

Microscale Analytical Potentiometry: Experimental Teaching with Locally Produced Low-Cost Instrumentation

Lilia Vierna¹, Arturo Garcia-Mendoza², Alejandro Baeza-Reyes²

(1. Biology Department, Autonomous National University of México;

2. Analytical Chemistry Department, Faculty of Chemistry, Autonomous National University of México, Mexico)

Abstract: MicroISE, microbiosensors and microreference electrodes built with low cost locally produced materials are presented, to perform experiments to determine several analytes in instrumental analysis teaching. Creativity in experimental learning emphasizing ecological and green aspects are achieved.

Keywords: low cost, microISE, microbiosensors, ionic liquids

1. Introduction

Microscale laboratory has been widely used in General Chemistry mainly in Synthetic Chemistry (inorganic and organic chemistry). Analytical Chemistry approaches just concern to titrimetric determinations with acid — base indicators using 5 mL pipets as burets to teach semi quantitative analysis aspects. Chemical Instrumentation has been developed mainly for basic or applied research so it is difficult to access to such devices in teaching laboratories. In our laboratory, we have developed low cost equipment with locally materials to perform micropotentiometric measurements to teach Instrumental Analytical Chemistry: pH microsensors based on electro generated conductive polymers or W^0 rods, $AgCl$ or Ag_2S microcrystal with Ag^0 transduction to measure chloride and sulfide anions and also microbiosensors based on fresh vegetable tissue to detect hydrogen peroxide, urea and ascorbic acid in several samples including foods, isotonic solutions and microbial systems.

2. Experimental Design.

2.1 Solid State Microsensors

The pH determination is achieved with a combined micropotentiometric system: A drawing carbon rod covered with polyaniline, PANI, obtained applying a direct potential, 9V, pulse according to Figure 1.

Microreference electrode is made by introducing a Cu^0 rod in a plastic tip that contains water or a $Cu(II)$ 10 mM solution. A piece of cotton is used as liquid junction separation. The PANI electrode can be substituted by a W^0 micro rod fixed in a plastic tip as well. Both pH solid-state sensor and microreference electrode are fixed in a 25 plastic vessel to performed pH measurements connected to a simple voltmeter as shown in Figure 2.

Alejandro Baeza-Reyes, Ph.D., Professor, Analytical Chemistry Department, Faculty of Chemistry, Autonomous National University of México; research areas: electro analytical chemistry. E-mail: baeza@unam.mx.

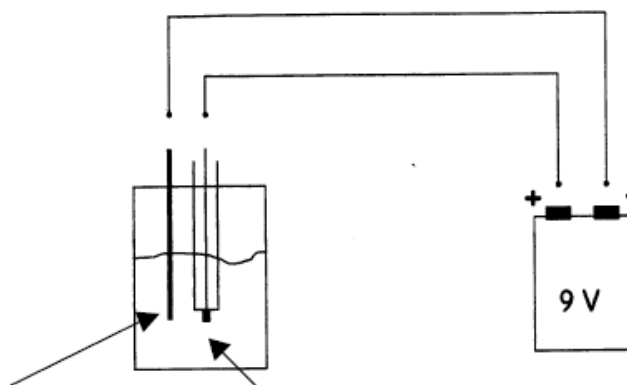


Figure1 Anodic Polyaniline Recovering of a Micro Carbon Rod in A 0.1 M Aniline Bisulphate Dissolved in A 0.5 M Sulfuric acid. A 30s 9 V Potential Pulse is Applied.

Silver — silver chloride microreference electrodes have been used successfully in potentiometric experiments as well. This kind of electrode is constructed by means of an Ag^0 wire with electrochemical covering of $AgCl$. This procedure is easily reproducible with a 9V battery using the Ag wire as anode and a carbon rod as cathode in a hydrochloric acid 0.1 M solution, by 10 seconds. A single plastic tip with KCl saturated solution can be used as first chamber, however a second chamber has shown better results whenever the double junction in the electrode restricts diffusion of analytes towards the reference electrode.

