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Portable Multispectral Colorimeter for Metallic Ions Detection and Classification

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Abstract

In the present work, a portable device system applied in the detection and classification of different metallic ions was proposed and developed, aiming at its application in the monitoring of hydrological systems like rivers, lakes and groundwater. Considering the system features, a portable colorimetric system was developed by using a multispectral optoelectronic sensor. All the technology of quantification and classification of metallic ions using Optoelectronic Multispectral sensors was fully integrated in the embedded hardware FPGA technology and software based on virtual Instrumentation (NI LabView ®). The system was used as a colorimeter by using the chromogen reagent of 1-(2-pyridylazo)-2-naphthol (PAN) as an indicator and the results obtained together with the signal processing and pattern analysis using the method of the linear discriminant analysis, allowed to obtain excellent results in detection and classification of Pb(II), Cd(II), Zn(II), Cu(II), Fe(III) and Ni(II) ions, with almost the same level of performance in relation to those obtained from the UV-VIS spectrometers of high spectral resolution.

Keywords: portable environmental monitoring systems; metallic ions detection; colorimetric system

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1. Introduction

The heavy metals ions have showed strong threats to human health because they have a lot of toxic properties and additionally showed to be bio-cumulative in the natural environment. Since these ions are thrown into river and lakes near the cities, it could contaminate the vegetable food and animals compromising all the food chain [1]. In this sense, great effort has been made by the scientific community in order to develop devices and systems for metal ions detection. Electrochemical devices were initially proposed and in the last few years these kind of devices achieved high sensitivity and, in some special cases, also high selectivity by using nanomaterials as active electrodes [2-4]. However, these types of devices normally suffer the interferences from the electromagnetic noise sources. In order to avoid this kind of noise, many dyes molecules or also bio-indicator molecules have been proposed and used successfully by using as detection signal the absorption (colorimetric) and fluorescent emission spectra. In general, these metallic ions detection processes have been used on test bench spectrometer. For example, the Anabas testudineus was used as a bio-indicator for Hg and Pb metal ions detection using ion exchange chromatography spectrometer, the experimental setup of this assay needs complex procedure for separation and purification of samples [5]. The aminopyridine shift bases molecules were used for Ni(II), Zn(II), Fe(III) and UO_2(II) ions detection by colorimetric and flourogenic method using conventional spectrometer. These procedures showed that colorimetric allow selectivity for Ni(II) and Zn(II) ions and selectivity only to Zn(II) when in addition it was used fluorescence technique [6]. A sucessful review paper showed colorimetric technique as good suitable procedure for metal ions detection especially when it is used functionalized gold nanoparticle absorption spectra shift for ions detection [7]. The dyad biodipy-rhodamine molecule was used for three-valent ions (Al(III), Cr(III), Fe(III)) detection by monitoring fluorescence emission change due to energy transfer from biodipy to rhodamine moiety, this dyad molecule did not show any selectivity between these ions, additionally it was reported that the dyad could be also used as imaging indicator in the biological cell culture [8]. The carbon dot terminated with carboxylate groups was applied as chemo sensor for many metallic ions detection by using the photoluminescence quenching of these dots, however the selectivity only to Fe(III) , Pb(II) and Hg(II) was achieved after buffer solution switching for each kind of ions [9].

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The single pyridine-linked anthracene-base molecule was used for the detection of various metallic ions throughout the change of photoluminescence emission and this dye also showed selectivity to Pd(II) ion when in addition it was used SDS surfactant in the sample solution [10]. A portable microfluidic system for microbial biosensor was reported to detect Pb(II) and Cd(II) ions, the reason why the author used inverted fluorescence microscopy spectrometer [11]. The Plasmon resonance fiber optic-based sensor was proposed for metal ions detection using the peak resonance shift [12]. A review paper reported many different carbon nanoparticles structures to detect Hg(II), Cu(II) and Fe(III) ions by fluorescent off, fluorescence on and ratiometric detection mechanism, even though these structures showed to be a good potential material for the metallic ion detection, they did not show selectivity and the detection mechanisms described here were very sensible to buffer used in the metallic ions solution [13]. The benzothiazolium-derived was proposed as colorimetric and fluorescent chemosensor for detection of Hg(II) ions, these molecules showed high selectivity for Hg(II) ion and the colorimetric and fluorescent calibration curve were achieved by monitoring the peak position changes (i.e. a specific spectral point) of absorption spectra and fluorescent spectra respectively [14]. The only main challenge on the metallic ion detection is to develop a recoverable system, in this sense it was reported a photonic colorimetric device based in the Bragg diffraction process. In this work, the sensor was doped with hydroxyquilonine molecules and the sensor had selective response for Pb(II) and Cu(II) ions with good reversibility [15]. The selectivity of optical sensor for metallic ions detection is still a big problem in this sense, some authors reported the matrix array indicators to overcome this problem, the array of 12 different thiophene-based compounds were used in order to detect and classify various metallic ions, the author suggest 100% of classification when it was used the fluorescence signal from the phiophene-based molecules and these signals were processing by linear discriminant analyses [16].

As we described above, all systems that used colorimetric or fluorescence techniques used the conventional test bench spectrometer and the selectivity of these systems are specific for some type of metallic ions. In these contexts, this article presents the development of a portable colorimetric and fluorescent chemical detection system, for metallic ions detection in liquid media. The system is based on the optoelectronic

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multispectral sensor as the detector and the white light emitting diode has been used as an excitation source. All components of the system such as excitation, detection and test calibration curves have been controlled by real time embedded National Board acquisition system programed with LabVIEW software from National Instrument Company. The system was tested using the (2-pyridylazo)-2-naphthol (PAN) molecules as colorimetric indicator and the achieved results showed that this system could detect and classify many metallic ions at the same time (Pb(II), Cd(II), Zn(II), Cu(II), Fe(III) and Ni(II). The portable system proposed, together with signal processing technique, could apply to metallic ion detection in situ environment such as river and lakes.

