Determination of heavy metals contamination using a silicon sensor with extended responsive to the UV

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Abstract. Due to its potential risk to human health and ecology, the presence of heavy metals in water demands of techniques to determine them in a simple and economical way. Currently, new developments of light emitters and detectors open a window of opportunities to use optical properties to analyze contaminated water. In this paper, a silicon sensor developed to extend its sensitivity up to the UV range is used to determine heavy metals in water. Cadmium, Zinc, Lead, Copper and Manganese mixed in pure water at different concentrations were used as test samples. The photocurrent obtained by the light that passes through the samples was used to determine the optical transmittance of pure and contaminated water. Preliminary results show a good separability between samples, which can be used for qualitative and quantitative detection of such heavy metals in water.

1. Introduction
The presence of heavy metals in water, natural or due to environmental pollution, has received considerable attention of the research community in the last years due to its potential risk to human health and ecology. The toxicity of heavy metals such as cadmium, zinc, lead, mercury, copper, manganese, and others, can have harmful and even lethal effects on the human body, depending on the concentration and frequency of consumption. Regarding environmental aspects, recent studies indicate an increasing of heavy metals concentrations in lakes or rivers, frequently correlated with an increased industrial activity in the region [1, 2, 3]. As a result, techniques and methods for monitoring concentration of toxic metals within legally defined limits acquire special relevance.

A number of techniques have been developed over the years for analysis of heavy metals concentrations in water, many of them based on spectrophotometric methods. Among these, atomic absorption spectrometry (AAS), inductively coupled plasma (ICP)-atomic emission spectrometry and ICP-mass spectrometry have been broadly reported with several variants. AAS assesses concentration of analyte in a sample based on the absorption of optical radiation by free atoms. The radiation flux with and without a sample is measured, the absorbance is then translated to analyte concentration using the Beer-Lambert Law [4]. In atomic emission spectrometry (AES) the analyte is exposed to a flame, and the thermal energy excites the atoms into electronic states that emit light when they return to the original state. Radiation wavelength and intensity provide information about identity and amount of the element in a sample [5]. ICP-AES makes use of inductively coupled plasma to produce excited atoms, which emit the radiation detected in the spectrometer. In reference [6], flame atomic absorption spectrometry (FAAS) is used for the determination of some heavy metals, presenting a new

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cloud point extraction procedure for the separation and preconcentration of metals in water and food samples. In reference [7] the authors present a novel continuous powder introduction microwave-induced plasma atomic emission spectrometry method (CPI-MIP-AES), for trace determination of metals in ground and tap water samples after preconcentration on activated carbon. Another technique for the analysis of heavy metals in liquids is Laser Induced Breakdown Spectroscopy (LIBS). In this technique a highly energetic laser pulse is focused onto the sample producing a microplasma with molecular and atomic excited states, which will emit the expected radiation to be detected in the spectrometer. Reference [8] presents a method using LIBS in which a wood slice is used as a liquid absorber to transform liquid sample analysis to solid sample analysis. Another liquid to solid sample analysis using LIBS is presented in reference [9], where liquid solutions are converted into solid pellets of calcium hydroxide by mixing with calcium oxide. X-ray fluorescence spectrometry (XRFS) is another well-known technique, which has been used to analyze heavy metals content in water. XRFS is based on the emission of fluorescent X-rays from a sample, which has been excited by bombarding with high-energy X-rays. References [10] and [11] present studies using XRFS. Detection of heavy metals in water using surface plasmon resonance spectroscopy (SPRS) combined with anodic stripping voltammetry is presented in reference [12]. SPRS is based on the principle of resonance when the frequency of incident light matches the natural frequency of surface electrons oscillating against the restoring force of positive nuclei. Another technique often used in water analysis is Ion Chromatography (IC). Experiments on detection of heavy metals in water using IC with ultraviolet detection are reported in references [13, 14].

Besides all the efforts already mentioned, there is a tendency to take advantage of new light emitters and sensors to provide simplest and economical analytical methods. For example, in reference [15] our group has reported a silicon sensor that extends the silicon response, normally in the visible to near infrared (VIS-NIR), to the ultraviolet (UV) region. The sensor combines a PN junction with a film of Silicon Rich Oxide (SRO) with the property of converting UV radiation into VIS-NIR light. SRO obtained by Low Pressure Chemical Vapor Deposition (LPCVD) has demonstrated to have a higher emission of visible to near infrared emission when illuminated with UV light [16]. Figure 1 shows the wavelength range used to obtain the SRO emission, also in the inset is presented the typical photoresponse of a silicon diode and the SRO emission. As can be observed, the wavelength coincidence between the emission and the detection can be used to extent the silicon range of detection. So, a silicon sensor has been developed that prolongs the response of the silicon up to 200 nm.

![Figure 1](image-url) **Figure 1.** Wavelength range used to stimulate a SRO film producing an emission centered at 750 nm. The inset shows the characteristic SRO emission and the typical photoresponse of a silicon PN diode (red line).
In this work, a preliminary study aiming to detection of heavy metals in water based on analysis of transmittance of incident ultraviolet light is presented. For that purpose, an experimental arrangement for measurement of transmitted light in the 200 to 400 nm UV range was developed. Cadmium, Zinc, Lead, Copper and Manganese in pure water solution at different concentrations were used as test samples. Preliminary results show a good separability between samples, which can be used for qualitative and quantitative detection of such heavy metals in water. Also, fabrication details and characteristics of the Si sensor with responsivity from 200 to 1000 nm are shown.

