

# Voltammetry Based Automated Instrument for In-situ and Online Measurement of Heavy Metals Concentration in Water

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**Abstract-** Data processing of measurement data is a topic of paramount importance in every measurement system. Obviously sensors, signal conditioning and microprocessor specifications dictate important metrological characteristics of an embedded measurement system, namely: accuracy, resolution, repeatability and reliability. However, nowadays smart sensing systems and advanced signal processing techniques can improve measurement system's performance and flexibility relaxing hardware specifications and associated cost. This paper pays particular attention to curve fitting based on Gaussian interpolation techniques. Experimental voltammetry data is used to evaluate heavy metals concentrations in water. Advantages of Gaussian interpolation techniques to detect heavy metals and associated concentrations will be highlighted using a comparative analysis with the results provided by classical interpolation methods.

## I. Introduction

Heavy metals are the stable metals or metalloids whose density is greater than 4.5 g/cm<sup>3</sup>. They are stable and cannot be degraded or destroyed, and therefore they tend to accumulate in soils and sediments. The principal man-made sources of heavy metals are industrial point sources and diffuse sources such as combustion by-products and traffic [1]. Lead, copper and cadmium are heavy metals of greatest concern to human health because of their toxicity and their potential to cause harmful effects at low concentrations [2-4]. Thus, monitoring of heavy metals concentration is a topic of paramount importance in order to preserve human life quality and ecosystems.

In traditional measurement applications, sensor's accuracy and specificity are crucial and dictate the main metrological characteristics of the measurement system. With the advent of sensors data fusion and sensor networking the hardware requirements can be relaxed and signal processing techniques can improve the performance and extend the capabilities of smart sensing systems. The greatly expanded computing capability of smart sensing systems allows an easy implementation of advanced measurement features that include error compensation, error correction, self-testing, self-calibration and the implementation of "plug-and-play" technology.

Efficiency and autonomy of power solutions for environmental monitoring [5-6] are also a topic of major importance because those applications demand an extended autonomy especially when battery charging solutions are not available near sensing units. In this context minimization of system's power consumption is a hard restriction that must be addressed in system's hardware and software design in terms of reliability and autonomy.

This paper considers a voltammetry based automated instrument for in-situ and online measurement of heavy metals concentration in water. A hardware solution based on a fully portable, hand held electrochemical analyzer for both laboratory use and field applications will be presented together with an auto-calibration solution that can be used to improve measurements accuracy. The software part related with data processing includes a Gaussian curve fitting algorithm that is particularly suited to perform heavy metals identification and concentration evaluation. The minimization of the number of calibration and measurement points, directly related with the voltage increment used in each measurement cycle (voltage scan), is an issue of paramount importance because of their influence on measurement rate, accuracy and power consumption.

## II. System Description

### A. Hardware

Figure 1 represents the measurement and calibration system block diagram. The system includes a set of pumps with motors (Jabsco 42510), three peristaltic pumps (Watson Marlow 102R), two 3 way electro valves (Burket 6014), a temperature sensor (AD22103), a nitrogen cylinder (Air Liquide B03), an embedded PC (e-PC) and a potentiostat unit (PG 580).

