

# Autonomous Nanosensor System for Monitoring and Quantifying Arsenic in Water

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## ABSTRACT

In present work, we have developed a system for detection and quantification of arsenic in water, based on surface plasmon resonance. Studies that we have done with self-assembled monolayers on gold substrate type Au(111) allowed us to evaluate the behavior and evolution of the substrate as it is reuse, which led us to perform a protocol for functionalization in aqueous medium to ensure autonomous and repetitive use of the substrate which makes it possible sensing concentrations close to 5 parts per billion. We have developed a novel self-functionalization system of monolayers on Au(111) for recognition and fixation of arsenic, that makes possible to use In situ of the substrate repeatedly (over 100 times). The system is equipped with a wireless communications module that allows the configuration of a network of sensors dedicated to mapping and monitoring arsenic concentrations produced by anthropogenic and natural causes in drinking water.

**Keywords:** nanosensor, plasmon resonance, arsenic.

## 1 INTRODUCTION

The presence of arsenic in drinking water and food contaminated by the use of certain types of fertilizer has become an issue of great impact on human health. It is estimated that over 130 million people in more than 70 countries are at high risk from consumption of arsenic present in food or water contaminated. Accepted levels of arsenic in drinking water are below 10 parts per billion, which requires the use of appropriate methodologies and instrumentation for monitoring and quantifying these levels of contamination. Furthermore, for the tasks of mapping concentrations of arsenic in aqueous matrices and investigation of causes and sources of these metals, is necessary to develop measurement systems and methodologies for identification and quantification with a high degree of portability and accuracy. Current methods for measuring concentrations of arsenic in water, although of high quality and precision, require complex preparation protocols and instrumental infrastructure. This justifies the development of portable and economic systems able to quantify arsenic concentrations in water contaminated with the level of sensitivity required.

We have developed an autonomous sensor with gold substrates type Au(111) self-functionalizable, economic, portable, useful for to make In situ measures, equipped with a wireless communications module that allows the configuration of a network of sensors dedicated to mapping and monitoring arsenic concentrations.

## 2 DESIGN Y CONFIGURATION

### 2.1 Gold Substrate

In this project, thin films of Au(111) grown on glass with refractive index 1.51 type are used. Due to the low adherence of gold to the glass, an intermediate film of Titanium with 5nm in thickness is used. The average Au film thickness is 50nm.

The diffraction pattern obtained is shown in Figure 1. Using Bragg's law and from the value of the lattice constant for gold, the Miller indices for the corresponding peaks were obtained. The XRD pattern of the gold film on glass surface shows diffraction peaks corresponding to (111), (200), (220) respectively. The higher diffraction peak intensity corresponding to the plane Au (111) is located in  $38.3^\circ$  and is parallel to the glass surface. The peaks (200) and (220) of less intensity are located in  $44.4^\circ$  and  $64.8^\circ$  respectively. This distribution corresponds to a cubic face centered structure and allows us to verify experimentally that is a surface Au(111).

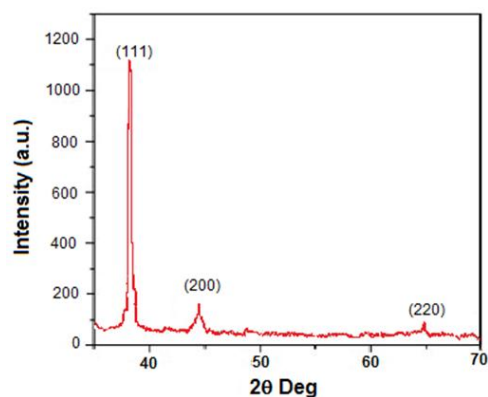


Figure 1. Diffraction pattern of the gold substrate.

### 2.2 Self-assembled monolayers

In this work, thin films of Au (111) grown on glass with refractive index equal to 1.51 are functionalized with n-alkanethiols with different chain lengths using different immobilization strategies on gold surfaces. The evolution of self-assembled monolayers on Au(111) substrate with different substances was studied. These studies allowed the research team to evaluate the behavior and evolution of the substrate as it is reused, which led us to perform a formal protocol for functionalization in aqueous medium at room temperature and to ensure autonomous and repetitive use of the substrate.

Functionalization of the gold surface with n-alkanethiol, was performed at room temperature and in aqueous media. Specifically for dithiothreitol DDT, it was possible to obtain monolayers of good quality for capturing the arsenic as indicated by the graph in Figure 2.<sup>1</sup>

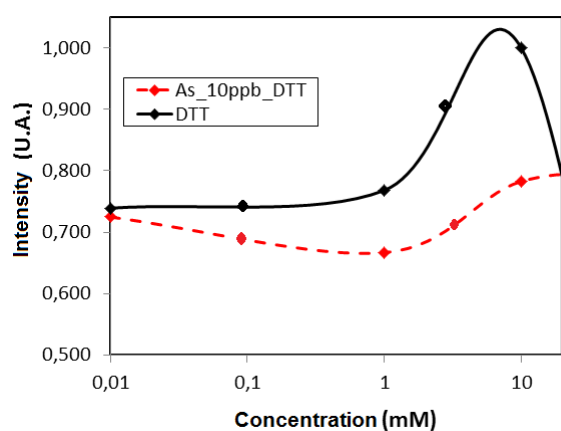


Figure 2. Curve for absorption of Au(111) self-assembled with DTT in aqueous solution at different concentrations (solid line) and subsequent conjugation of As (dashed line). Concentration of the molecular entity under which a higher level of identification of arsenic occurs is 10mM.

