STUDY AND CONSTRUCTION OF AN AMPEROMETRIC POTENTIOSTAT SUITABLE FOR USE IN ENVIRONMENTAL MONITORING

Laura Mihaela LELUȚIU, Marius Dan BENȚA

Transilvania University of Brasov, Romania, Dep. of Electrical and Engineering
(lelutiulaura@gmail.com, marius.bentea@unitbv.ro)

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Abstract: *The paper presents some new requirements and trends concerning applications of amperometric biosensors and some practical problems for the environmental monitoring. The goal of this work was to build and study an amperometric potentiostat suitable for use in environmental monitoring. The amperometric potentiostat is an interface circuit which can adapt the biosensor for detection of pesticides in actual water samples. A rapid, simple, and sensitive amperometric potentiostat for direct total micro analysis measurement was developed. The large purpose of our work is creation of fast chemical test-systems with quite enough low detection limits and enough high selectivity. This paper presents some experimental studies of this apparatus.*

Keywords: *biosensors, amperometric, potentiostat, environmental, monitoring*

1. INTRODUCTION

In the last years the need for analytical devices to be used for environmental, industrial or medical controls has been growing very quickly. Today, the capability of sensors is a decisive factor in determining whether a system is of practical use or not. The development of new sensors for monitoring the complex matrix of physical, chemical, and biological entities is critical to our ability to deal with evolving environmental problems. Recently, pollution of environmental water and soil by pesticides has received much attention due to the use of large amounts of pesticides in agriculture and related activities. Small concentrations of such eco toxicants in soil and food products are the reason for many diseases in the population. Because similar compounds were produced as possible nerve poisons, a further area of application is in the military [1]. The application of enzymes as catalysts in organic solvents has led to the important development of organic-phase biosensors. However, the use of pure organic solvents leads to many problems, such as the incompatibility with enzyme, substrates and supports. The activity of enzymes is strongly dependent on their hydration layer, which is essential for their conformational flexibility. Therefore, an enzyme activity is influenced by the presence of organic solvents that interact with the aqueous layer around the enzyme molecule. Organic solvents can induce extensive changes in enzyme activity and specificity.

This is because the enzyme structure and activity depend on several non-covalent interactions, such as hydrogen bonding, ionic, hydrophobic, and Van der Waals interactions [2].

Therefore, important aspects of biosensors are the immobilization procedure for the enzyme on the electrode surface, and the selection of the solvent and electron communication between the electrode and the enzyme. Environmental monitoring involves three basic steps: collection of a representative environmental sample; extraction, separation, other sample pre-treatment; and finally, chemical analysis to determine the identity and quantity of material present in the sample.

2. CONSIDERATIONS ABOUT APPARATUS

Environmental monitoring involves three basic steps: collection of a representative environmental sample; extraction, separation, other sample pre-treatment; and finally, chemical analysis to determine the identity and quantity of material present in the sample. For an amperometric measurement a defined potential is applied at a working electrode with respect to a reference electrode while the circuit is closed by means of a counter electrode. Most electrochemical work with an electrochemical cell is achieved using what is called a potentiostat. Potentiostats are amplifiers used to control a voltage between two electrodes, a working electrode and a reference electrode, to a constant value. Both electrodes are contained in an electrochemical cell. Some designs have been proposed for VLSI potentiostats. Each of these designs amplifies smaller currents to the μA range and then measures the input current by calibrating their design at higher current range. By converting input current directly into time we eliminate amplifying circuitry, avoid matching problems and save on area and power consumption [3].

We have designed a potentiostat circuit that accepts an electrical signal, proportional to current flowing through the electrolyte (in the electrochemical cell) and measure the time it takes to charge or discharge a capacitor. For construction of suitable potentiostat we must study a simplified one. We can be seen below a simplified schematic of a potentiostat. A potentiostat is an electronic device that controls the voltage difference between a working electrode and a reference electrode. The potentiostat implements this control by injecting current into the cell through an auxiliary electrode. In almost all applications, the potentiostat measures the current flow between the working and auxiliary electrodes. The controlled variable in a potentiostat is the cell potential and the measured variable is the cell current. A potentiostat typically functions with an electrochemical cell containing three electrodes and that is true for both field probes and lab cells:

- Working Electrode: Electrochemical reactions being studied occur at the working electrode. This is analogous to testing using weight loss coupons. The working electrode can be bare metal or coated.
- Reference Electrode: A reference electrode is used in measuring the working electrode potential. A reference electrode should have a constant electrochemical potential as long as no current flows through it.
- Auxiliary Electrode: The Auxiliary electrode is a conductor that completes the cell circuit. The auxiliary (counter) electrode in lab cells is generally an inert conductor like platinum or graphite. In field probes it's generally another piece of the working electrode material [4].

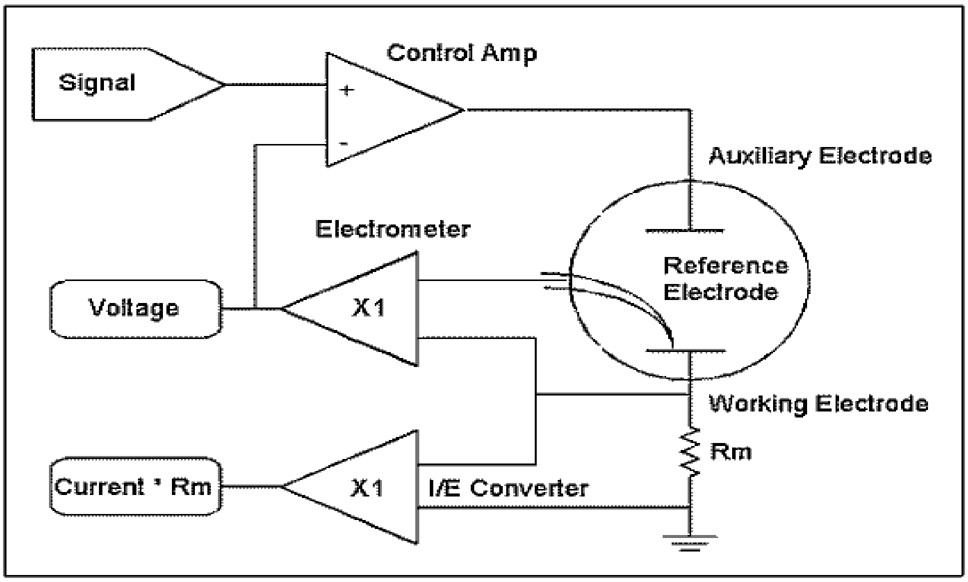

FIG. 1. A schematic diagram of a Potentiostat

Additional components are:

- Electrometer: The electrometer circuit measures the voltage difference between the reference and working electrodes. Its output has two major functions: it is the feedback signal in the potentiostat circuit and it is the signal that is measured whenever the cell voltage is needed. An ideal electrometer has zero input current and infinite input impedance.
- I/E Converter: The Current to Voltage (I/E) converter in the simplified schematic measures the cell current. It forces the cell current to flow through a current measurement resistor. The voltage drop across that resistor is a measure of the cell current.
- Control Amplifier: The control amplifier is a servo amplifier. It compares the measured cell voltage with the desired voltage and drives current into the cell to force the voltages to be the same. Under normal conditions, the cell voltage is controlled to be identical to the signal source voltage.
- The Signal: The signal circuit is a computer controlled voltage source. It is generally the output of a Digital to Analog (D/A) converter that converts computer generated numbers into voltages.
- Galvanostats and Zero Resistance Ammeters (ZRAs): Most laboratory grade potentiostats can also be operated as galvanostats or ZRAs(Zero Resistance Ammeter). Galvanostat is an electronic instrument that controls the current through an electrochemical cell at a preset value, as long as the needed cell voltage and current do not exceed the compliance limits of the galvanostat. Also it is called "amperostat." [5].

An interesting application is when the coupling current between two nominally identical electrodes is measured.

If both electrodes were identical then very little coupling current would flow. In real situations these electrodes will be slightly different, one being more anodic or cathodic than the other and a small coupling current will exist.