2. Experimental procedures

The portable embedded system for detection of different metallic ions by colorimetric method uses a photodetector optoelectronic chip, composed of 18 sets of photodiodes (3 x 6) encapsulated in a same enclosure, MMCS6CS type, manufactured by the MAZeT company. In this device, there are three groups of 6 photodiodes symmetrically distributed in a circular structure of 2 mm diameter. Each group of photodiodes has a spectral dielectric filter that selects the specific wavelength band so that the complete array of photodiodes covers the spectral region from 380 nm to 780 nm where each group with specific filters are sensible to the band centered at 425, 475, 525, 625, 575 and 675 nm respectively, additionally there is one group of 6 photodiodes that do not have any filter i.e., unfiltered array (PW). The photodiodes are connected directly in two integrated transimpedance amplifiers MTI04CS type which have four channels with programmable gains. The amplifiers chips are manufactured by MAZeT company. The gain selection is achieved by combining 3-bit binary entrance of the MTI04CS integrated circuit, allowing up to 8 different stages of amplification levels. After the amplification step, the signals from the photodiodes are multiplexed and directed to a processing and signal acquisition module in order to get the electrical signal (V_{DC}) that corresponds to light intensity that arrived at each groups of photodiodes array of the multispectral sensor. As light source, a white LED (P_{MAX} = 120 mW, IF = 30 mA), manufactured by the company Laser Roithner Technik (B3B-440-JB) was used. This source was set up at the front side of the quartz cuvette that contains the sample solution. The LED was fed with constant current source. The acquisition, control and processing of signals are performed based on FPGA technology, which was developed based on virtual instrumentation software (NI LabView ®), manufactured by National Instruments, NI model myRIO-1900. Figure 1 shows the schematic diagram of portable embedded system for detection of heavy metal ions (Cu(II), Zn(II), Ni(II), Cd(II), Pb(II), and Fe(III)) by the colorimetric method using chromogen reagent and multispectral optical sensor.

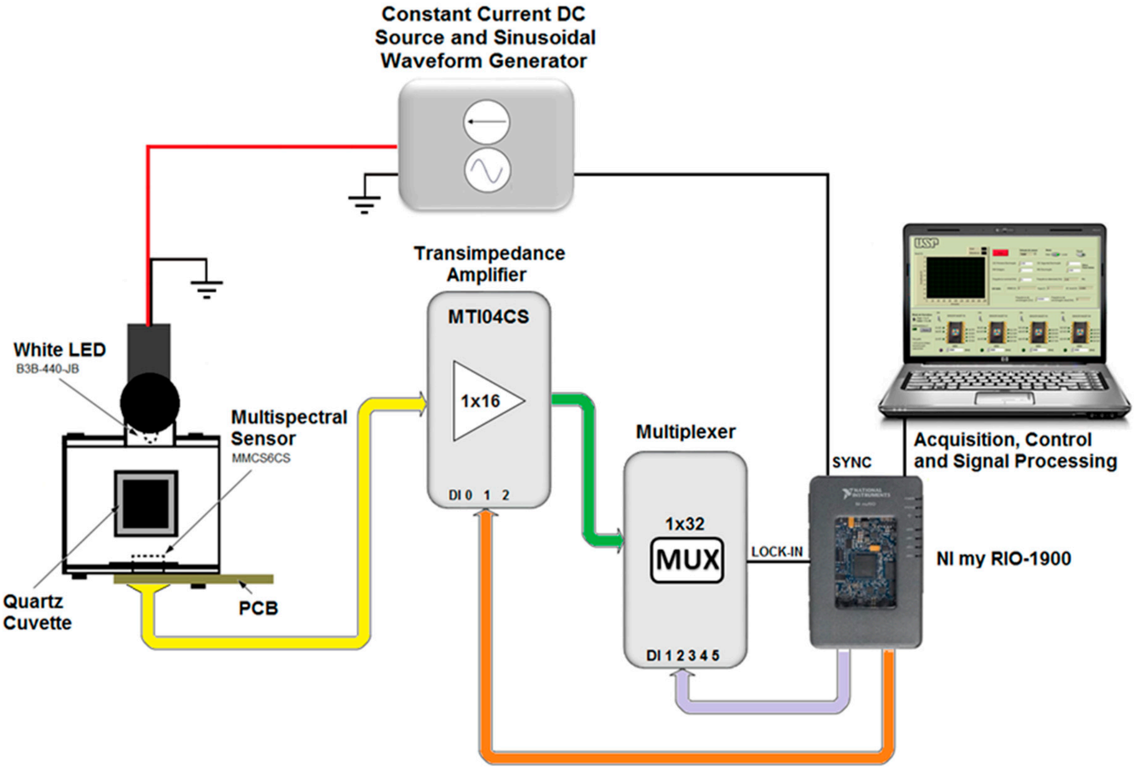

Figure 1. The schematic diagram of portable colorimetric system built with the multispectral optoelectronic sensor.

The solution with different metal ions was prepared with reagents of 99.9 % purity. All reagents were acquired from Sigma-Aldrich Chemistry (São Paulo, Brazil) and DI water was purified with a Milli-Q system Gradient. Standard solutions for the different metals were prepared in water DI, with suitable dilution of 250 ppm of salts of copper sulphate ($CuSO_4$), zinc sulfate ($ZnSO_4$), nickel chloride ($NiCl_2$), cadmium chloride ($CdCl_2$), lead nitrate ($Pb(NO_3)_2$), iron (III) nitrate (FeN_3O_9). The pH values of ionic solutions were read by a pH meter, LUCA-210 model, manufacturer Lucadema and unmodified according to

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those values obtained after the process of dilution of salts in water, as it is shown in the Table 1.

