

# Electrochemical Sensor with Polymer Thick Film Printed Electrodes

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**Abstract:** *The assurance of a high level of safety regarding the food market has been one of the main concern issues of the European Commission. In this sense the affirmed documents name the pesticides as a major hazard factor. For these residuals the maximum quantity is strictly limited, especially for children. A sensor with detection capabilities in this sense will be presented. The actual sensor is a three electrodes system realized in thick film technology using specific silver and carbon conductive depositions. The measurement principle is based on chronoamperometry technique which consist in applying a constant potential and monitoring the current evolution. Using a specific enzyme, the sensor can be used for detection of residuals contained in aliments. The presented results show the first step in this process, the detection of thiocholine for which the sensors have shown a good detection capability.*

## 1. INTRODUCTION

In the last two decades, the research in the field of biosensors has shown an important increase as the need for non-expensive analytical instrumentation, rapid and easy to use and capable to deliver in short time valuable qualitative and quantitative information about the composition of a specimen and all these with a very simple probe preparation procedure [1-4]. Biosensors are analytical instruments which use the sensitivity and selectivity of an bio-receiver attached on a surface of an physical transducer, in our case an electrochemical sensor. Following the bio detection process between the bio-receiver and the specific analyte it results a biochemical and/or physical chemical signal /property which can be translated by the transducer in a measurable quantity [5].

The presence of residuals in many food products is an issue of maximum concern for the European Commission. In this sense two documents were adopted: The green book (1997) and The White Paper on Food Safety (2000). A maximum importance is given to the pesticides for which the maximum quantity is strictly limited, especially for children. A

sensor with detection capabilities in this sense will be a “must have” tool in order to analyze the aliments conformity. In present there are in use some classes of sensor with detection capability of food residuals, most of them are expensive and cumbersome, being possible to be used only in laboratories. The sensor that was developed is realized in thick film technology based on specific silver and carbon conductive depositions.

## 2. PRINCIPLE OF OPERATION

### 2.1. Electrochemical sensor basics

Chronoamperometry is a powerful electro-analytical technique that offers a high sensibility selectivity and precision using a relatively non-expensive measurement apparatus. It has applicability in various domains among them we mention the determination of species with biological meanings as (medicaments, vitamins, metallic ions, aminoacids, peptids, proteins, nucleic acids, steroids, enzymes, co-enzymes etc.). Chronoamperometry belongs to a class of electro-analytical techniques where the current intensity at the surface of a working electrode in the

electrolysis process is measured as a function of the potential applied to it.

The electric potential applied to the working electrode acts as the driving force for an electrochemical reaction, the potential itself being the controlled parameter, that determines the electrolysis of chemical species (reduction or oxidizing) at the surface of the working electrode.

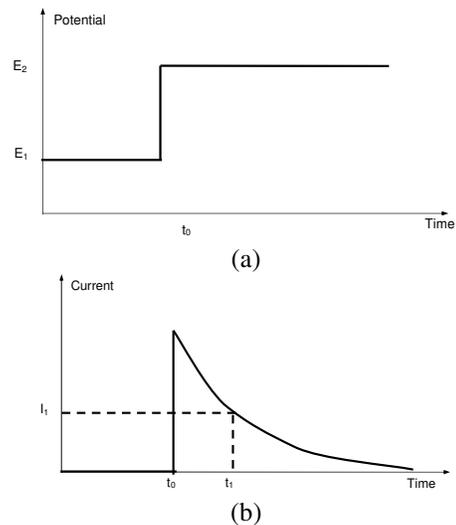
The current intensity at one electrode is given by the Cottrell equation, that in case of a planar electrode and a linear diffusion has the form given in 1:

$$i = \frac{nFAD^{1/2}C^0}{(\pi \cdot t)^{1/2}} = K \cdot t^{-1/2} \quad (1)$$

with  $C^0$  concentration of electro-active species in solution,  $D$  diffusion constant of the respective species,  $t$  time,  $F$  Faraday's constant  $C=96485$  C/mol,  $A$  the surface area,  $n$  number of electrons exchanged between the ion or molecule and the electrode

According to Cottrell equation the current intensity goes to zero when the time tends to infinite. This is due to the progressive increase of concentration near the electrode surface.