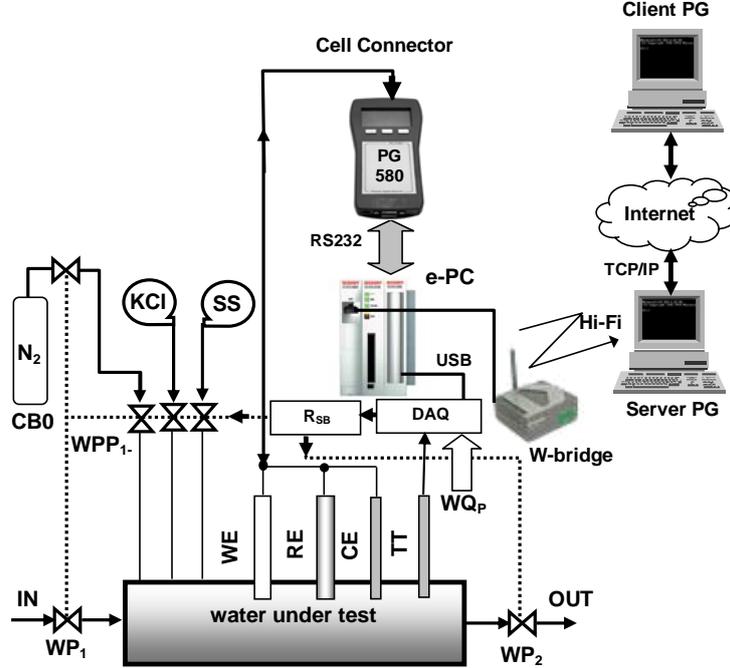


Figure 1. Measurement and calibration system block diagram: e-PC- embedded PC, PG 580- potentiostat unit, WPPi- peristaltic pumps, WP – regular pumps, SS- standard solutions, KCl- support electrolyte, TT- temperature transducer, CB0- nitrogen cylinder, R<sub>SB</sub>- 24 V relay switching box, DAQ- data acquisition board, WE- working electrode, RE- reference electrode, CE- counting electrode, W-bridge- 2.4GHz Ethernet wireless bridge DWL-810+

The embedded PC is a robust unit from Beckhoff [7] that includes a power supply unit, a CPU module, flash memory and RAM, USB interfaces and communications capabilities via the built-in Ethernet and RS232 interfaces. The operating system (Windows XP Embedded) is contained in a compact flash expansion slot.

The PC communicates through RS232 interface with the potentiostat unit (PG580) using an ActiveX control software module (PG580-12) and the Ethernet interface provides access to wireless transmission through a 2.4GHz Ethernet wireless bridge (DWL-810+). A multifunction data acquisition board (NI USB-6008) [8] with 12 bits resolution and 10 kS/s sampling rate provides a low-cost interface with the temperature transducer (TT), the relay switching box (R<sub>SB</sub>) and with additional water quality parameters (WQ<sub>p</sub>) sensing units. A single powered supply temperature sensor with signal conditioning and a temperature sensitivity equal to 28 mV/°C, AD22103 [9], generates an output that varies linearly with temperature:

$$V_{\text{out}} = \frac{V_{\text{PS}}}{3.3} (0.25 + 0.028 \cdot T) \quad (1)$$

being  $V_{\text{PS}}$  the power supply voltage and  $T$  the measured temperature in Celsius degrees.

The temperature information together with Nernst equation (2) is used to compensate the errors caused by temperature variations:

$$E = E_{\text{ref}} - \frac{RT}{nF} \ln \left( \frac{a_{\text{red}}}{a_{\text{ox}}} \right) \quad (2)$$

where  $R$  represents the ideal gas constant,  $T$  the temperature in Kelvin,  $F$  the Faraday's constant,  $n$  the charge number of the electrode reaction,  $a_{\text{red}}$  represents the chemical activities of all of the species that appear on the reduced side of the electrode reaction and  $a_{\text{ox}}$  represents the chemical activities of all the products that appear on the oxidized side of the electrode reaction.

Temperature variations cause deviations in the standard electrode potentials in aqueous solutions affecting the voltage values associated with the current peaks [10]. Metals identification based on voltage values must then consider the temperature of the solution in order to avoid measurement errors caused by a wrong identification of metals that exhibit adjacent current peaks in the voltammogram. A reference temperature of 25°C is used to normalize experimental voltages values of the voltammogram curves.

The potentiostat unit allows heavy metals concentration measurements based on standard techniques such as cyclic voltammetry, chronoamperometry, square wave, and differential pulse voltammetry [11-13]. The PG580 unit is remotely controlled by the e-PC. The experimental parameters and data display are implemented on the PC in a Windows software application that provides full, detailed graphs, and filing of data objects. The main metrological characteristics of the potentiostat unit includes: an optional connection for up to 5 working electrodes, 16 bits current measurement resolution, current measurement between 1 nA to 1 mA in 7 decade ranges, current measurement accuracy lower than 0.5%, an applied potential resolution of 16 bits (61  $\mu$ V) and electrode input impedance equal to  $10^{11}\Omega$  in parallel with 5 pF capacity.