Table 1 - The pH values of prepared ionic solutions for colorimetric assays.

Ionic solution of 250ppm	*pH*
Cu(II)	4.0
Zn(II)	4.5
Ni(II)	4.5
Cd(II)	4.5
Pd(II)	4.5
Fe(III)	3.0

The chromogen reagent of 1-(2-pyridylazo)-2-naphthol (PAN) was diluted with methanol in order to get a concentration of 100 µM. Before each data acquisition, a volume of 2.5 ml of the PAN solution prepared was added into a quartz cuvette and then, small additions of appropriate volumes of metal ions Cu(II), Zn(II), Ni(II), Cd(II), Pb(II), Fe(III) were performed in order to get concentrations of 1 to 10 ppm respectively.

The multispectral sensor MMCS6CS response in the presence of metal ions of Pb(II), Cd(II), Zn(II), Cu(II), Fe(III) and Ni(II) was based on spectral change measurement of the optical transmittance spectra of a PAN solution, due to the action of different ions. In this case, the light intensity transmitted and received by the array of photodiodes was converted by transimpedance amplifiers (MTI04CS) in V_{DC} voltage values and stored by the acquisition, control and processing module (myRIO-1900). The transmittance was determined relative to the reference signal which corresponded to the response of each photodiode of different arrays to the transmitted white light through the solvent used in the preparation of the solutions samples.

Before each signal reading, a volume of 2.5 ml of prepared PAN solution (100 µM) was added into a cuvette of quartz which has square shape of 10 mm each side. After, a calibrated pipette, model P100 (20-100 µ l), Gilson Pipetman, was used to add a small volume of metal ions diluted in water in order to get a concentration of ions in the range of 1 to 10 ppm. During the experiment, the ambient temperature was kept at 26 °C.

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3. Results and Discussions

In order to compare the performance of our proposed portable colorimeter first, the transmittance spectra (T) was obtained of PAN (sensitive molecule) and of solutions of this molecule in environments containing metal ions of Pb(II), Cd(II), Zn(II), Cu(II), Fe(III) and Ni(II), respectively. The spectra were obtained by UV-VIS spectrometer Cary 50 model, Varian and presented in Figures 6(a) – 11(a), which can be seen in the supplementary information (Appendix).

Then, the portable colorimeter which was built with the multispectral sensor MMCS6CS was used to obtain the transmittance spectra of the PAN solution containing the different metallic ions so that the solutions had the same condition of the ones used with the UV-VIS spectrometer. The transmitted light signals were detected with the 6 (six) photodetector outputs terminals MAZeT that correspond to the responses of the array of photodiodes with band pass optical filters centered at 425, 475, 525, 575, 625 and 675 nm , respectively. These signals were conditioned by using the digital LOCK-IN amplification process. The transmittance spectra were determined comparing the signal from the PAN solution relative to the signal corresponding to solvent (methanol) used for PAN solution preparation. The equation 1 gives the transmittance relation that was obtained using the detected signals on the photodiodes array.

$$T = \frac{I_{\text{sample}\ (\lambda)}}{I_{\text{solvent}\ (\lambda)}} \qquad (1)$$

Where: $I_{\text{sample}}(\lambda)$ is the current generated by the photodiode array with optical filter centered at wavelength of λ when the samples were the PAN solution without or with metal ions respectively.

I_{solvent} is the current generated by the photodiode array with optical filter centered at wavelength of λ when the sample only corresponds to solvent (methanol).

The transmittance spectra for different metal ions and at different concentrations obtained this way are depicted in the Figures 6(b) – 11(b) in the supplementary information (Appendix).

The spectra results with UV-VIS spectrometer and portable system clearly show that the presence of metal ions in the solutions of PAN molecules changes the transmittance

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bands profile and these changes are related to color change of the original solution (PAN solution free of ions). The spectrum turn-up is a result of the PAN molecules complexation with the metal ion, via Ortho-hydroxyl group that is close to the phenolic ring and the heterocyclic nitrogen Atom [17-18].

The spectra, obtained with the multispectral sensor MMCS6CS, certainly have lower quality than the spectra obtained with conventional UV-VIS spectrometer, since the multispectral sensor system has a discrete number of spectral points (6 filtered sensors). However, it is observed in the Figures 6(b) to 11(b) that the profiles of the discrete spectra follow the same trend in the change of spectra that were obtained with UV-VIS spectrophotometer. It is important to point out that the spectral range of the set of 6 (six) filtered sensors are limited to a range between 380 and 780 nm. In this sense, in order to obtain a more accurate comparison, the regions of bands of wavelengths in the ultraviolet region (275-375 nm), seen in the spectra with UV-VIS spectrometer have been suppressed for quantitative analyses.

Before the colorimetric analyses, the sensitivity response of our proposed system was compared with that obtained with conventional spectrometer. For this proposal, it was analyzed the transmittance coefficient at 525 nm, which is a sensible spectral point that changes significantly with metal ions concentrations. So, we define a response function at this point to both the spectrometer and multispectral MMCS6CS system, using the following equation 2.

$$\text{Response} = \frac{\mathrm{T_0} - \mathrm{T}}{\mathrm{T_0}} \tag{2}$$

Where: T_0 and T are the transmittance coefficients of PAN solution without and with metallic ions respectively.