2. Experimental
The Si sensor was built on (100) P type epitaxial silicon wafers, the anode was done either by implanting or by thermal diffusion of phosphorous into the P type wafer. On the PN junction a SRO layer was deposited [17]. The active area used in this study was 1500 square micrometers. Average optical power was measured using an International Light model IL1400 radiometer. The currents were measured with a Keithley model 6517A electrometer. The set up used to measure the relative transmittances is shown in figure 2. For more detail on the experimental procedure refer to [18]. The relative transmittance, $T_r$, was measured in the wavelength range of 200 to 900 nm. However, data in the range of 200 to 400 nm is enough to determine the contamination. The relative transmittance ($T_r$) was defined as the ratio of the photocurrent produced by light passing through contaminated water ($I_c$) and that of pure water ($I_p$) as shown in equation (1). An example of relative transmittance is shown in figure 3.

$$T_r = \frac{I_c}{I_p}$$  \hspace{1cm} (1)

Figure 2. Experimental setup, the Xe lamp and the monochromator of the spectrofluorometer is used as a monochromatic light source.

Figure 3. Relative transmittance as function of incident wavelength for the five metals used with 5000 ppm.

3. The sensor
Figure 4a shows the current density as a function of the wavelength for our sensor and two commercial Si sensors. The dark current density in our devices is in the order of pA/cm². The well-known relationship in equation (2) was used to determine the responsivity of our UV silicon sensor, UVSis. In this formula $J_p$ is the photocurrent density and $P_0$ is the optical power density.

$$R = \frac{J_p}{P_0}$$  \hspace{1cm} (2)

Figure 4b shows the typical responsivity measured for the UVSis. As can be seen, from 200 nm the response increases having a maximum around 300 nm. Then, the responsivity starts to reduce in agreement with figure 1. After 400 nm a PN silicon photodetector standard response is observed, therefore demonstrating that the SRO layer really contributes to the sensor sensitivity in the UV
Figure 4b can be used to estimate the efficiency of emission of SRO. The sensor’s responsivity in the range of 700 nm is 0.3 A/W, meaning that per each watt of light impinging in the sensor, a 0.3 A photocurrent will be obtained. Now, if 1 W of 270 nm radiation shines on the sensor that will be converted into 700 nm light that produces only 0.1 A. It has to be considered that not all light converted from UV into VIS will reach the sensor’s surface. Let us suppose that only 50% of the generated VIS light will reach the sensor, then a photocurrent of 0.15 A should be obtained. However, only around 70%, 0.1 A are obtained. That is an indication that the SRO film is a really good wavelength shifter, converting most of the UV radiation into visible light.

Figure 4. a) Current density and b) responsivity as a function of wavelength for the UVSis. The current density is compared with two commercial Si diodes.

4. Heavy metal detection

The relative transmittance, $T_r$, was measured in the wavelength range of 200 to 400 nm. The results show clearly discernible curves for the different metals and concentrations. Figure 3 shows the transmittance curves for the different metals used with a concentration of 5 000 ppm. 100 ppm was the minimum quantity clearly determined. In this wavelength range, the $T_r$ and the concentration follow a quadratic relationship. In a simple way this relationship can be used to determine the metal and its concentration, experimentally an error of less than 5% was found.

In order to automatically classify the different contaminated solutions, a database was created with the relative transmittance obtained at five different wavelengths in the range 250-300 nm, which were found to give the most discriminative values associated to the greatest variances. Separability on data clustering was tested through Euclidean distance classification, which is a well-known pattern recognition technique. The object under test is assigned to the nearest prototype among the $p$ classes using the minimum-Euclidean-distance criteria, equation 3, where each prototype is obtained as the mean vector of the $m$ samples in each class, equation 4. In this work, the number of classes corresponds to $p = 5$ (five contaminating metals), and $m = 3$ (number of samples associated to each contaminating metal). Figure 5 shows the Euclidean distance obtained from the samples in the database to each prototype. Inter and intra-class statistical analysis indicates that an adequate data clustering with good data separability can be obtained through the described method. Further experimentation using non-linear classification based on neural networks is currently in progress.

$$d_{ip} = \sqrt{\sum (\bar{x}_p - x_i)^2}$$  \hspace{1cm} (3)
\[
\bar{X}_P = \frac{1}{m} \sum_{j=1}^{m} \bar{X}_j
\]  

Additional experimentation aiming to the generation of a comprehensive database should be carried out in order to come up with a complete technique evaluation. Those experiments should include more contaminants at different concentrations, as well as combinations of them, which could take advantage of the non-linear classification capabilities of the neural network.

**Figure 5.** Euclidean distance from database samples to the five prototypes.

5. Conclusions
A silicon sensor with responsivity from 200 to 1000 nm was used to determine the transmittance of pure and contaminated water. The sensor combines the light emission properties of a Silicon Rich Oxide film with the detection capabilities of a PN silicon junction. The efficiency of emission was estimated from the measured responsivity. The optical transmittance of Cadmium, Zinc, Lead, Copper and Manganese mixed in pure water at different concentrations were measured from 200 to 900 nm. However, only data obtained from 240 to 340 nm was enough to obtain relevant information to determine the contaminant. Separability on data clustering was tested through Euclidean distance classification in order to automatically classify the different contaminated solutions. Our preliminaries results, using pure water and one contaminant at a time, show that it is possible to determine quantitatively and qualitatively heavy metals such as Cadmium, Zinc, Lead, Copper and Manganese in concentrations up to 100 ppm.

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