steps used for all the measurements with the portable quality analyzer are shown in Fig. 5.



(a) (b)

Fig. 4. Electrochemical behavior of water contaminated with E.coli for Au electrode (a), and Pt electrode (b).

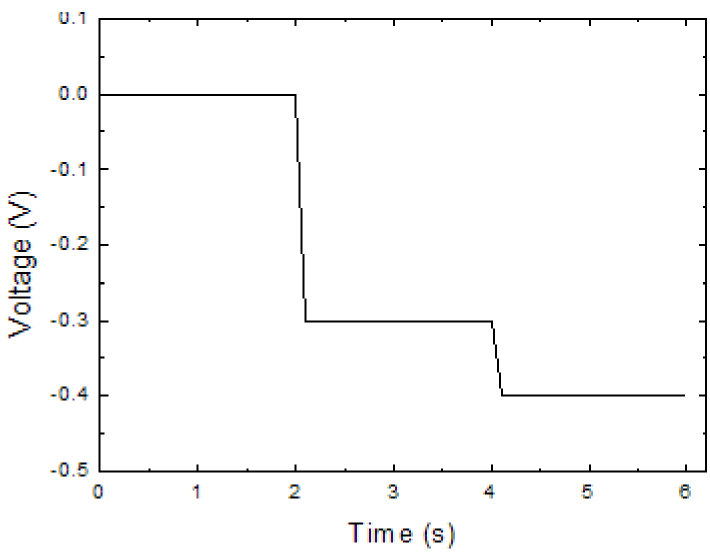


Fig. 5. Voltage steps used for the analyzer.

2.2. Laboratory Measurements

Water samples contaminated with different concentrations of E.coli where analyzed, using both the quality analyzer and the standard MF microbiological test.

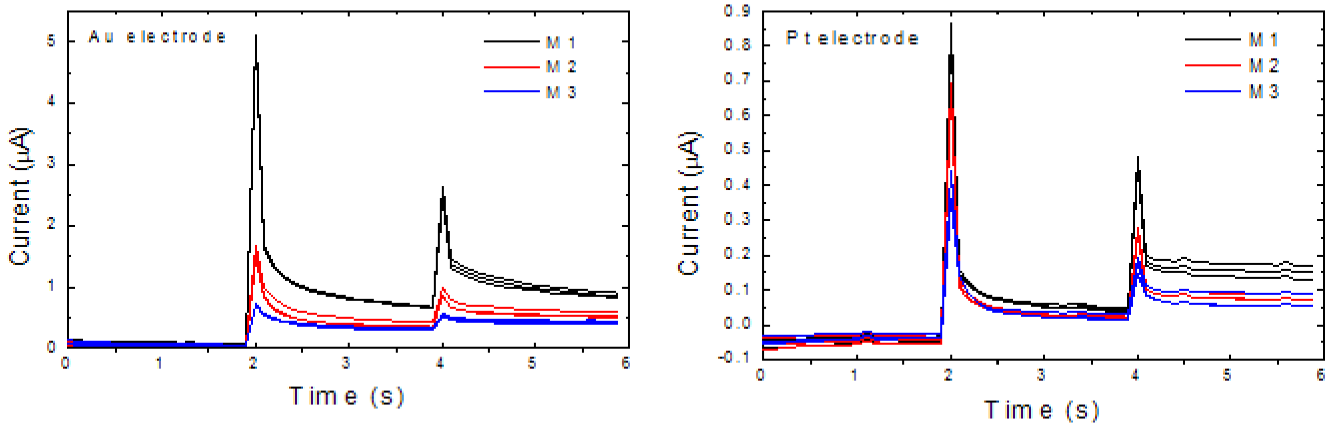
Three samples of E.Coli contaminated water were prepared in the laboratory. The E.coli concentration for each sample is shown in Table 1.

Table 1. E.coli polluted water prepared in the laboratory.

Sample	**M3**	**M2**	**M1**
Level of contamination	High	Medium	Low
CFU / 10ml. E.coli	Uncountable x 10^{-1}	Uncountable x 10^{-2}	554 x 10^{-4}

The three samples where measured with the portable quality analyzer three times each and randomly under laboratory conditions (25 ^{0}C, 67 % RH).