MicroISE based on $Ag^0 | AgCl_{(s)}$ to measure chloride ions or $Ag^0 | Ag_2S_{(s)}$ to measure HS^- , are prepared in a similar way by oxidizing a microsilver rod in HCl 0.1M for the former and Na_2S 0.1 M for the latter microsensor. In both cases the same microreference electrode can be used.

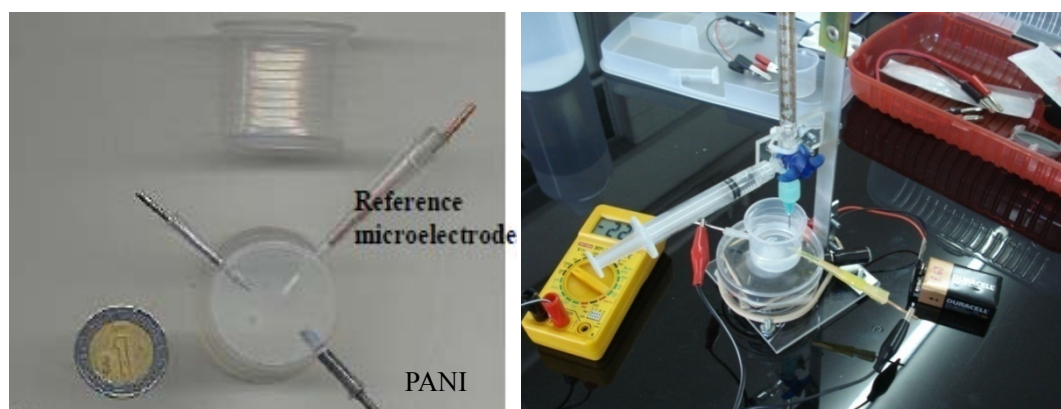


Figure 2 Typical Plastic Microcell Shown with Two Solid State Microsensors: W^0 and PANI as pH Sensors. Combined PANI-Microreference or W^0 -Microreference Electrodes Can be Used Alternatively Connected to a Multimeter to Determine pH.

2.2 Microbiosensors

A microchamber to put fresh tissues of vegetal containing a certain active enzyme is built by placing a C^0 or a W^0 rod transducer into a plastic tip cut properly to form a small chamber as shown in Figure 3.

A piece of fresh potato is used to profit the peroxidase activity to determine H_2O_2 in samples dissolved in a pH = 7 phosphate buffer solution, PBS. A paste formed with soybean flour obtained directly by grinding soybean grains in distilled water is used to determine urea since this tissue presents a high urease activity. A skin cucumber extract with PBS present ascorbic acid oxidase activity used to measure ascorbic acid content.

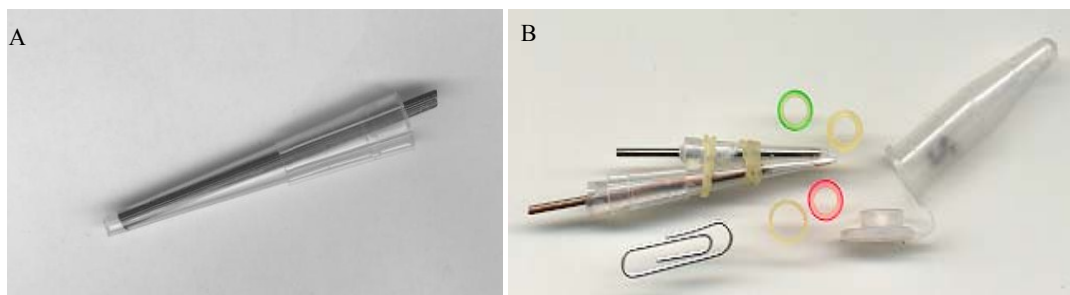


Figure 3 Microchamber (A) to Built Microbiosensor Based on Fresh Vegetable Tissues Combined with A Microreference Electrode (B).