## B. Software

The software of the measurement system, developed in LabVIEW, includes different modules. There are four main software modules associated with the following tasks: initialization and configuration (e-PC and PG580), data acquisition, evaluation of heavy metals concentration and data transmission. Figure 2 represents a simplified flowchart of the measurement and curve fitting programming routines.

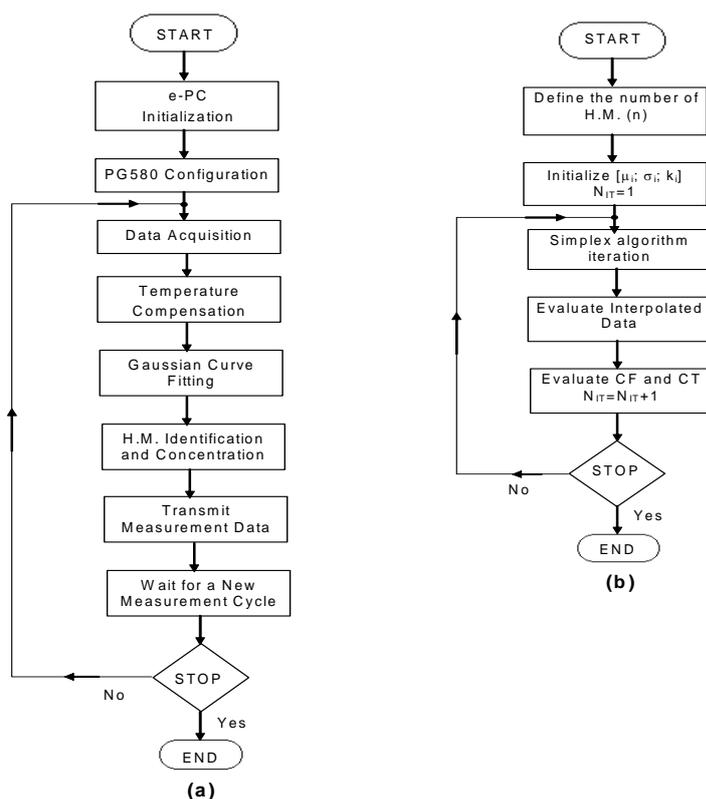


Figure 2. Flowchart of the measurement (a) and curve fitting (b) programming routines

The PG580 is configured for differential pulse experiments (*PSPSetDiffPulseVoltametry*) being possible to define the sweep potential, the pulse height, the pulse width, the scan increment and the step time. The measurement current and voltage range are programmed using the *PSConfigure* command and the sample rate is programmed by the *PSCalcDAQSampleRate* command. Auto-ranging capabilities are also setup in order to improve dynamic range and measurement accuracy. The voltage scan increment and voltage range is established paying particular attention to the minimum number of steps and scan range that are required to detect the heavy metals contents in the water under test with a given accuracy.

The Gaussian curve fitting algorithm uses a modified version of the Nelder-Mead algorithm [14-15] and the number of Gaussian functions ( $n$ ) is equal to the number of current peaks (different heavy metals) contained in the voltammogram data. Each primary Gaussian function ( $GF_i$ ) is defined by the following relationship:

$$GF_i(V) = k_i \cdot e^{-\frac{(V-\mu_i)^2}{2\sigma_i^2}} \quad GF(V) = \sum_{i=1}^n GF_i(V) \quad (3)$$

where  $k_i$  represents the amplitude,  $\mu_i$  the mean and  $\sigma_i$  the standard deviation of each primary Gaussian function ( $GF_i$ ).

The Gaussian interpolated curve parameters associated with the means and amplitudes of each primary Gaussian function are used to obtain heavy metals identification and concentration, respectively. The standard deviations are also important to evaluate the overlapping degree between Gaussian curves and to validate the interpolation results.