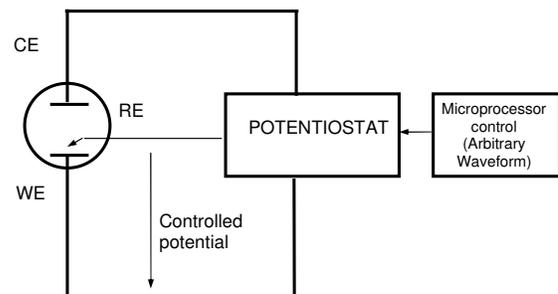
In the measurement process, chronoamperometry method implies the setting of working electrode potential starting from a value at which the Faraday process doesn't exist to a value for which the concentration of electro-active species became effectively zero. The presented sensor uses a stationary working electrode and an un-stirred solution because the diffusion process must be the governing factor for the reactant and electrode reaction products transport. During the measurement the electrode surface must be unchanged. During the measurement the dependence of the electrolysis current is monitored. The graph intensity-time reflects the change in concentration gradient near electrode surface. This implies a gradual expansion of the diffusion layer, associated with the reactant exhaustion and hence the decrease of concentration gradient during time. So, by measuring the current evolution it is possible to have information about the concentration of the electro-active species. Typical graphs involved in chronoamperometry are presented in figure 1 a) and b).



**Fig. 1.** Principle of chronoamperometry a) Step waveform b) current response.

In our experiments the current  $I_1$  was read after a time  $t_1 - t_0$  of 100 seconds.

The complete sensor includes an electro-chemical three electrode system and as measuring equipment a potentiostat. In case of a three electrode system, the working electrode –(WE) is the one where the chemical reaction takes place. The electrical signal is measured against the counter-electrode (CE) or auxiliary electrode –(AE) which is not necessary to be realized from catalytic material, and the third electrode is the reference electrode –RE, see figure 2. This is used to measure and correct the electrochemical potentials generated between electrodes and electrolyte. This third electrode enhances the function by compensating the error caused by the working electrode polarization.

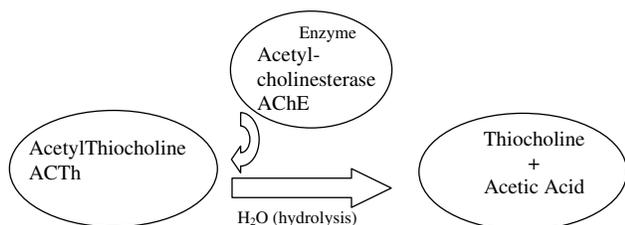


**Fig. 2.** Three electrode electrochemical sensor and measuring instrumentation (potentiostat).

Another technique that is widely used is the cyclic voltammetry. In this case the potential is varied in a specific interval following a determined cycle with a determined rise speed (scan rate -SR). In this time, the current is monitored, the results being graphically displayed in form of a cyclic voltammogram, see fig. 7.

The presented sensor is based on three electrode system and the reference electrode is Ag/AgCl, KCl. For our sensor a so called buffer solution is employed. This is a solution with a controlled neutral pH that gives no response (no peak) on the voltammogram and also generates the required quantity of KCl necessary for the reference electrode functioning.

The chemical species involved in the process are presented in figure 3.



**Fig. 3.** Reaction that takes place during sensor operation.

The enzyme Acetylcholinesterase (AChE) acts as a catalyst for this hydrolysis reaction of Acetylthiocholine (ACTh), during which thiocholine and acetic acid are obtained. From this both products only thiocholine can be electrochemically oxidized. So, during the electrochemical process the oxidation reaction which transforms thiocholine in ditio-bis-choline will be detected.

In order to prepare the experiment three major steps are necessary:

1. Cyclic voltammetry with a buffer solution
2. Cyclic voltammetry with thiocholine presence
3. Chronoamperometry with Acetylthiocholine and Acetylcholinesterase

Steps 1 and 2 are preparatory steps for the real detection in step 3. The voltammogram of the buffer solution and no other chemical reactants is used as a check measurement, where no peak must be detected.