Figures 2 and 3 depict the calibration curves of responses obtained by UV-VIS spectrometer and multispectral sensor MMCS6CS, in different concentrations of metals ions, at a wavelength of 525 nm, respectively. It is observed that, for both systems, the response curves for this spectral point (525 nm) present the same profile, showing the compatibility of the sensitive results of our proposed system with the results obtained by conventional UV-VIS spectrometer.

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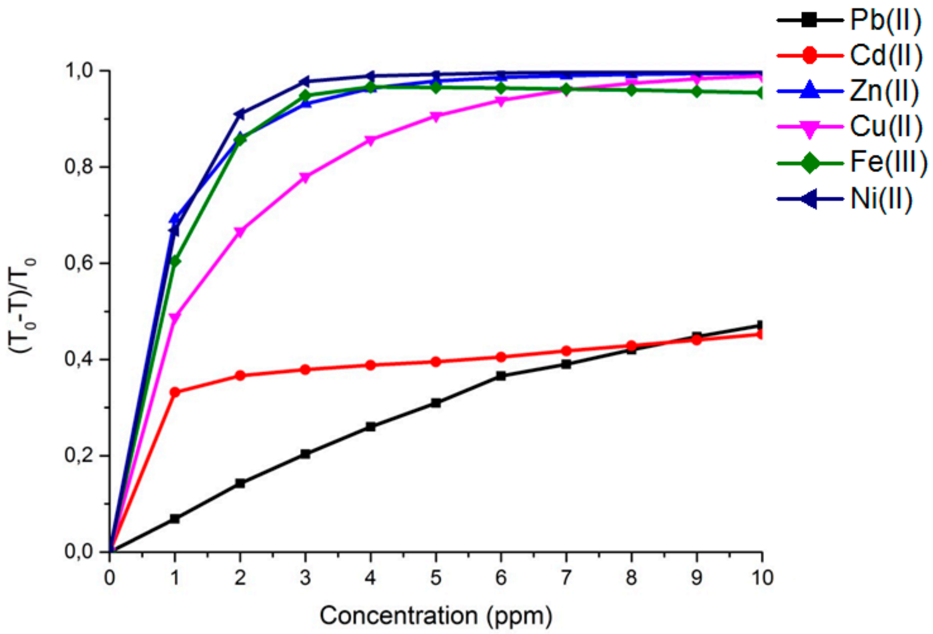

Figure 2. The response curves obtained from the transmittance spectra at 525 nm which were gotten with the UV-VIS spectrometer for different metallic ions at different concentration.

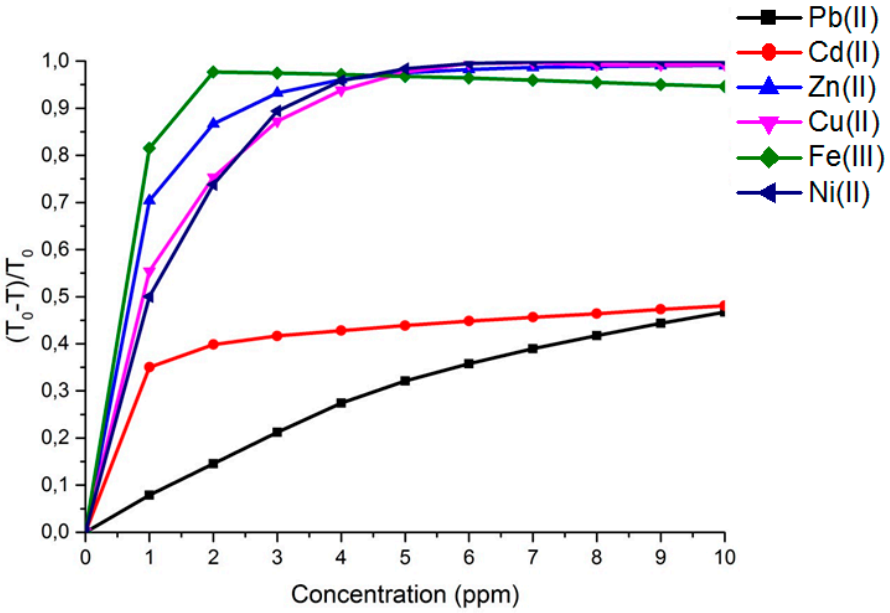

Figure 3. The response curves obtained from the transmittance spectra at 525 nm which were gotten with portable colorimetric system based in multispectral sensor for different metallic ions at different concentration.

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The most relevant results reported in this work are related to the classification power of different metallic ions achieved with the proposed portable colorimeter system. The classification procedure was achieved by using the Fisher linear discriminant analysis. For this procedure we used a set of 20 data for each type of ions of which ten data were used for training process and the other ten data were used for testing process. In the case of the spectra from the UV-VIS spectrometer, first the transmittance curves were fitted with seven harmonic functions.

$$T(\lambda) = A_0 + \sum_{j=1}^{7}\left[A_j sin(jK\lambda) + B_j cos(jK\lambda)\right] \tag{3}$$

Where: λ is the wavelength of excited light, K is the fundamental frequency of harmonic series.

The sixteen parameters K, A_j and B_j (j=1,2,….7) were used as the input data for linear discriminant analyses (training and testing process). It is important to point out that different authors proposed the classification process using the colorimetric technique by using the spectral point where the significant variation of transmittance (or absorbance) coefficient happened [9]. This strategy certainly loses the profile change of all the transmittance bands. In this regard the fitting process proposed in this work preserved the intensity and shape variation of the spectral bands on the classification process.

In the case of multispectral MMCS6CS portable colorimeter, we have the six spectral points for transmittance spectra, so these six transmittance coefficients were directly used as the input data for linear discriminant analyses.

