



# Integration of diffusive gradient thin-film devices and functionalized electrode sensing matrix for discriminative detection of heavy metals in water environments

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## Abstract

This study presents a novel approach combining diffusive gradient thin-film devices and a sensing matrix of functionalized electrodes for discrimination and quantification of heavy-metals in water environments. The experimental setup uses four sensing units with interdigitated gold-plated electrodes and an ionic conductive hydrogel. Impedance measurements were conducted using a gain/phase analyzer in the frequency range from 10 MHz to 0.1 Hz. Principal component analysis was applied to enhance data interpretation. The results showed distinct clusters for cobalt (Co<sup>2+</sup>) and manganese (Mn<sup>2+</sup>) ions at concentrations ranging from 10 to 100 ppm, indicating the potential for discrimination between water samples contaminated with these analytes. The integration of IoT and low-cost instruments enables real-time monitoring, wireless transmission of data, and cloud storage. This research contributes to the development of cost-effective methods for heavy metal detection and environmental monitoring, facilitating improved water quality assessment and prompt risk mitigation.

## Introduction

Heavy metal ions are significant contributors to water contamination in rivers, lakes, seas, and oceans, posing a risk to human health even at low concentrations. These non-biodegradable elements, when accumulated in organs and tissues, can lead to various diseases, including liver, lung, bone, and respiratory system cancers, as well as cardiovascular and neurological problems, due to their high toxicity [1, 2]. Heavy metals originate from both natural and industrial sources, with industrial activities releasing

considerably larger quantities of these substances. They can disperse through various means, impacting food chains, drinking water sources, and the entire biosphere, thereby compromising ecosystems and biodiversity [3–5].

To address the challenges posed by heavy metal contamination, several well-established analytical techniques have been developed for analysis and speciation of these elements. Examples of these techniques include Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), X-ray Fluorescence Spectroscopy (XRF), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), and Neutron Activation Analysis (NAA) [6]. These techniques are extensively employed in laboratories to determine the concentration and speciation of various metal ions.

The technique of diffusive gradient in thin films (DGT), which was pioneered in the 1990's in the UK, is an environmental chemistry technique used to detect and quantify elements and compounds present in aqueous environments [7]. Since its inception, this technique has found widespread applications in various research fields. For instance, it is utilized to determine in situ concentrations of labile inorganic species, perform chemical analysis of solutions, evaluate the bioavailability of trace metals in water and soil (potential sources of environmental pollution), and has industrial applications, particularly in the mining sector, as well as in

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fluvial and marine aquatic environments [8]. A DGT device commonly comprises a sequential arrangement of a filter membrane, a diffusive gel, and a resin embedded with a binding gel. The components of the device are securely positioned within a lid using a plastic base and, when immersed in a liquid medium, this assembled configuration enables the capture and accumulation of elements present in the surrounding liquid. Therefore, the devices are deployed in the environment of study and collected after the accumulation time (days or weeks) for laboratory analysis using standard analytical techniques.

Besides the traditional analytic techniques, thin film sensors have been extensively proposed as a valuable means of detecting heavy metals [9–13]. These sensors can be custom-designed and functionalized to suit different applications, types of liquids, and volatiles, allowing for the selection of suitable organic or inorganic materials, conductive or semiconductor materials, and their precursors. The versatility of thin film sensors enables a wide range of applications [14]. Moreover, the manufacturing process for these sensors is cost-effective in terms of both processing and operation. Thin film deposition techniques such as drop-casting, spin coating, spray coating, and layer-by-layer deposition are user-friendly and have low operating costs. These sensors can be utilized for the analysis and detection of metal ions in sensor array systems, enabling rapid identification of the presence or absence of heavy metals in liquid samples before undergoing further analysis and identification [15, 16].

Although established analytical techniques such as AAS, ICP-MS, XRF, ICP-OES, and NAA are effective in metal ion analysis applied to DGT devices deployed in water environments, they need sophisticated laboratory facilities and qualified operators to prepare the samples for analysis and carry out the experiments. Moreover, there is a considerable delay between the collection and the analysis. In this sense, thin film-based sensors are an interesting alternative for low-cost and real-time (or, at least, faster) detection of heavy metals contaminants. In the present paper, we propose the coupling of a thin-film impedimetric matrix sensor to a DGT-like device, aiming the real-time detection of heavy metals in aquatic environments.

