# Construction of a low-cost detector to identify dissolved metals in aqueous media by fluorescence spectroscopy: design and perspectives.

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**Abstract**. We have constructed a low cost fluorescence detector model to determine the presence of some heavy metals in an aqueous medium. In particular, we focus on metals which cause public health problems in our country. We did the first tests with standard samples of Hg (II). The innovative features of this instrument are its small dimensions (9 $dm^3$) and the low cost of materials used in its construction.

## 1. Introduction

The determination of contaminants of the heavy metal kinds in aqueous media is supported through American and European procedures and rules [1, 2, 3]. These rules guide the traceability and repeatability of measurements of these contaminant. In them, sampling and conservation are included, which implies an increase in the costs of such analysis.

There exist some specific laboratory instruments to detect metal contaminants dissolved in aqueous media. All of them are made for a specific size and high cost for acquisition data and its operation [4] to smaller size but also very expensive [5]. In the case of metal contaminants in aqueous media, spectrometry equipment is based on atomic absorption or plasma-mass technologies. All these use the spectral detection method, i.e. the emission spectrum of an aqueous sample previously excited by a high frequency source (plasma) or non-ionizing radiation (UV light), is detected and interpreted. Taking this last exciting method, we have developed a low cost instrument that can be used “in situ” requiring only that the sample is stabilized without conservation or transportation.

The initial plan to construct this instrument for water analyses was divided in two steps: First, an analytic method to prepare the samples. Second, the electronic prototype development itself. In the first step, we made use of the chemical properties of the 8-hydroxyquinoline to build the chelates in metals previously dissolved in aqueous media to obtain fluorescence when irradiating [4, 5]. Our prototype was built to have control mechanisms to excite the sample by a UV source and to detect the fluorescence light into the 390-410 nm range [6].

## 2. Design and construction

We our design on the concept of having a device able to detect the fluorescence emission coming from a physic-chemical reaction produced by a high power UV source (figure 1). This emission is sent to a

ATMega 2560 microprocessor coupled to a graphic interface which show qualitatively and quantitatively the contaminants in the analyzed sample [7, 8, 9].

For an analog electronic level, we selected three IN, one OUT and five control signals, all shown in the control interface. To detect the non-ionizing radiation, we implemented the ferricyanide silica ($SiFe(CN)_2$) photo-detector with three sensitivity channels working from 0.1 to 0.6 mV range (figure 2).

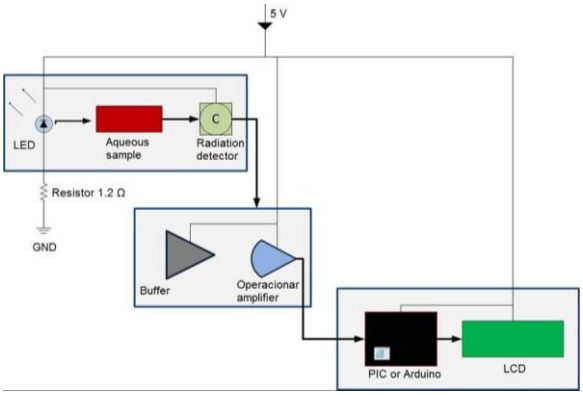


Figure 1. Conceptual design of the device.

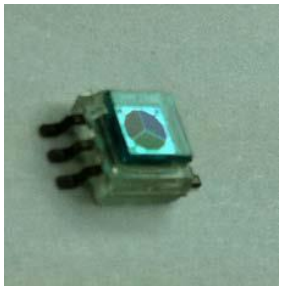

Figure 2. Three-channel radiation detector

For the UV source we acquired a high power LED (1W) in the 390-400 nm range mounted in a detection cell to avoid energy losses. This cell was designed to have all the components in a complete dark environment with the possibility, if required, to replace easily the emission source and the photo-detector (figure 3).

Figure 3. Detector cell and the emission source integrated

Once detected, the signal is amplified by a complement electronic circuit to avoid voltage drops. Then, the amplified signal enters the interpretation circuit zone where the corresponding algorithms were programed to show the presence of the contaminant source (figure 4).