The canonical score plots for training and testing process are depicted in the Figures 4 and 5, respectively.

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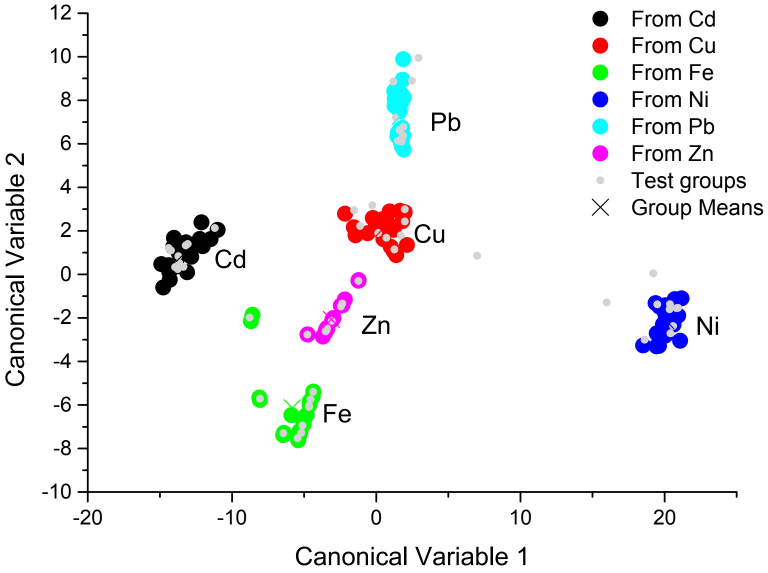

Figure 4. The canonical score plots for training and testing process built from the set of spectra data which were obtained with UV-VIS bench spectrometer. The Classification procedure was obtained by using the linear discriminant analyses.

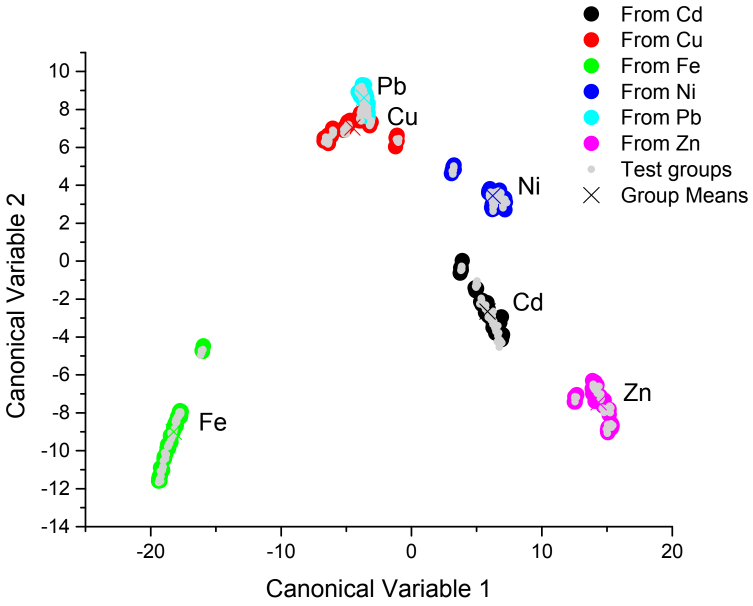

Figure 5. The canonical score plots for training and testing process built from the set of spectra data which were obtained with portable colorimetric system based in multispectral sensor. The classification procedure was obtained by using the linear discriminant analyses.

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The Figure 4 shows that the training process achieved an excellent classification for spectra data obtained with UV-VIS spectrometer since the different classes were clearly separated between them by hyperplanes. This Figure also shows the testing results and the error rates for all metallic ion recognition were 0% as it is shown in the Table 2.

Table 2. Classification counts and error rate of different metallic ions obtained after processing and analyzed the fitted parameter of transmittance spectra (obtained with UV-VIS spectrometer) by linear discriminant analyses method.

	Predicted group						
	Cd(II)	**Cu(II)**	**Fe(III)**	**Ni(II)**	**Pb(II)**	**Zn(II)**	**Total**
Cd	20 **100.00%**	0 0.00%	0 0.00%	0 0.00%	0 0.00%	0 0.00%	20 100.00%
Cu	0 0.00%	20 **100.00%**	0 0.00%	0 0.00%	0 0.00%	0 0.00%	20 100.00%
Fe	0 0.00%	0 0.00%	20 **100.00%**	0 0.00%	0 0.00%	0 0.00%	20 100.00%
Ni	0 0.00%	0 0.00%	0 0.00%	20 **100.00%**	0 0.00%	0 0.00%	20 100.00%
Pb	0 0.00%	0 0.00%	0 0.00%	0 0.00%	20 **100.00%**	0 0.00%	20 100.00%
Zn	0 0.00%	0 0.00%	0 0.00%	0 0.00%	0 0.00%	20 **100.00%**	20 100.00%
Total	20	20	20	20	20	20	120
				Error rate			
	Cd(II)	**Cu(II)**	**Fe(III)**	**Ni(II)**	**Pb(II)**	**Zn(II)**	**Total**
Prior	0,16667	0,16667	0,16667	0,16667	0,16667	0,16667	
Rate	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%

The score plot of training and testing process, which were obtained from the proposed portable colorimeter, is depicted in Figure 5. The cluster of different classes were almost totally separated by hyperplanes, except for the clusters corresponding to Cu(II) and Pb(II) ions, where it was not possible to draw a hyperplane which could separate these clusters. The testing process also shows the error rate for Cu(II) ion recognition of 10 % as it can be seen in Table 3, i.e., 10 % of Cu(II) ions samples were misunderstood as Pb(II) ions. Even though it was not possible to understand the samples for Cu(II) and Pb(II) ions, all the other metallic ions used in this work were successfully classified with error rate of 0% (Table 3). The classification results obtained with the portable multispectral colorimetric system almost showed to have the equivalent performance than those obtained with the conventional UV-VIS spectrometer, the 10% of misunderstood of Cu(II) and Pb(II) ions

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must be due to discrete spectral point of multispectral detector of our system, which loses fine details of bands shape changes.