The Fig. 6 (a) and (b) show the current response for the three samples.



(a) (b)

Fig. 6. Current signal for the three water samples measured three times each, from the gold electrode (a) and platinum electrode (b).

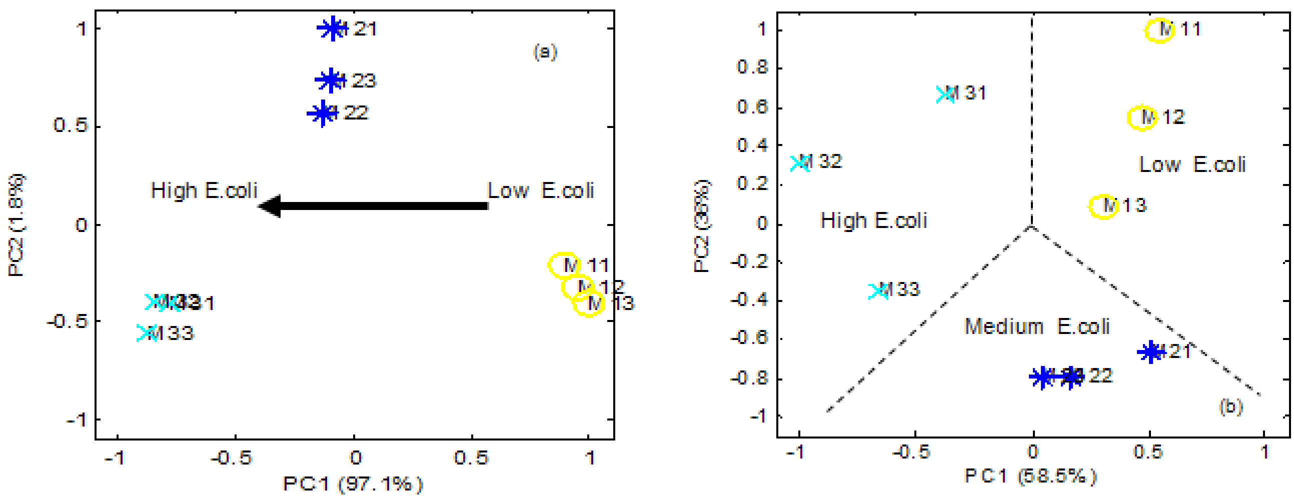
The data were analyzed using the developed PCA software. Each current pattern has 60 variables and each of the 9 measurements is an object.

The PCA score plot for each working electrode is shown in Fig. 7. In the notation M_{ij}, "i" represents the sample number, and "j" is the time the sample was measured.

2.3. In-situ River Water Measurements

The in-situ analysis was performed in a rural area of Yaurisque (13º 39' 37.24"S, 71º 55' 6.59" W), setting located 48Km from Cusco city.

Water samples were collected from Yaurisque River. This river carries residual water from a school and a little medical assistance center.



(a) (b)

Fig. 7. PCA score plot for the samples M1, M2 and M3 measured tree times each for gold electrode (a) and platinum electrode (b).

The solar disinfection individual units method (DSAUI method) [11] has been used to water decontamination. In this method recycled transparent PET soft drink bottles are filled with biological polluted water, and the filled bottle is exposed to solar radiation. Due to the UV-A and thermal radiation the amount of colony forming units are reduced dramatically. This technology is been used in several countries in Latin America [12].

The portable Delagua® water test kit was used to perform the MF microbiological test. The test showed presence of E.coli and pseudomonas in the Yaurisque River.

The decontamination process had duration of 4 hours and began at 10am. Each hour, a water sample from the decontamination bottle was collected. These collected samples were analyzed using Delagua® kit and the values are shown in Table 2.

Table 2. Concentration of E.coli measured during DSAUI decontamination.

Time	CFU/10 ml
Start	117 x 10 E.coli; 190 x 10 Pseudomonas sp.
T1 1 hour	60 x10 E. coli; 71 x 10 Pseudomonas sp.
T2 2 hours	19 x 10 E.coli
T3 3 hours	4 x 10 E. coli; 4x 10 Pseudomonas
T4 4 hours	2 x10 E. coli

Because Delagua® kit uses MF test, it takes at least 18 hours to analyze each sample. The analyzer developed needs only 15 seconds to obtain the current pattern correspondent to each sample.