In the second measurement the oxidation of the thiocholine produce the peak in the graph in fig. 7. The peak corresponds to an oxidation reaction and what is important is the value of the corresponding potential. At any value above this potential the reaction can take place. In applications where we can have multiple chemical species, we are interested in a low value of this potential in order to reduce the possible interferences (oxidation of other chemical species). At higher potential values it is possible that the oxidation of other reactant arrives.

Step 3 involves the applying of a potential at which the oxidation reaction takes place and to record the obtained current. The current gives practically the detection response, the slope of the current after a fixed time interval (100 s) being proportional with the concentration of ACTh.

### 3. PRACTICAL REALIZATION USING POLYMER THICK FILM DEPOSITIONS

Electrochemical sensors and biosensors found recently a lot of applications outside the laboratories. This was possible mainly by using new materials and new electrodes structures. One of the most attractive methods in realization of such sensors is the silk screen printing technology. This technology permits the realization of low cost sensors with various configuration and layouts. An important aspect is the use for these sensors of carbon electrodes, resulting disposable analysis cells, where the low cost requirement is mandatory. The carbon electrodes also provide a favorable low potential for the oxidation reaction. Supplemental, single walls carbon nanotubes can be used to modify the carbon electrode. The electrode system was Ag/AgCl. For the actual sensor the layout is presented in figure 4.

In order to realize the screen printing process of the structure, at least three printing layers were necessary.

- 1) silver deposition for reference electrode
- 2) carbon deposition for working electrode and counter-electrode
- 3) insulating protective deposition

The layouts of the deposition can be seen in figure 5. For the deposition the following pastes from Acheson were used:

a) silver based PTF ink Electrodag 725 A for reference electrode, b) carbon-based polymer thick film ink Electrodag PF 407 A for working electrode and counter-electrode, c) flexible dielectric polymer thick film ink Electrodag PF465 for the insulator.

In figure 6 the complete structure of one sensor and the panelized board are presented.



Fig. 4. Drawing of the sensor electrodes.

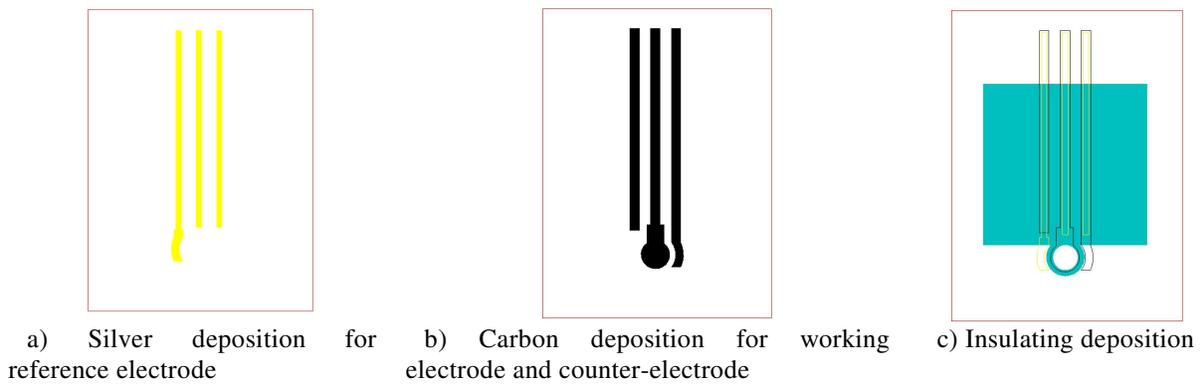
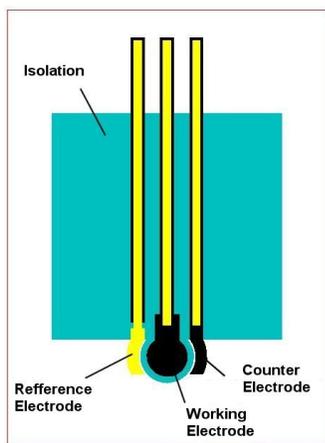
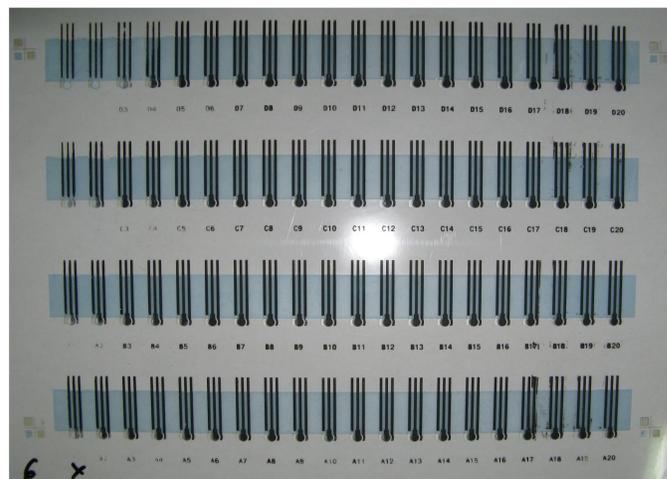