3. Experimental Results

MicropH sensor based on PANI was calibrated with several pH buffer solutions in order to determined the Nikolsky potentiometric behaviors. The selectivity of the PANI sensor to H^+ in presence of Na^+ , as example, was determined by a linear analysis of the type:

$$10^{\left(\frac{\Delta E}{60mV}\right)} = f\left(\frac{[Na^+]}{[H^+]_{BS}}\right)$$

since the corresponding slope yields the selectivity coefficient k_{Na^+,H^+} directly. Results obtained are shown in Figures 4 and 5.

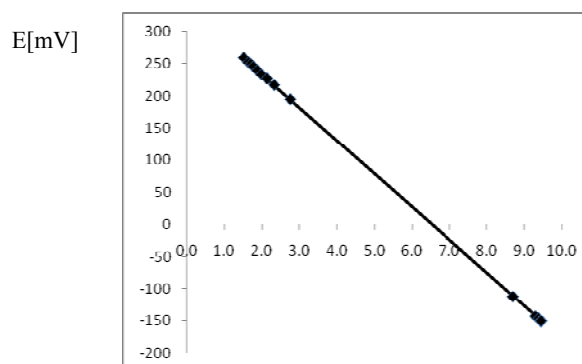


Figure 4 Typical Calibration Plot $E = f(pH)$ for PANI Solid State Microsensor Calibrated with Several Buffer Solutions, Linear Fitting Analysis Yields $E=336.7 mV-51.6pH$, $R^2 = 0.9998$.

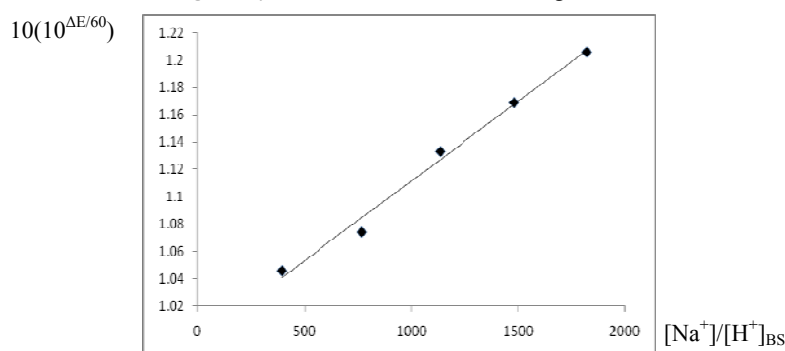


Figure 5 Plot $10^{\left(\frac{\Delta E}{60mV}\right)} = f\left(\frac{[Na^+]}{[H^+]_{BS}}\right)$, Where E_2 in Presence of $0.04 M < [Na^+] < 018M$, E_1 without Na^+ , in 5 mL of Biphtalate Buffer Solution pH = 4.0. Linear Fitting Analysis Yields $b = 0.9951 \approx 1$; $m = 0.0001$ and $r^2 = 0.9899$.

From the results presented above it is concluded that the proposed PANI solid state microsensor is suitable to determine pH in aqueous solutions.

Figure 6 shows a typical titration plot obtained with a W^0 microsolid state pH sensor.