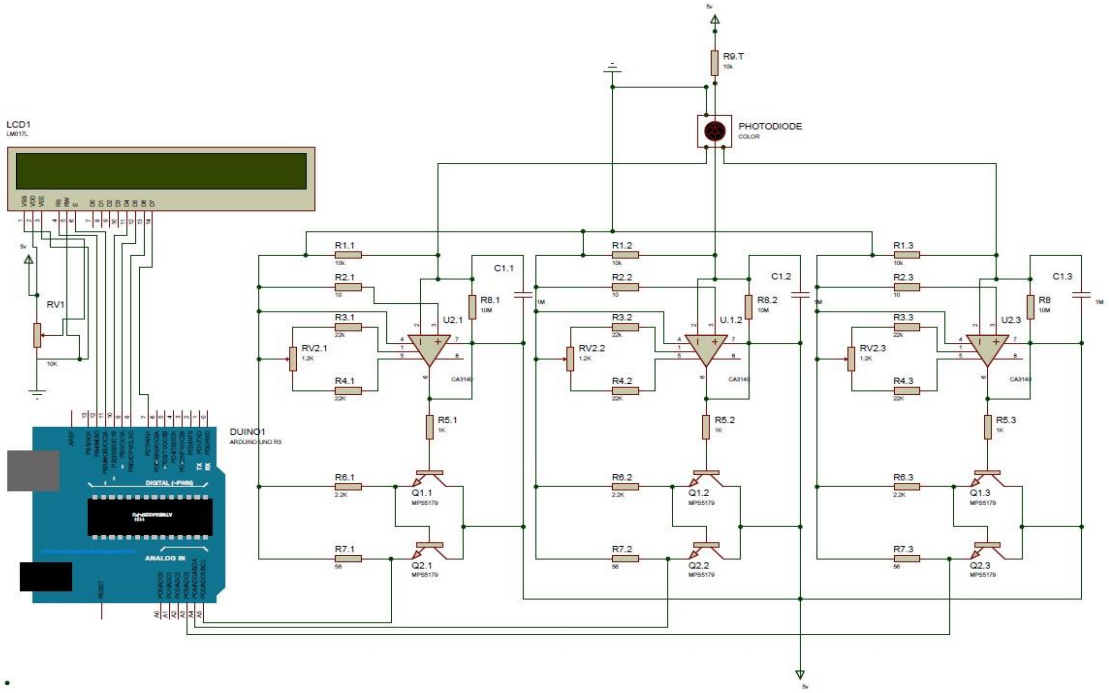


Figure 4. Electronic diagram of the microprocessor, photodetector and interface

To improve the detection, we again use the three signals from the photodetector for the graphical interface to identify the contribution of each of them to establish a statistical weight among them. The intention with this analysis is to obtain a cleaner final result of the real presence of the contaminant. All this is connected to a touch screen that functions as an interface between the control electronics, cell detection and UV emission source.

## 3. Results.

For the three-channel sensor, we measured the spectral response of ultrapure water to test the sensibility limits of our prototype. For this, we tested the response of the photodetector with different LEDs of different wavelengths. We try to check if the photodetector is able to give us a consistent signal to avoid saturation or a change in the linearity of its response and, if appropriate, seek alternatives to address this problem (figure 5).