### III. Experimental Results

Figure 3 represents the voltammogram experimental data for a solution with the following heavy metals' concentrations: 2.809  $\mu\text{M}$  ( $\text{Cu}^{2+}$ ), 0.861  $\mu\text{M}$  ( $\text{Pb}^{2+}$ ) and 0.445  $\mu\text{M}$  ( $\text{Cd}^{2+}$ ). Potentiostat setup is characterized by a voltage scan range between -800 mV and 50 mV, a voltage increment equal to 1 mV and a differential pulse voltammetry measurement method. The circles over the graph curve represent a set of 40 calibration points that were tested for the Gaussian curve fitting interpolation method.

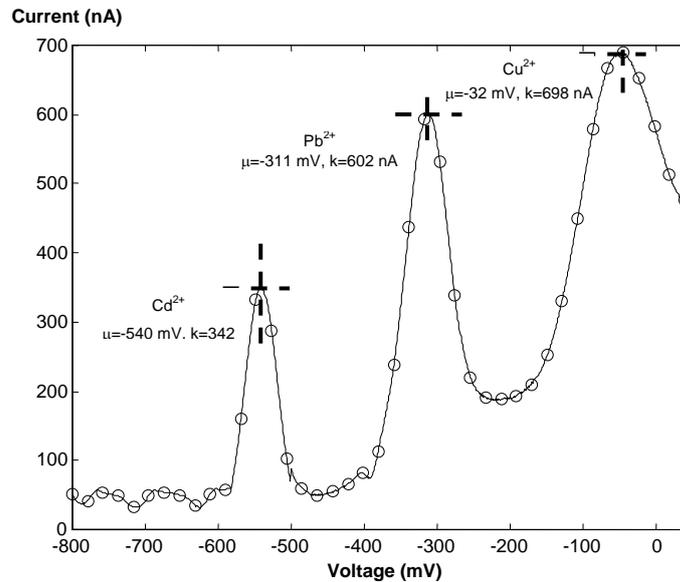


Figure 3. Voltammogram experimental data for a solution with the following heavy metals' concentrations: 2.809  $\mu\text{M}$  ( $\text{Cu}^{2+}$ ), 0.861  $\mu\text{M}$  ( $\text{Pb}^{2+}$ ) and 0.445  $\mu\text{M}$  ( $\text{Cd}^{2+}$ )

Figure 4, where the result of the Gaussian curve fitting algorithm is represented, clearly shows a good correlation between experimental data and interpolated data. The mean values and amplitude of each Gaussian curve corresponds to the standard voltage of each heavy metal and the amplitude is proportional to its concentration. The mean values ( $\mu_i$ ) and amplitudes ( $k_i$ ) associated with each primary Gaussian function, obtained after running the proposed Gaussian curve fitting algorithm for a set of 40 calibration points and a maximum number of iterations lower than 150 (3 times the number of primary Gaussian functions), are given by:

$$\begin{aligned} [\mu_{\text{Cd}}, k_{\text{Cd}}] &= [-541.8 \text{ mV}; 341.8 \text{ nA}] && \text{for Cadmium} \\ [\mu_{\text{Pb}}, k_{\text{Pb}}] &= [-311.2 \text{ mV}; 585.8 \text{ nA}] && \text{for Lead} \\ [\mu_{\text{Cu}}, k_{\text{Cu}}] &= [-31.1 \text{ mV}; 697.6 \text{ nA}] && \text{for Copper} \end{aligned} \quad (4)$$

These results correspond to a maximum absolute curve fitting error of 4.80 ppb (Lead) and an average absolute error equal to 1.62 ppb for the 3 heavy metals.