In an electrochemical cell, any change in the potential of the cathodic electrode, results in a flow of current in the electrolyte so the potential of the electrode is maintained. It is a fact that the biosensors require low-power electronics for providing the interface between biological electrode and signal processing devices (Fig. 2). The amperometric potentiostat is suitable for the above presented direct interfacing [6].

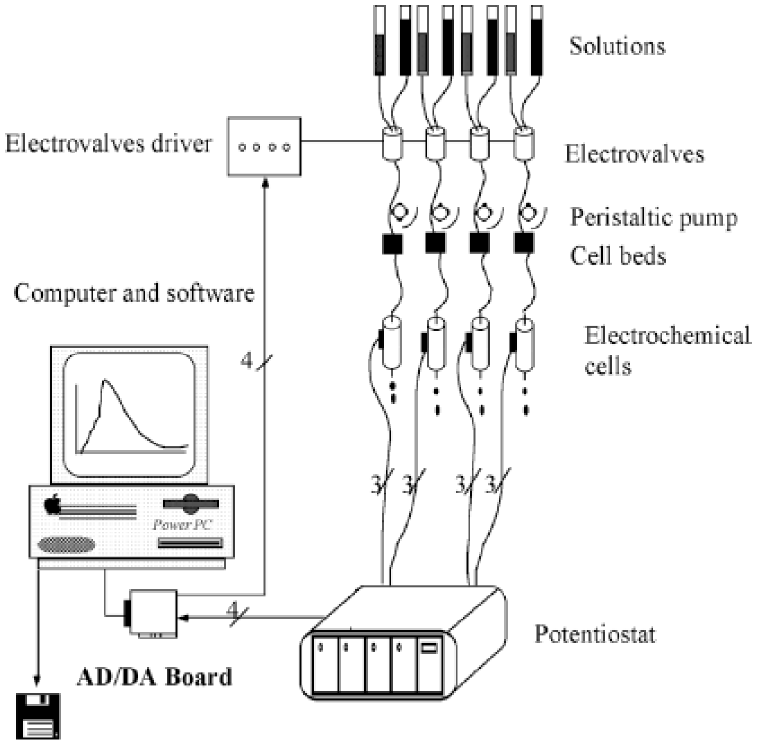

FIG. 2. The interface between biological electrode and signal processing devices

Basal incubating solutions or chemical stimuli are selected by the electro-valves. These valves can be manually operated or by a TTL signal generated by a computer digital output. A four-channel peristaltic pump is continuously perfusing the cell chambers or adrenal glands.

The emanating fluid is passed through the electrochemical cells for catecholamine detection. The potentiostats send the analogic signal (± 12 V) to a computer through a 12-bit AD/DA board.

3. CONSTRUCTION OF THE AMPEROMETRIC POTENTIOSTAT

Our presented amperometric potentiostat exhibits good linearity in the current range up to 200 nA when calibrated with highly stable thick-film resistors, with a detection limit of approximately 3 nA. In the embodiment tested, a sensitivity of just over 3 Hz/nA was achieved. The potentiostat was able to control the working electrode potential with respect to the counter electrode with a regulation of better than ± 2% under various complex load impedances. The circuit consumes 500 µW of power, achieved through the careful use of low-power CMOS amplifiers in the circuit design, and minimal quiescent current drain, and is therefore suitable for operation from standard 3 V Lithium coin cells. In fact, we developed a current-to frequency converter circuit. This apparatus has been designed by us for implementing the function of an amperometric potentiostat with a minimum number of components. The specific unique qualities of this current-to-frequency converter that make it particularly suited to this type of application are high input impedance, necessary to obtain accurate amperometric measurements, and the direct production of a pulsed digital output, compatible with low-voltage CMOS logic gates, using only a few components [7].

4. EXPERIMENTAL DETERMINATIONS

The experimental measurements were accomplished using physical methods of conductivity and potentiometry. For low current densities, the error arising from the dependence of the potential from the cell current may be neglected and a two-electrode set-up is sufficient for amperometric investigations. The constructed converter exhibits good linearity in the nanoampere current range that is relevant for many chemical and biosensor electrodes.