Fig. 5. The three deposition layers.



(a)



(b)

Fig. 6. Details of sensor layout (a) Layout of the sensor with the tree superposed layers, b) panelized project 20x4.

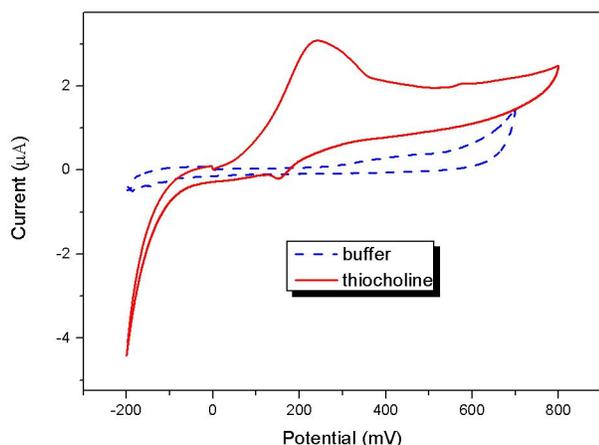
The printing was done on a DEK 248 screen printing machine and a 3mm polyester (mylar) substrate was used. Amperometric measurements and cyclic voltammetry studies were carried out using a Autolab PGSTAT 12 computer controlled potentiostat (Eco Chemie, Utrecht, Netherlands).

#### 4. RESULTS

Following the measuring principle presented above, the sensor configuration was used in the laboratory for thiocholine detection.

Cyclic voltammetry and amperometric measurements were performed for characterization of the sensor.

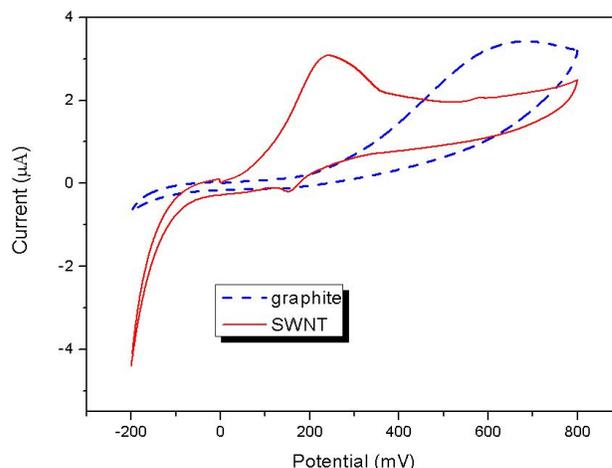
Single-walled carbon nanotubes (SWNTs) present interesting electrochemical properties, which allow detection of electrochemically active compounds at low applied potential. The graph in figure 7 shows and demonstrates the capacity of the SWNTs to promote de electrochemical oxidation of thiocholine.



**Fig. 7.** Cyclic voltammograms for a SWNT modified SPE (SR = 50 mV/s).

In an experiment done for comparison purposes, no peak was recorded in phosphate buffer 0,1 M, pH=7 but in the presence of thiocholine 1 mM an oxidation peak was observed at a potential of about 220 mV. Generally, the electrochemical oxidation of thiocholine is irreversible, but using SWNT electrode a reduction peak appears at 180 mV. Anyway the process is not reversible because the peaks height is very different.