Table 3. Classification counting and error rate of different metallic ions obtained after processing and analyzed the output signal from the multispectral sensor by linear discriminant analyses method.

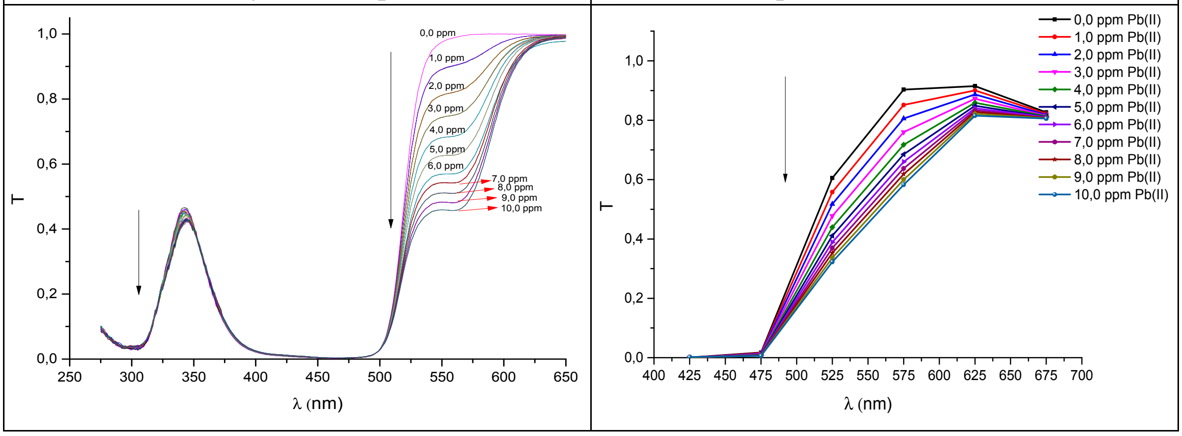
	Predicted group						
	Cd(II)	**Cu(II)**	**Fe(III)**	**Ni(II)**	**Pb(II)**	**Zn(II)**	**Total**
Cd	50	0	0	0	0	0	50
	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%
Cu	0	45	0	0	5	0	50
	0.00%	**90.00%**	0.00%	0.00%	10.00%	0.00%	100.00%
Fe	0	0	50	0	0	0	50
	0.00%	0.00%	**100.00%**	0.00%	0.00%	0.00%	100.00%
Ni	0	0	0	50	0	0	50
	0.00%	0.00%	0.00%	**100.00%**	0.00%	0.00%	100.00%
Pb	0	0	0	0	50	0	50
	0.00%	0.00%	0.00%	0.00%	**100.00%**	0.00%	100.00%
Zn	0	0	0	0	0	50	50
	0.00%	0.00%	0.00%	0.00%	0.00%	**100.00%**	100.00%
Total	50	45	50	50	55	50	300
				Error rate			
	Cd(II)	**Cu(II)**	**Fe(III)**	**Ni(II)**	**Pb(II)**	**Zn(II)**	**Total**
Prior	0,16667	0,16667	0,16667	0,16667	0,16667	0,16667	
Rate	0.00%	10.00%	0.00%	0.00%	0.00%	0.00%	1.67%

4. Conclusions

In the present work, a portable device system applied in the detection of different metallic ions was proposed and developed, aiming at its application in the monitoring of hydrological systems like rivers, lakes and groundwater. A portable colorimetric system was designed and developed embedded in board acquisition of National Instruments. The system applied as a colorimeter by using the chromogen reagent of 1-(2-pyridylazo)-2-naphthol (PAN) as an indicator along with the signal processing and pattern analysis using the method of linear discriminant analysis, allowed to obtain excellent results in the detection and classification of Pb(II), Cd(II), Zn(II), Cu(II), Fe(III) and Ni(II) ions, with almost the same level of performance in relation to those obtained from the UV-VIS spectrometers of high spectral resolution. All the technology of quantification and classification of metallic ions using Optoelectronic Multispectral sensors were fully integrated in the embedded hardware FPGA technology and software based on virtual Instrumentation (NI LabView ®).

The portable system developed in this work suggests its application in environmental control in situ and in real time, in such a way that it can be integrated into a network of sensors that can provide data continuously and receive commands to control environmental monitoring centers. In addition, the proposed system can be applied for the detection of various types of gases simultaneously since the different dyes molecules sensitive to different types of gas and with different spectral responses could be integrated in the active area of multispectral sensor, in this case it will be used the absorption or photoluminescence spectra of dyes molecules since our portable system provided an easy process to switch the source of white light emitting diode (used for absorption spectra obtention) by emitting laser diode at specific wavelength, which will be used as a source to excite the dyes molecules for photoluminescence emission.

5. Appendix



a) The UV-VIS Cary Varian spectrometer

b) The Multiespectral MMCS6CS sensor

Figure 6. The transmittance spectra of the chromogen reagent of 1-(2-pyridylazo)-2-naphthol (PAN) solution containing the Pb(II) ions at different concentration corresponding to: a) The UV-VIS Cary 50 – Varian spectrometer b) the Multiespectral MMCS6CS sensor.