This graph shows changes in the monolayer absorbance experienced when it is exposed to a water sample with arsenic.

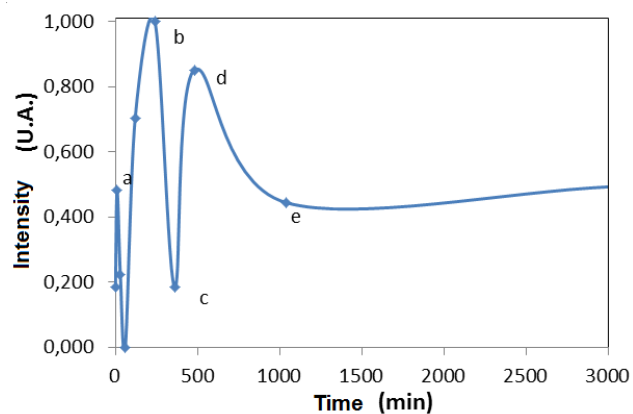


Figure 3. Absorbance by a thin layer of Au (111) functionalized with DTT at different times between 10 and

30000 min in aqueous solution at a concentration of 10 mM. Areas of the curve associated with the steps of self-assembly: a-b) physisorption. b-c-d) chemisorption, and d-

e) Planning and Ordering and constant densification. The functionalization time of the monolayer is very important to design the sensor. We have identified as desirable time 8 hr, as shown in Figure 3.

The temperature at which the functionalization process was performed is 15 °C. In summary, the operating parameters for the process of self-functionalization (for the case of the DTT) of the sensor are:

1. Temperature: 15oC.
2. Molarity of DDT: 10 mM.
3. Time of functionalization: 8 hr.

## 2.3 Architecture and technical aspects

The present system utilize the well known Kretschmann geometry<sup>2</sup> which is the most common approach to excitation of surface plasmon by prism coupling in total attenuation method. (ATR). Among the companies that use this kind of technology to his high-sensitivity measurement solutions, we could mention the following: Biacore AB<sup>3</sup>, Reichert Technologies<sup>4</sup>, Bio-Rad Laboratories Inc.<sup>5</sup>, Horiba Ltd.<sup>6</sup>, Metrohm USA Inc.<sup>7</sup> and Biosensing Instrument Inc.<sup>8</sup>

The system consists of two storage units of 300 mL, one for supply and the other one to reuse and pretreatment of the samples. The Kretschmann configuration is present in the sensor reader unit of chemical species, which is continuously consulted by a robust programmable logic control unit, which is the principal data reader, processing and recorder. The data can be consulted in a net environment, through his communication GSM modem unit. Furthermore, his battery pack unit, guarantee an autonomy of at least three months working on the field. These units are indicated in the block diagram of the figure 3 and 4. The table 1. Summarizes the system principal technical aspects.

Description	Unit	Value
Net connection. (0-5)	Subj*.	3
Weight.	Kg.	< 8
Operating temperature.	°C.	(5) a 45
Sensibility.	ppb.	5 a 100
Uncertainty	%	15% (95% C.Int.)
Toxic Consumables. (0-5)	Subj*.	3
Reusables consumables. (0-5)	Subj*.	4
Power	W.	< 900
Price	USD.	< 1800
Safety (0-5)	Subj*.	4
Easy to use. (0-5)	Subj*.	3
Innovation (0-5)	Subj*.	4
Time to reading	Min.	< 30
Kind of measurement.	Subj*.	As3
Can read other ions (0-5)	Subj*.	0

Table 1: Technical aspects. \*5 is the best, 0 is the worst..