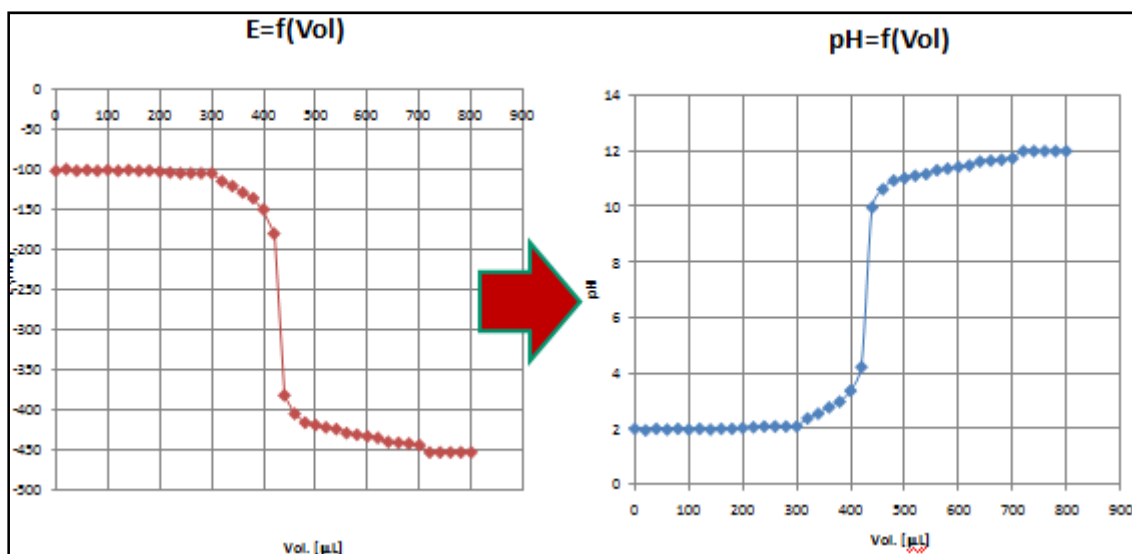


Figure 6 Typical Titration plot, $pH = f(v)$, of 0.5 mL HCl 0.1 M with NaOH 0.0998 M, monitored with a W^0 Microsolid State pH Sensor and a $Cu^0|H_2O||MicroreferenceElectrode$, A linear Fitting Analysis Yields $E = 84mV-28pH$, $r^2 = 0.9964$.

PANI micro pH sensor has been used successfully in non-aqueous solvents. Indeed in pure acetonitrile this sensor has shown a linear behavior, $E = 244.89-20.39pH$, $r^2 = 0.9923$, calibrated spectrophotometrically with bromochresol blue in this solvent (results not shown).

On the other hand, it is very well known Liquid Ionics are a special family of solvents with amazing properties; nevertheless the high cost of them has complicated and discouraged the searching for new physicochemical parameters. We have been able to evaluate the electrochemical behavior of ferrocene and p-benzoquinone in several ionic liquids media, in order to compare electrochemical reactivity in these media. A suitable microcell was designed for potentiometric, cyclic voltammetric, chronoamperometric and chronopotentiometric experiments with small solvent volumes, $V < 500 \mu L$. Also, a set of microelectrodes was designed for this task, included a micro-reference electrode based in each ionic liquid. As a matter of fact, p-benzoquinone reduction was studied in two ionic liquids: tetrafluoroborate of 1-butyl-3-methylpyridinium, [bmpy][BF₄] and tetrafluoroborate of 1-ethyl-3-methylimidazolium, [emim][BF₄]. In both media, two experimental conditions were used: pure ionic liquids and buffered acidity levels. A buffer of methanesulfonic acid and sodium methanesulfonate prepared in these media was used. A W^0 microelectrode was designed and used as an acidity levels sensor together with a $Ag^0/AgCl_{(s)}$ micro reference made in those media. A Nernstian potential — concentration linear behavior was found using perchloric acid as leveling agent acidity levels, as shown in Figure 7.

For potentiometric assays, tungsten sensor presented a differential response to different levels of acidity in [bmpy][BF₄]. Its performance was tested in various evaluations volumetric *Lutidine* with $HClO_4$, which was obtained in the typical evolution potential during the analytical operation as can be seen in Figure 8. This methodology has allowed us to reduce costs and waste materials.