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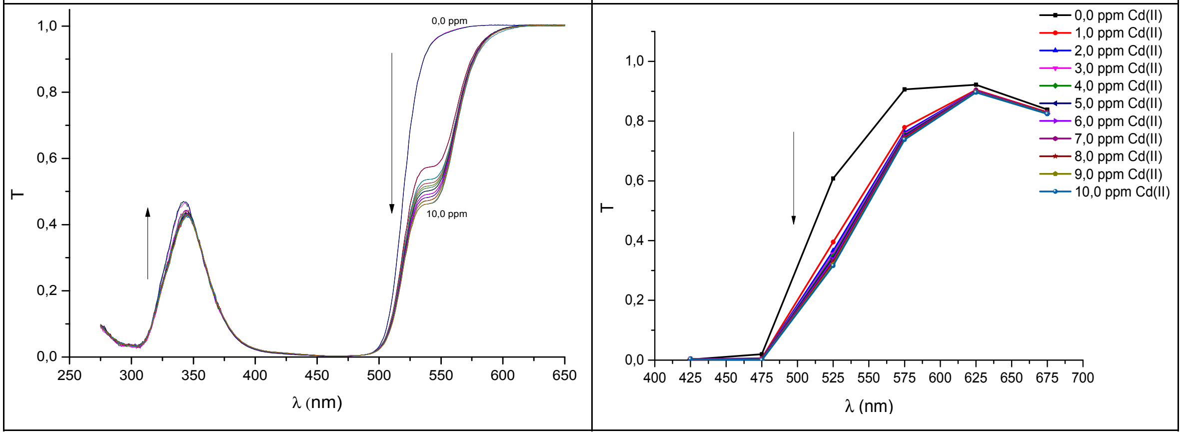
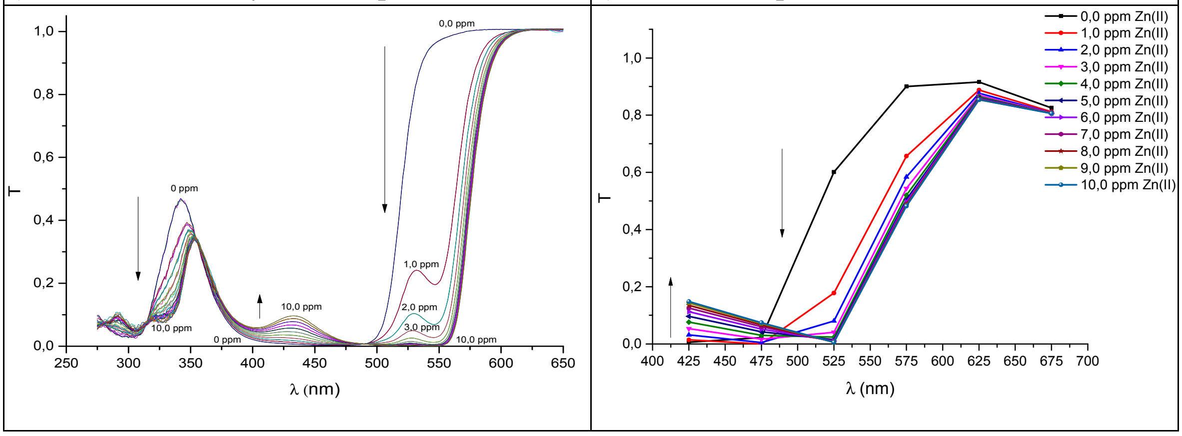


a) The UV-VIS Cary Varian spectrometer

b) The Multiespectral MMCS6CS sensor

Figure 7. The transmittance spectra of the chromogen reagent of 1-(2-pyridylazo)-2-naphthol (PAN) solution containing the Cd(II) ions at different concentration corresponding to: a) The UV-VIS Cary 50 – Varian spectrometer b) the Multiespectral MMCS6CS sensor.



a) The UV-VIS Cary Varian spectrometer

b) The Multiespectral MMCS6CS sensor

Figure 8. The transmittance spectra of the chromogen reagent of 1-(2-pyridylazo)-2-naphthol (PAN) solution containing the Zn(II) ions at different concentration corresponding to: a) The UV-VIS Cary 50 – Varian spectrometer b) the Multiespectral MMCS6CS sensor.

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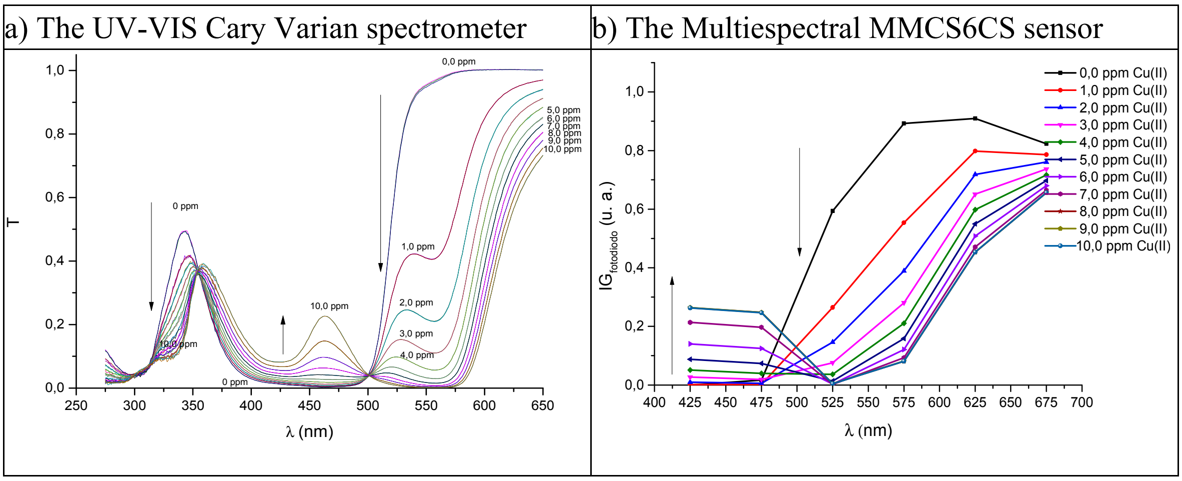
a) The UV-VIS Cary Varian spectrometer
b) The Multiespectral MMCS6CS sensor