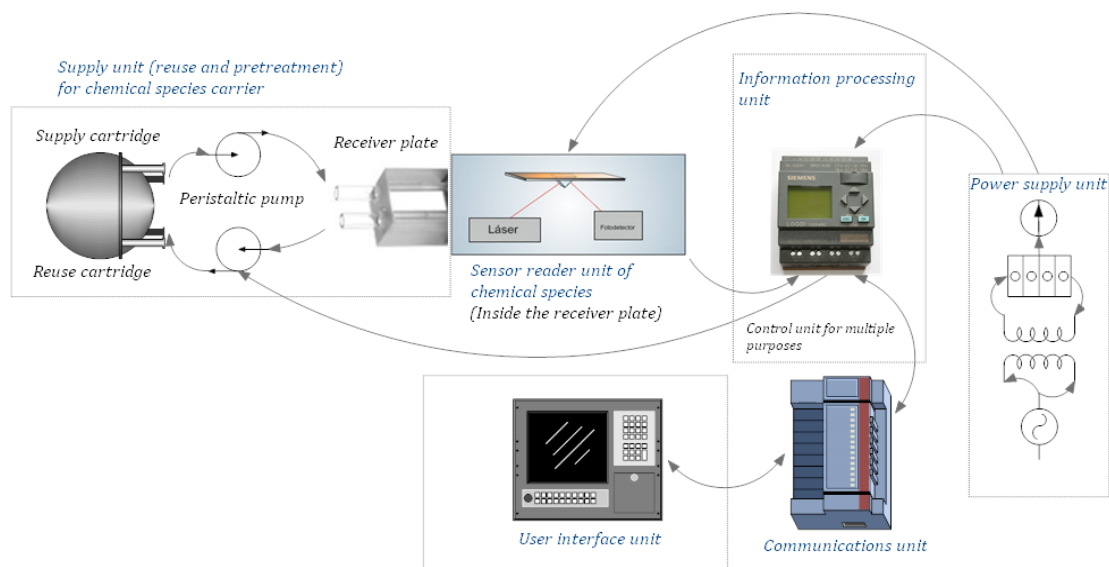


Figure 3. Schematic diagram for the NanoSensor System.

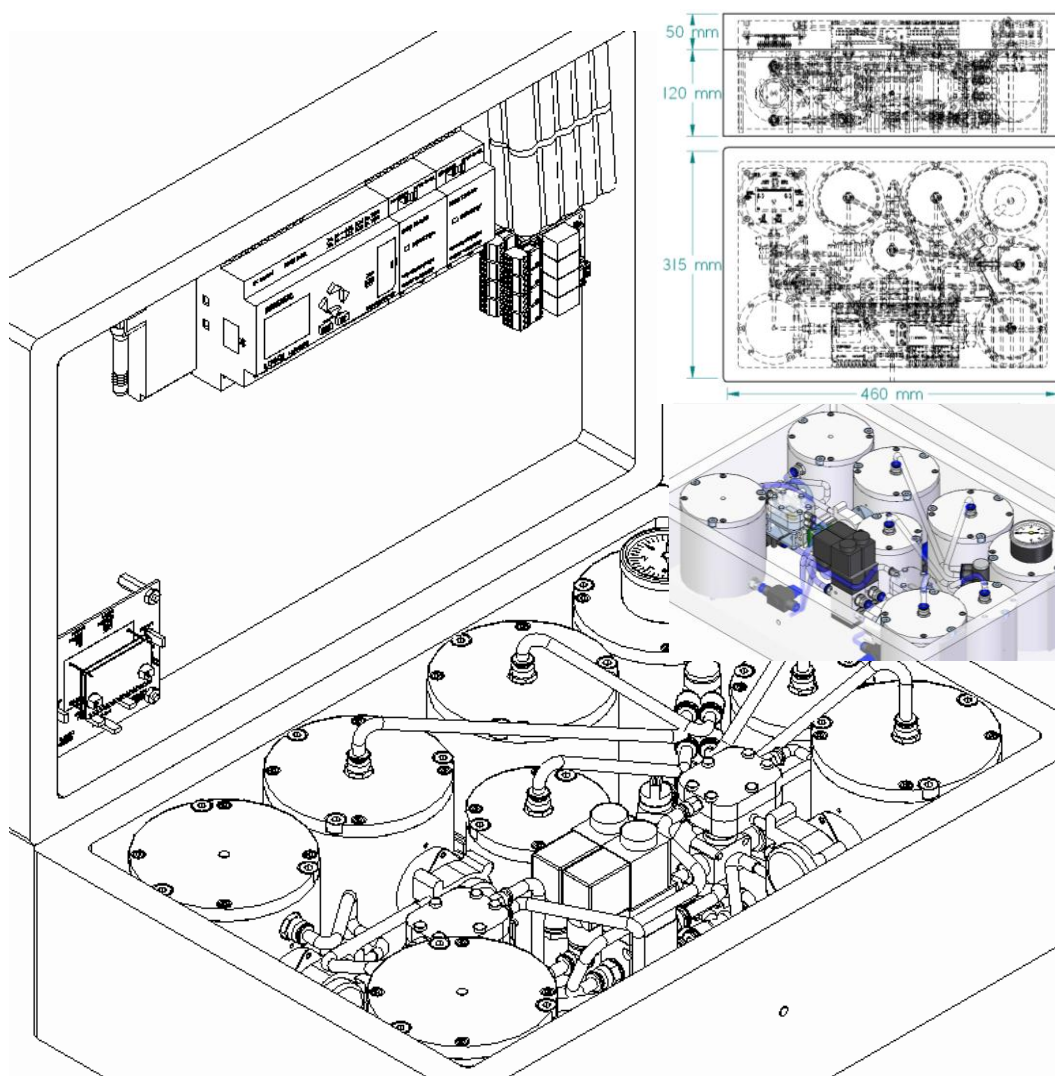


Figure 4. Isometric view with the total sizes of the Nanosensor system.

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