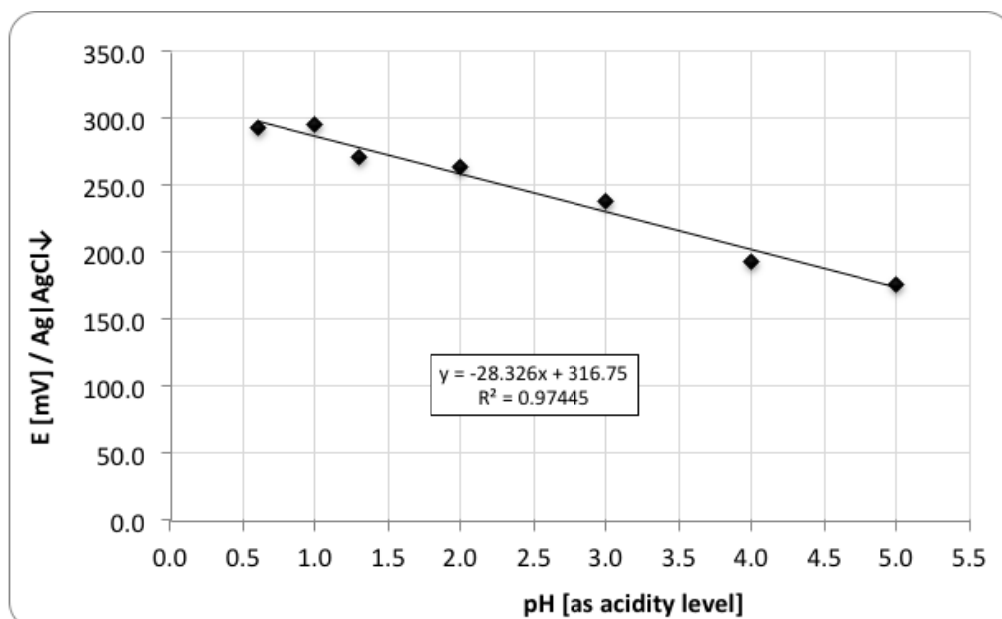


Figure 7 Typical Potentiometric Calibrationplot Obtained for a W^{θ} Micro Sensor for Acidity Levels in [bmpy][BF₄], Experiments Were Performed using A Multimeter to Determine the Potential in Each Solution.

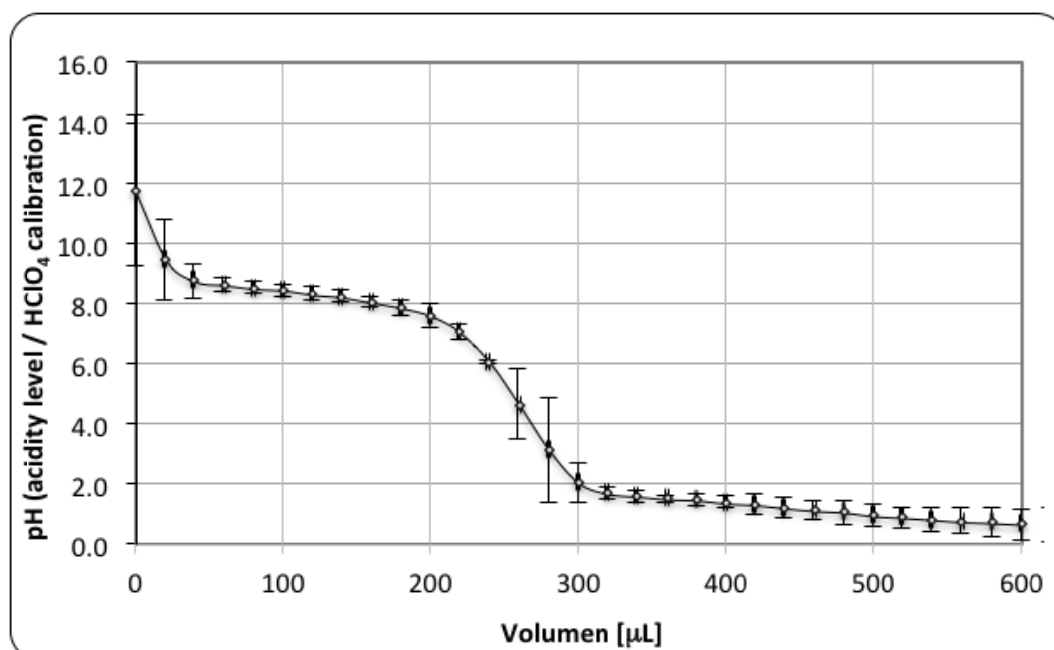


Figure 8 Titration Plot, $pH = f(v)$, of 0.5 mL Lut 0.1 M with $HClO_4$ 0.1 M, Monitored with a W^{θ} Microsolid State pH Sensor and a $Ag^{\theta}|AgCl(s)$ Microreference Electrode in [bmpy][BF₄].