Figure 9. The transmittance spectra of the chromogen reagent of 1-(2-pyridylazo)-2-naphthol (PAN) solution containing the Cu(II) ions at different concentration corresponding to: a) The UV-VIS Cary 50 – Varian spectrometer b) the Multiespectral MMCS6CS sensor.

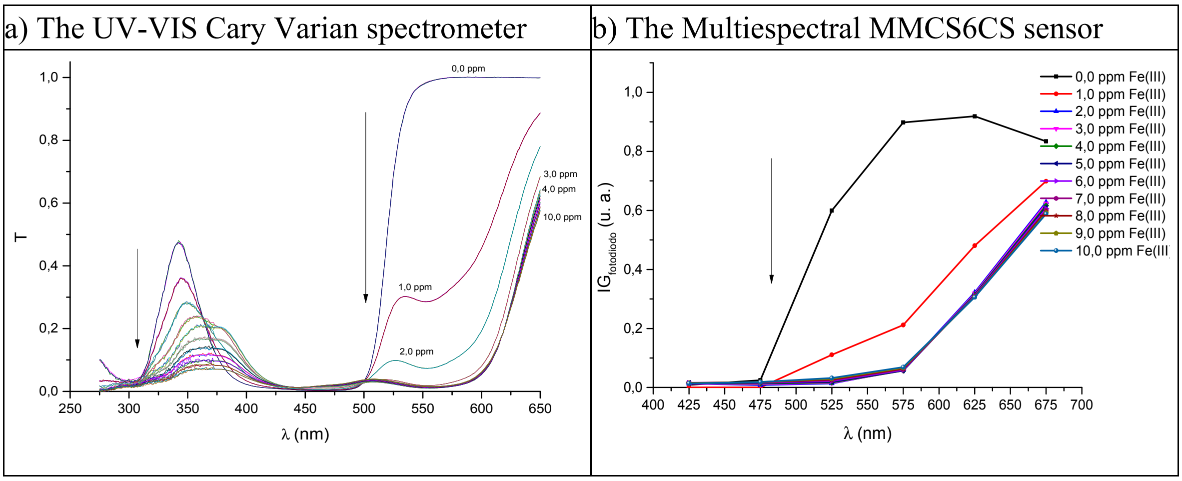
a) The UV-VIS Cary Varian spectrometer
b) The Multiespectral MMCS6CS sensor

Figure 10. The transmittance spectra of the chromogen reagent of 1-(2-pyridylazo)-2-naphthol (PAN) solution containing the Fe(III) ions at different concentration corresponding to: a) The UV-VIS Cary 50 – Varian spectrometer b) the Multiespectral MMCS6CS sensor.

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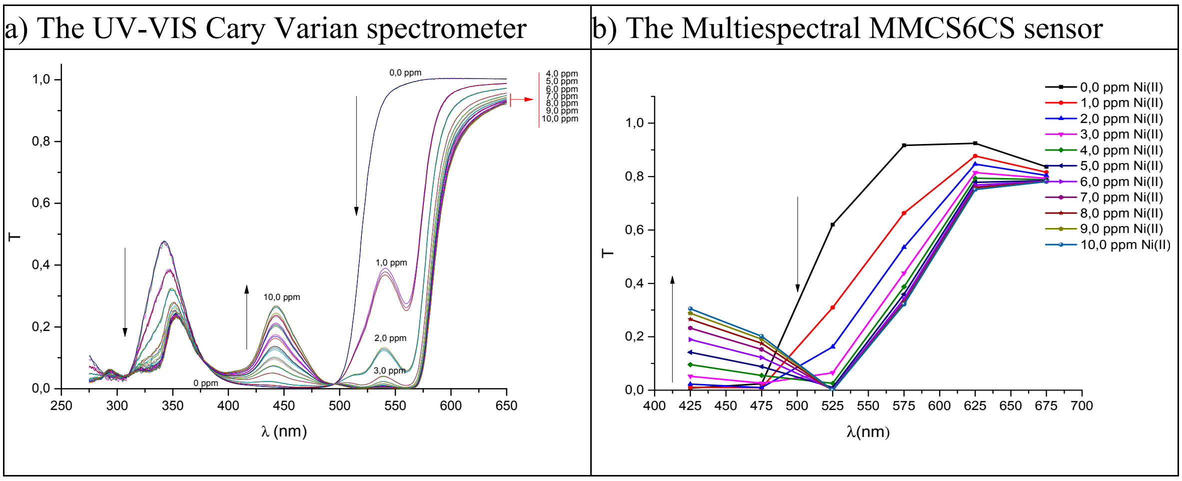
a) The UV-VIS Cary Varian spectrometer

b) The Multispectral MMCS6CS sensor

Figure 11. The transmittance spectra of the chromogen reagent of 1-(2-pyridylazo)-2-naphthol (PAN) solution containing the Ni(II) ions at different concentration corresponding to: a) The UV-VIS Cary 50 – Varian spectrometer b) the Multispectral MMCS6CS sensor.

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