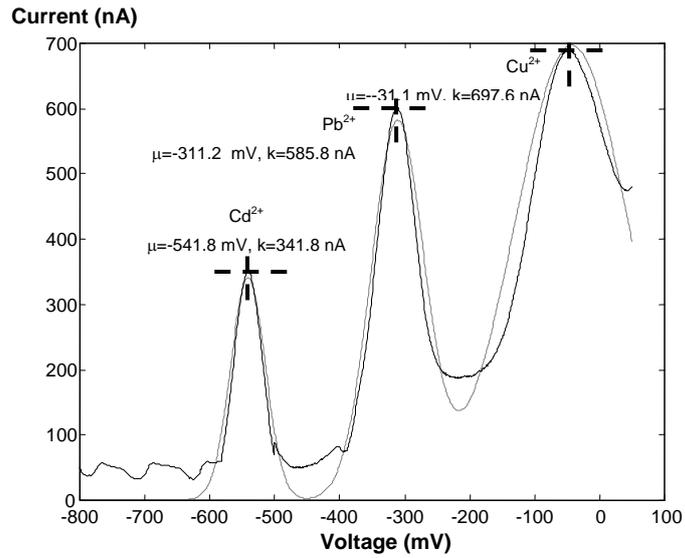


Figure 4. Results of the Gaussian curve fitting algorithm: experimental data (continuous line) and interpolated data (dashed line)

Figure 5 shows the interpolation error obtained with the Gaussian curve fitting algorithm and the error obtained with the best LMS polynomial curve fitting (polynomial degree=15) using the same set of 40 calibration points. The maximum error of the Gaussian interpolation is almost 5 times lower than the LMS polynomial interpolation error and the deviations between interpolation and experiment data around current peaks, which are crucial for a correct metal identification and concentration evaluation, are also much lower for Gaussian interpolation (shadowed areas).

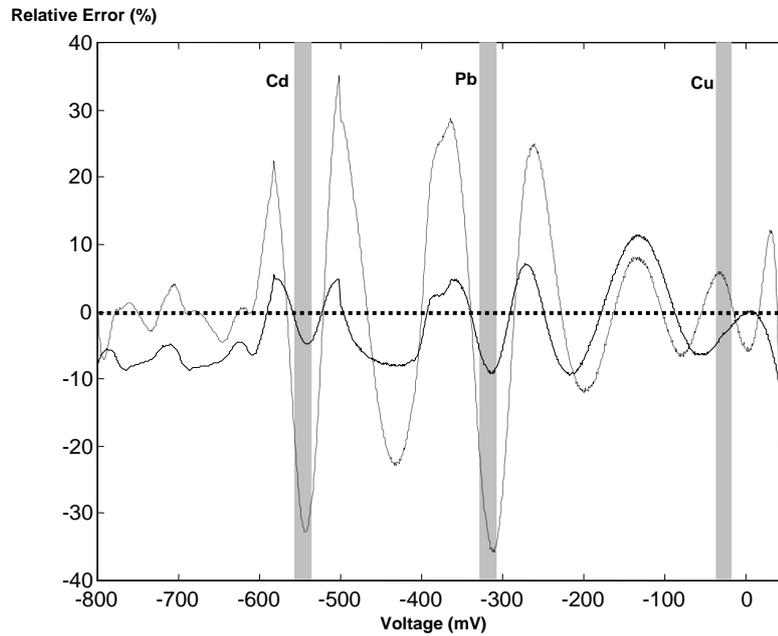


Figure 5. Interpolation errors: Gaussian curve fitting algorithm (continuous line) and best LMS polynomial curve fitting (dashed line)

#### IV. Conclusions

The hardware solution presented in this paper enables an automated measurement of heavy metals concentration in water. Measurement accuracy is improved based on self-calibration techniques supported by a set of calibration solutions with well known heavy metals concentrations. Particular

attention was dedicated to the errors caused by dissolved oxygen (nitrogen cylinder) in water and temperature variations.

This paper also underlines the main advantages of curve fitting techniques based on Gaussian interpolation to obtain heavy metals concentrations from voltammogram data. Curve fitting results associated with the means and amplitudes of each primary Gaussian function are used to identify metals and to evaluate their concentrations, respectively. Results from Gaussian interpolation are not affected by the typical numerical oscillations of polynomial interpolation and computational processing load can be substantially reduced specially when a small number of heavy metals need to be identified and their concentrations evaluated. Moreover, considering the symmetry of the current peaks contained in typical voltammogram curves, the proposed Gaussian curve fitting method preserves symmetry and the interpolated data is never affected by numerical oscillations as long as the number of primary Gaussian functions is equal to the number of voltammogram curve peaks.

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