The chloride microISE can be used to monitoring titration plots of $AgNO_3$ solutions with NaCl standard (Mohr Method). Figure 9 shows a typical calibration plot to determine chloride in 1 mL standard NaCl solutions.

It has been possible to work with halides mixtures with these microelectrodes. Several experiments have shown that it is feasible to find their respective concentrations without prior sample treatment. Figure 10 shows the potentiometric titrations of a mixture of halides with no more than 1 mL of silver nitrate 0.1 M. *No salt bridge is needed.*

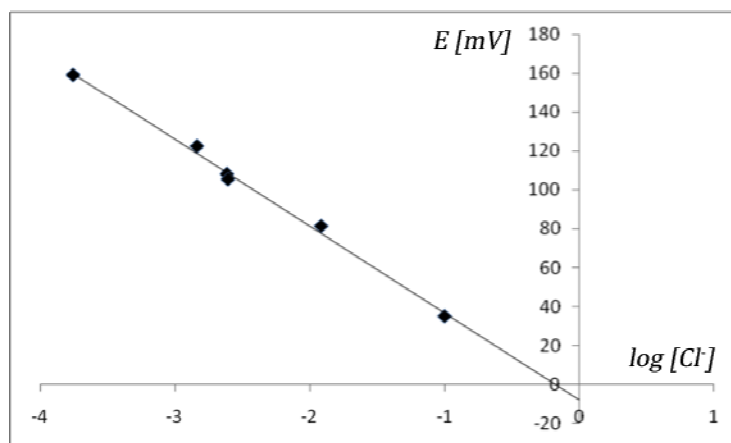


Figure 9 Calibration Plot $E = f(\log[Cl^-])$ Obtained with Several 1 mL NaCl Standard Solutions. MicroISE: $Ag|AgCl(s)$, Microreference of $Cu^0|H_2O$. A linear Fitting Analysis Yields: $E = -7.9mv - 44.65\log[Cl^-]$, $r^2 = 0.9950$.

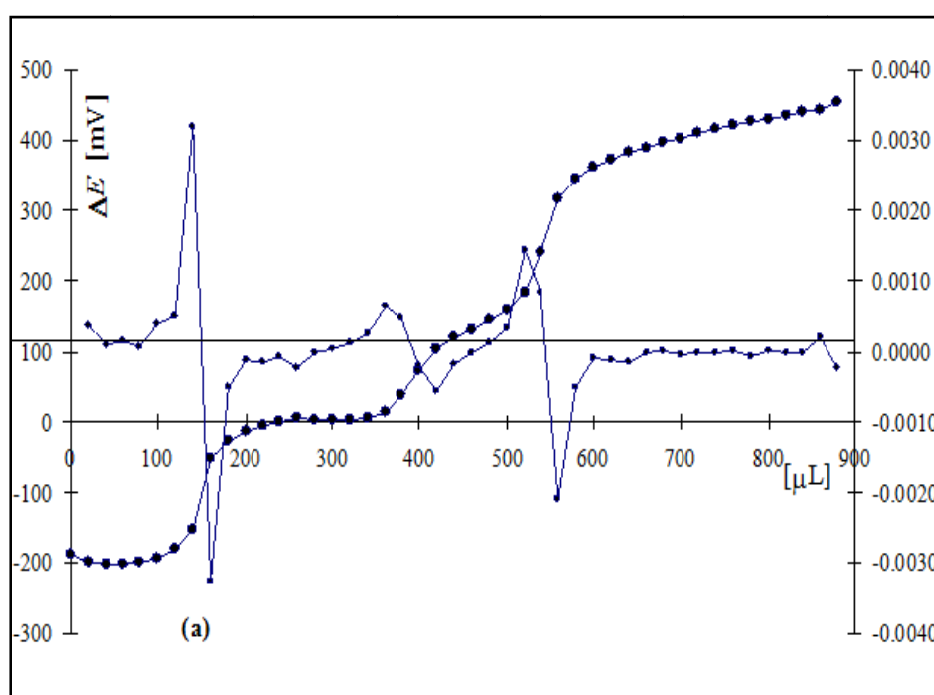


Figure 10 Titration Plot of 500 μL of a Mixture of NaCl, KCl and KI Aprox. 0.1 M with $AgNO_3$ 0.1 M Using MicroISE: $Ag|AgCl(s)$, Microreference of $Cu^0|H_2O$ Potentiometric System, $\Delta(\Delta E/\Delta v) = f(\Delta v_{av})$. Plot is Also Shown.