This particular design has a very low-power consumption, and may easily be adapted to meet the requirements of different electrode-based amperometric sensors. Our aim was to obtain the calibration curve for the potentioststat. It was measured the dependency between the current and frequency and the results obtained are shown in Table 1.

f [Hz]	15	20	40	60	90	120	150	200
I [nA]	50	65	120	180	270	340	420	620

We processed the experimental data by making use of a tblcurve and orrigin soft. in figures 3, 4 and 5 there is represented the dependency between the current-to-frequency calibrations curves obtained for the potentiostat. different currents were sequentially set with high-ohmic thick-film resistors connected across the working and counter electrode terminals of the potentiostat. the current value was calculated from the radio of the measured electrode potentional difference to the measured value of the applied resistance.

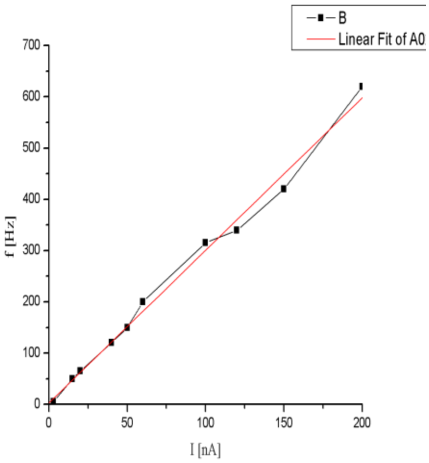

FIG. 3. The current-to-frequency calibration curve of the potentiostat. obtained by making use of a ORRIGIN SOFT-(a) Linear current range

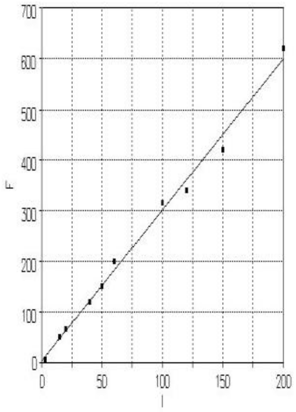

FIG. 4. The current-to-frequency calibration curve of the potentiostat obtained by making use of a TBLCURVE SOFT, with resistive loading to the electrode terminals.

By processing the experimental data by making use of a TBLCURVE and ORRIGIN SOFT there was established the equation of the curve of dependency of the current-to-frequency. The Figure 4 show that the current-to-frequency transfer function is linear between approximately 4 and 200 nA, and extends up to currents of 700 nA. In the linear region, after processing the experimental data, the output frequency there was obtained by the the following equation:

$$f_{out} = 2.8472 + 2.9769\ I_{cell} \qquad (1)$$

where I_{cell} is the electrode current in nA. We find that the zero offset of the converter is 2.8472 nA, and the sensitivity is 2.9769 Hz/nA.

5. CONCLUSIONS

The above constructed potentiostat exhibits good linearity in the nanoampere current range that is relevant for many chemical and biosensor electrodes. This apparatus has been designed by us for implementing the function of an amperometric potentiostat with a minimum number of components. This particular design has a very low-power consumption, and may easily be adapted to meet the requirements of different electrode-based amperometric sensors. The requirements for environmental monitoring are not easily satisfied, but step by step the aim is to establish more reliable and rational sensors. Important challenges remain in the area of environmental sensing. The scope of these challenges ranges from monitoring global atmospheric phenomena to detecting alternations in the structure of DNA. To be effective, the measurement, electronics and control components, and sub-systems, in particular sensors and sensors systems have to be developed in parallel as part of computer-controlled manufacturing systems. Adequate solutions have been found for most practical measurement problems, but there are applications where the available solutions are not fully satisfactory. Still, a few general environmental sensing trends can be identified. In assessing the risks to human health from chemical hazards, increasing emphasis is being placed on measuring individual exposures, with personal monitors or through analysis of biological fluids. New instruments and methods being developed show promise for continuous, in situ monitoring of toxic compounds. The environmental analytical community continues to search for portable analytical techniques that can give reliable, on-site results for a variety of matrices and a host of analyzes. New technology, new principles for reliable sensors are expected to be developed. To meet both present and anticipated requirements, new and improved methods are needed. It is now recognized that these methods must be based on the powerful techniques employing computer-assisted information systems and production methods.

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