In figure 8 a comparative study between a graphite based electrode and a SWNT modified electrode is presented. Oxidation of thiocholine could be achieved at approx. 650 mV for graphite working electrode. Presence of SWNT reduces the oxidation potential with more than 400 mV. A comparison in term of sensitivity was also realized (table 1).



**Fig. 8.** Thiocholine detection at the surface of a graphite and SWNT modified working electrode (SR = 50 mV/s, phosphate buffer 0,1 M, pH=7).

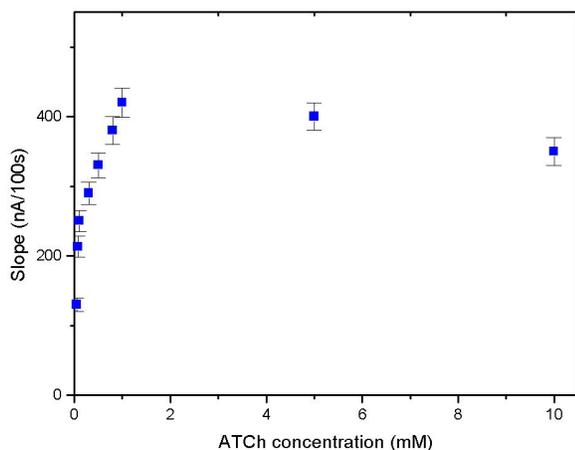
Experimental data demonstrates that the peak current for SWNT based electrode is approx. 10 times higher than the peak current for unmodified electrode.

Working electrode	$E_p$ (mV)	$I_p$ ( $\mu$ A)
graphite	657 mV	2.2
SWCNT	234 mV	0.18

**Tab.1.** Cyclic voltammetry parameters for graphite and SWNT modified electrodes.

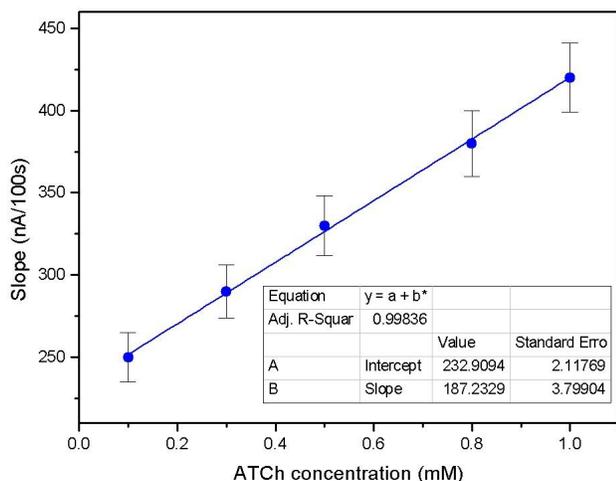
The sensor with SWNT modified electrode was tested for thiocholine monitoring during the enzymatic hydrolysis of ATCh in the presence of 1 UI of AChE. ATCh concentration was varied between 0.05 and 10 mM. Amperometric measurements were performed at an applied potential of 300 mV. Kinetic calibration curve was realized by representing the analytical signal at 100 s after enzyme injection, as in fig. 1b. Each time the measurement was started with

new enzyme and new reactants concentrations. The results are presented in figure 9.



**Fig. 9.** Calibration curve for ATCh.

It can be seen that with increasing ATCh concentration the “speed” of reaction increases, i.e. the current as output signal increases after measurement time interval. It can be seen that a saturation occurs and if very concentrated solutions are used the speed can also decrease, as result of the very complex interaction with the enzyme. For the linear domain more experiments were done and the linear fitted results are presented in figure 10.



**Fig. 10.** Linear response range for ATCh calibration (n=5).

A linear response range was observed between 0.1 and 1 mM ATCh with a sensitivity of 187 nA/mM.

## 5. CONCLUSIONS

The structure realized in thick-film technology using polymer thick-film pastes (PTF) printed on mylar plastic substrate was able to be used for Thiocoline detection. Modified electrodes with SWNT has allowed an effective low-potential amperometric determination of ATCh using AChE in solution. This is a first step in using the sensor for food residuals detection. Further step involve AChE immobilization for development of a biosensor for pesticide detection, where the organic-phosphorous species inhibit the enzyme.

## ACKNOWLEDGMENT

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