The above calibration plots has been successfully used to control chloride content in commercial Isotonic Saline Solutions and chloride content in commercial french-fries potatoes samples.

Figure 11 shows a typical calibration plot to determine sulfides, HS^- , from asulpho-bacterial culture media. Determination is performed in a borate buffer solution pH = 9.2 by the standard additions method and Gran Plot data processing method:

$$\left(10^{\left(\frac{\Delta E}{-30mV}\right)}\right) (V_0 + v_{agr}) = 10^{\left(\frac{K}{-30mV}\right)} C_{std}(v_{agr}) + 10^{\left(\frac{K}{-30mV}\right)} (C_x V_0)$$

where $V_0 = 200 \mu L$ sample; $v_{agr} = 0, 10, 20, 30$ and $40 \mu L$ of a standard solution of $NaHS$ 0.1 mol/L in buffer solution. Sulphide content in the analyzed sample is obtained according to: $C_x = \left(\frac{-C_{std}(v_{abs})}{V_0}\right)$

where v_{absc} is the extrapolated volume value for $\left(10^{\left(\frac{\Delta E}{-30mV}\right)}\right)(V_0 + v_{agr}) = 0$. From the Gran Plot obtained, $Y = 5 \times 10^{-6}X + 7 \times 10^{-8} = 0$, $X = v_{absc} = 0.014 \text{ mL}$, then:

$$C_x = \left(\frac{-0.1M(0.014 \text{ mL})}{0.2 \text{ mL}}\right) = 7.0 \times 10^{-3}M = 7.0 \text{ mM}$$

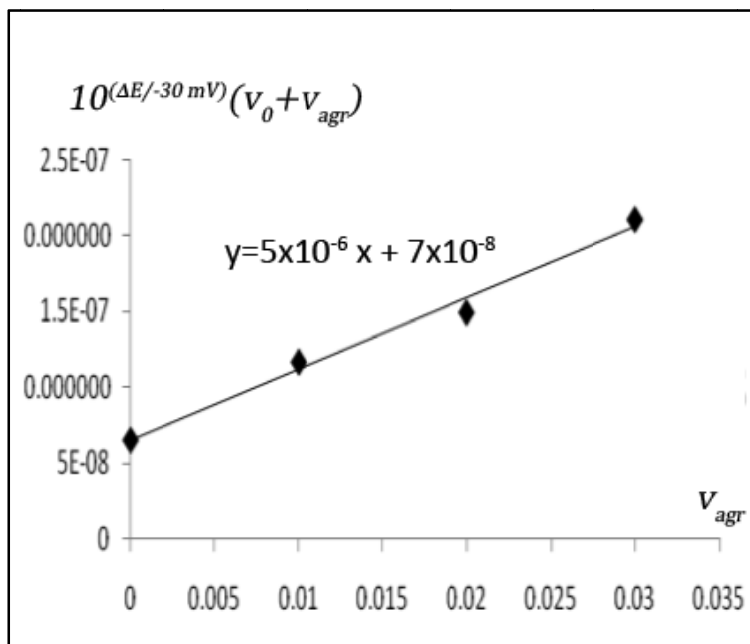


Figure 11 Gran Plot for Micropotentiometric Determination of Sulphides with $Ag^0|Ag_2S(s)$ Microsensor in Asulphurbacterial Culture Media