The current signals obtained for each time and for each electrode are shown in the Fig. 8 and Fig. 9.

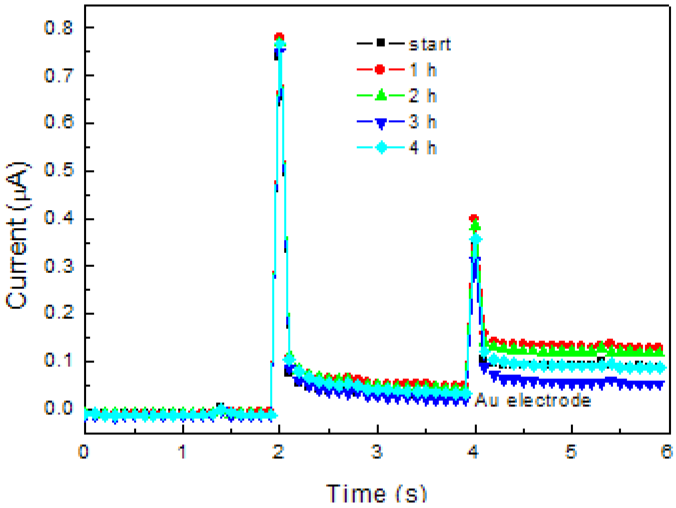


Fig. 8. Current signals for gold electrode, while the river water is decontaminating.

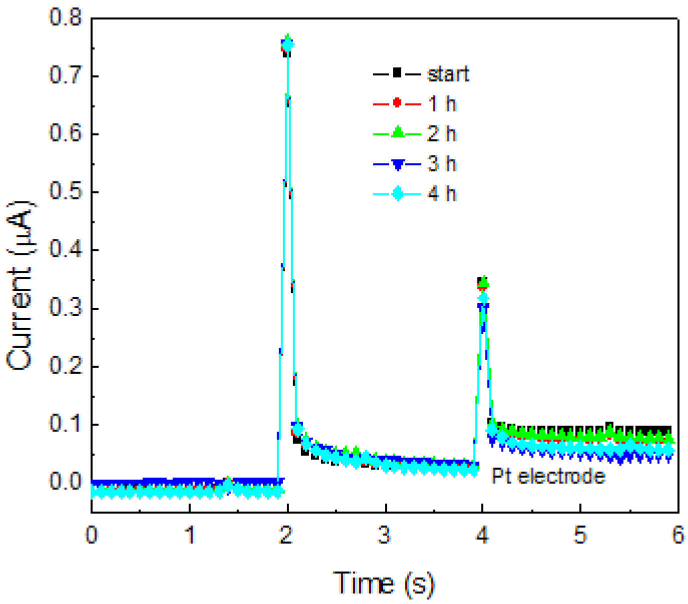


Fig. 9. Current signals for gold electrode, while the river water is decontaminating.

The data were analyzed using the developed PCA software. The six objects represents the time the samples were collected. As in the previous case there are 60 variables. In the Figs. 10 and 11 the scores respectively the PCA plots for gold and platinum electrodes are shown.

3. Conclusions

A portable water analyzer based on a voltammetric electronic tongue has been developed. The voltage steps suitable for E.coli detection were 0.0 V, -0.3 V and -0.4.

In the laboratory measurements it was noticed that the gold electrode had the best performance, enabling the equipment to differentiate clearly between samples.