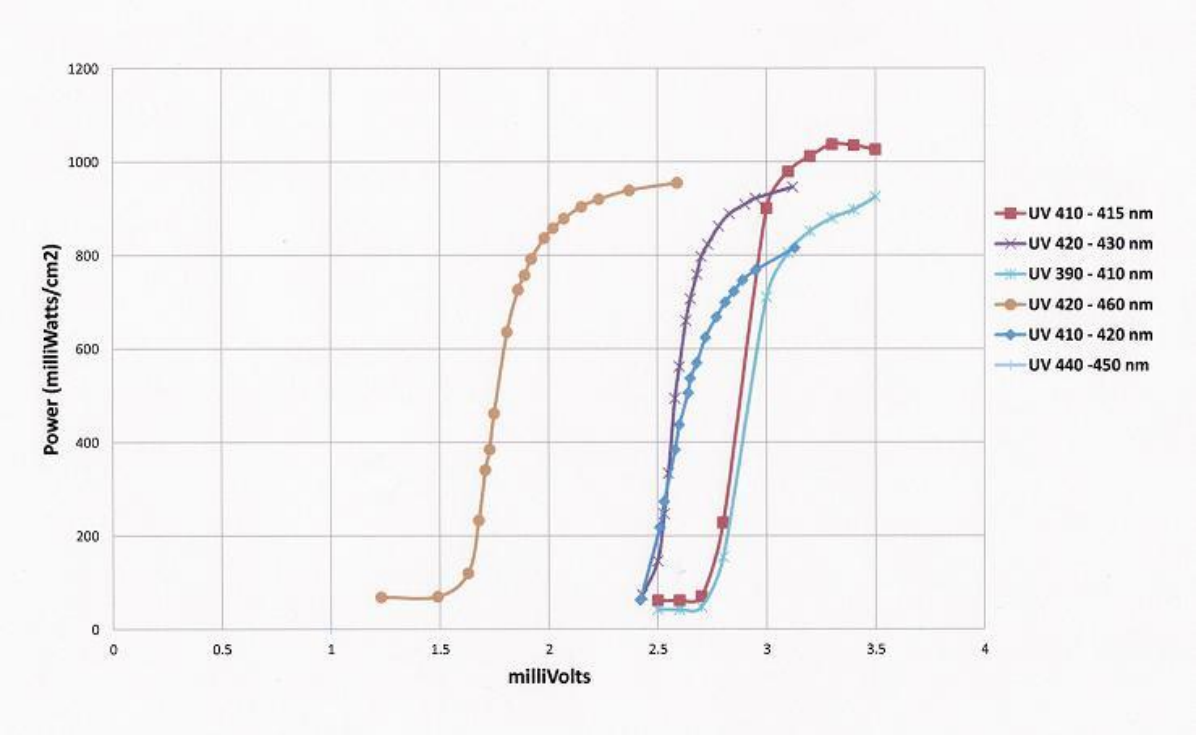


Figure 5. Photodetector response at different wavelengths for each high power LED

To obtain the calibration curve, we measured Hg standard samples of different concentrations to establish the detection methodology. Then, we test this methodology using a mixture of 8-hydroxyquinoline with pH of 8.5 and Tris-hydroxyaminometane [9]. We use high-power LED in the range of 390-410 nm with a concentration range for 0.02 to 0.2 mg/l obtaining few significant deviations compare to different sample dilutions; we developed 9 tests of this kind (figure 6).

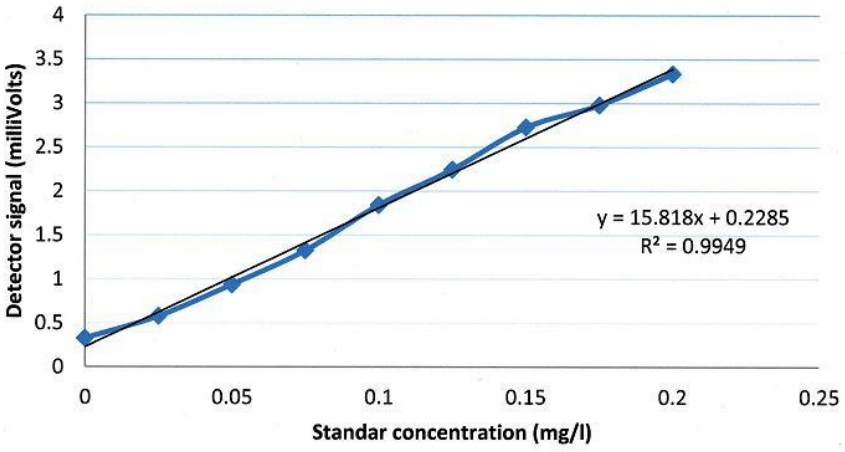


Figure 6. Calibration curve for Hg.

The limit of detection was obtained by calculating three times the standard deviation of ten measurements reagent blank between the slope "*m*" obtained by the calibration curve; in case of LD = 0.0021 mg / l, and the uncertainties presented values range from 0.13% for the reagent blank to 0.25% for the standard of 0.2 mg / l of Hg.

We say that there are variations in measurements due to the presence of chemical reagents. In this sense, we performed a series of tests at very high concentrations of two species of the same analyte; mercuric chloride and mercuric nitrate, in order to try to differentiate a soluble a partially insoluble substances in a basic medium. Notice that the behavior detection is not entirely linear and does not lose continuity (figure 7).