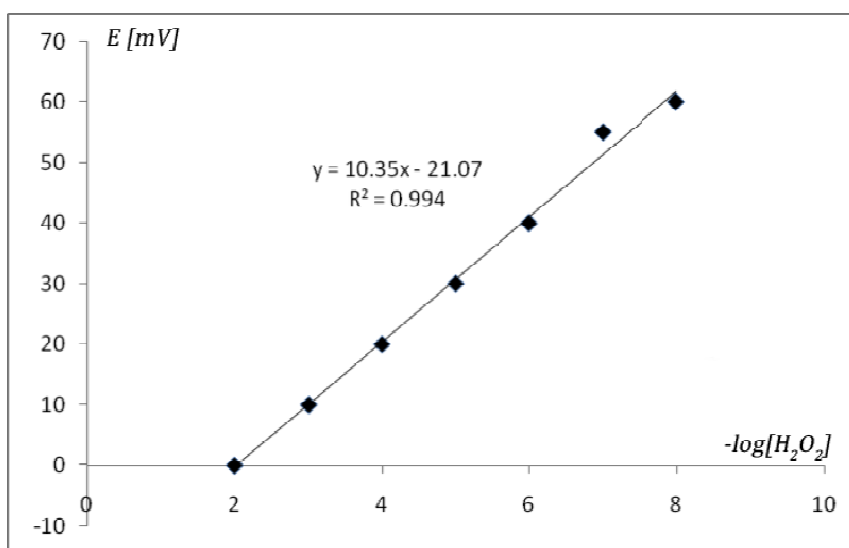


Figure 12 Calibration Plot $\Delta E = f(-\log[H_2O_2])$ Performed with Abiosensor Based on Fresh Potato Tissue Combined with A Microreference Electrode $Cu^0|H_2O||$. Linear Fitting Fata Is Shown As Well

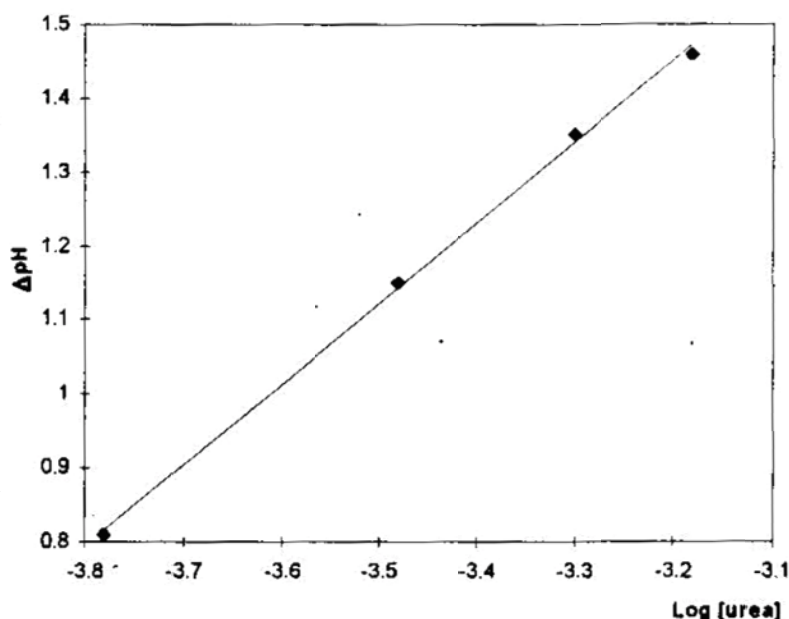


Figure 13 Shows a Typical Calibration Plot Obtained with A Fresh Soybean Flour Paste to Determine Urea in 1 mL, pH = 5 Buffered Standard Solutions, An Inner W^0 pH Microsensor Was Used As Signal Transductor
 $\Delta pH = 4.95mV + 1.09 \log [urea]$, $r^2 = 0.9994$.

The latter biosensors have been employed successfully in determining the corresponding analytes in food samples.

Suitable calibration plots has been obtained for microbiosensors based on fresh cucumber extracts in PBS buffer solutions as well.

4. Conclusions

From the results shown above it is clear that the microsensors proposed responds properly to several analytes of interest. In all cases the use of reactive are minimized and the generated residues as well. The use of low cost materials minimizes operation and reparation costs. The oneself-designing promotes creativity in analytical instrumentation as well. Besides these sensors can be used in several types of samples even in complex media.

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