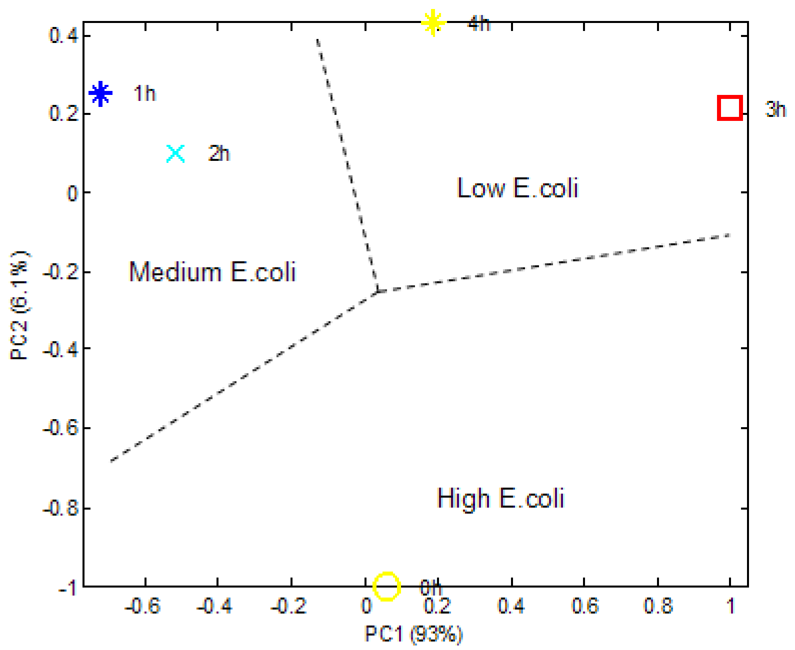


Fig. 10. PCA score plot for river water decontaminating in time for gold working electrode.

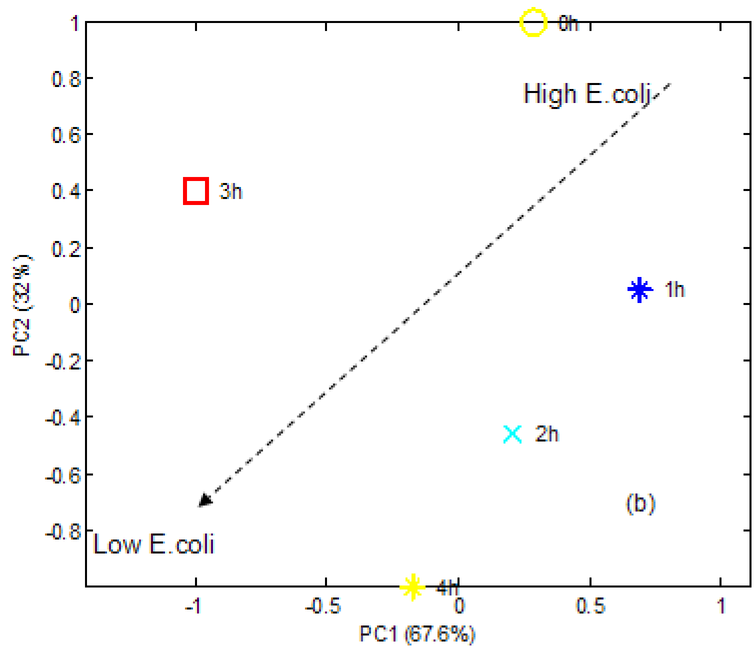


Fig. 11. PCA score plot for river water decontaminating in time for platinum working electrode.

In the in-situ measurements the equipment shows a good separation between the initial sample (high E.coli concentration) in respect to the other samples (medium and low E.coli concentration), which matches with the real value of CFU given by the standard MF test. The gold electrode enables good separation between high, medium and low E.coli concentration.

Only one working electrode was needed to differentiate between samples. Each one of 60 variables from the current pattern acts like a virtual sensor. This fact will simplify the maintenance of the working electrode which is one of the main concerns in systems that use array of several sensors.

The use of the two-electrode electrochemical cell and solid working electrodes increased the roughness of the analyzer for in-situ measurements.

The system (pump and potentiostat) uses a battery and the time needed to take the sample into the Teflon® liquid cell, obtain and register the current patron was less than 1 minute for both electrodes. The PCA analysis of the total data was less than 30 s. All the time needed was dramatically less than the 18 hours the standard MF method needs to obtain the E.coli concentration.

The main obstacle to build this equipment is the price of the potentiostat (US $ 5 000), to develop a cheap potentiostat based on a microcontroller should be the next step for this equipment.

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Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc.

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Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

- Physical, chemical and biosensors;
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- Theory, principles, effects, design, standardization and modeling;
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- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
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