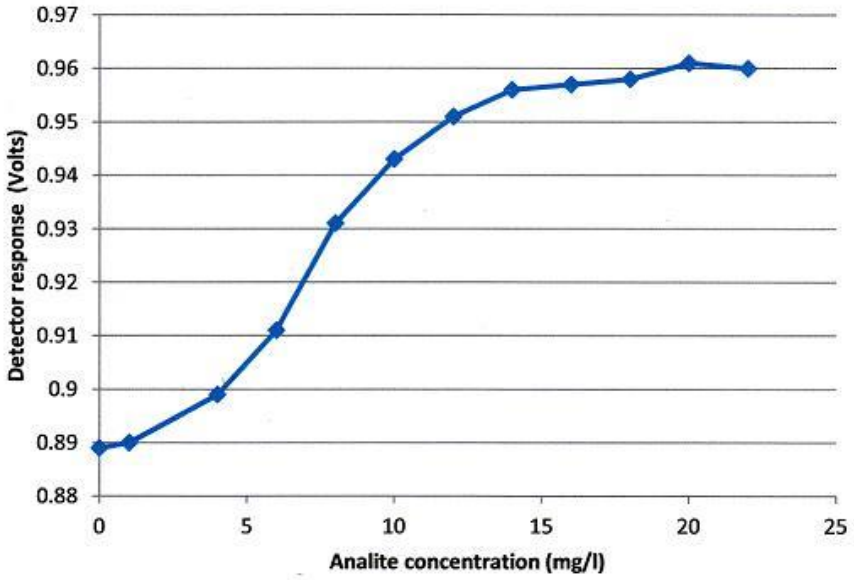


Figure 7: Detector response to high concentrations for mixture for two analytes.

With this procedure of applying fluorescence phenomena to identify contaminants in aqueous media, chemically previously treated, that our prototype can be applied to detect other metallic contaminants dissolved in water [10, 11].

## 4. Discussion

Fluorescence of metal complexes dissolved in aqueous media is a property that can be used to determine its presence not only qualitative, but quantitative. In this sense, the metal complexes of Cd, Zn, Cu, Pb and As, formed with chelating solutions also can be detected with our instrument. The instrument response to these complexes have still to be characterized for, first, to know if the detection is entirely possible and, second, to find the detection limits of the instrument. It is clear that these metals in water, which represent a public health problem in our country, are not found in pure form. They appear always in association with other components as oxides, sulfates, nitrates or acids; and these chemical combinations contribute as a detection problem.

## 5. Conclusions

By achieving fluorescence emissions detection for Hg for ranges between 0.02-0.25 mg / l we verified the usefulness of our instrument. The range of fluorescence of the sensor used, powered by the operational amplifier ensures applicability for detecting metal contaminants dissolved in water with a low price and fully portable device. The portability of the instrument, which is one of the added value, allows us to appreciate its application directly "in situ" to take immediate actions to contribute on the problem of water contamination. This instrument is not intended to replace the studies conducted by certified laboratories and centers; rather it is a viable option for presumptive analysis in areas or places causing health problems due to water pollution.

## References

[1] NMX-AA-051-SCFI-2001 Análisis de Agua – Determinación de metales por absorción atómica en aguas naturales, potables, residuales y residuales tratadas – Método de prueba SEMARNAT
[2] 2005 *Water Analysis Handbook* 3 ed HACH
[3] Clesceri L Greenberg A and Eaton A 2008 Methods for the examination of water and wastewater 20th edition *Oxford Academic Press* **1475**
[4] Lakowicz J 2006 Principles of Fluorescence Spectroscopy *Springer-Verlag* **954**
[5] IOE-CP Spectrometers 2015 *http://www.spectro.com/products/optical-emission-spectroscopy-metal-analyzer/trace-metal-analysis-spectrolab* [last access: February 8 2016]
[6] Fluorescence Method Development 2015 *http://www.dionex.com/en-us/webdocs/113591-Handbk-FLD-3000-Method-Develop-AN7* [last access: February 17 2016]
[7] Zhang H Qiang-Li and Jiang Y 2007 8-Methoxyquinoline based turn-on metal fluoroionophores *Tetrahedron Letters* **48** 3959 – 3962
[8] Valuer B and Brochon J. C 2001 New Trends in Fluorescence Spectroscopy. Applications to Chemical and Life Sciences *Springer- Verlag* **496**
[9] Soraka K Vithanage R and Phillips D 1997 Fluorescence Properties of Metal Complexes of 8-Hydroxyquinoline-5-sulfonic Acid and Cromatographic Applications *Anal. Chem.* **59** 629–636
[10] García-Colín L Dagdug L and Picquard M 2010 Introducción a la Física Biológica *El Colegio Nacional* **1295**
[11] Yan Z and Yan-Bin J 2015 Combined Toxic Effects of Heavy Metals and Antibiotics on a Pseudomonas fluorescens Strain ZY2 Isolated from Swine Wastewater Int.J.Mol.Sci. **16** 2839-2850