## Experimental details

### Thin-film matrix fabrication

In our experiments, the impedimetric sensing matrix utilized four sensing units, each consisting of a pair of interdigitated gold-plated planar electrodes. These electrodes were produced using photolithography techniques on a printed circuit board (PCB) by TEC-CI, Brazil. The sensing area of each sensor unit measures approximately 5.8 mm × 3.0 mm, with

a separation between the electrodes (L) of 160 μm and a total width (W) of 40.8 mm. The W/L ratio is approximately 255. Out of the four sensing units, three were functionalized by drop casting polymeric thin films, while the fourth unit remained as a "bare" electrode without any film deposition.

For the deposition of the polymeric films, appropriate solvents were used. Poly(3-hexathiophene) (P3HT) was deposited from a toluene solution (0.2%, w/w), poly(o-methoxy aniline) (POMA) from a chloroform solution (1%, w/w), and poly(vinyl carbazole):2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PVK:PBD) from a toluene solution (0.5%, w/w). The drop casting method was employed for the deposition of these polymeric thin films. Figure 1a shows the PCB with the electrodes and the selective drop casting deposition of the thin films.

### Ionic conductive hydrogel preparation

The diffusive gel utilized in the sensing devices was composed of an ionic conductive hydrogel. This hydrogel was created through UVA (370 nm) curing of a 1:1 mixture of poly(ethylene glycol) (PG) and poly(ethylene glycol) diacrylate (PGA). Additionally, a small amount (0.67% molar ratio) of phenyl bis(2,4,6-trimethylbenzoyl)-phosphine oxide (BAPO) was included as a photoinitiator. All the reagents used in the gel preparation were purchased from Aldrich-Merck.

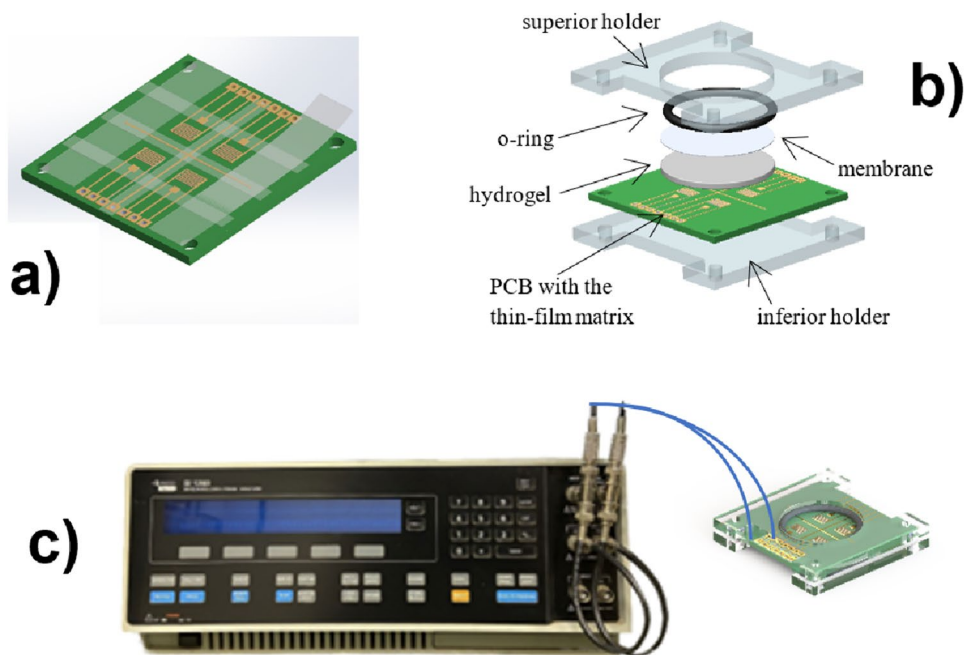
The precursor solution containing the hydrogel components was drop-casted onto a Petri dish until covering the entire surface. The amount of the precursor solution used was enough to produce films of approximately 1 mm thick. Subsequently, the curing process was carried out for 10 min under exposition to a UV lamp (centered at 370 nm). After the cross-linking reaction, the film was cut into a 20 mm diameter disc which was washed with deionized water at least three times to eliminate any residual reagents.

### Mounting of the sample holder

To provide proper protection and stability, the sensing device was enclosed within a custom-designed case made of laser-cut acrylic (PMMA). This case was specifically designed for the purpose of housing the device.

The device assembly involved sandwiching the printed circuit board (PCB) with the functionalized electrodes, along with the conductive/diffusive hydrogel and a filtering membrane made of PVDF with 0.22 μm pores (Durapore<sup>®</sup>, Merck), between two PMMA pieces, as shown in Fig. 1b. An o-ring was incorporated to prevent any leakage of the test water from the region of interest. The upper part of the sample holder featured a 20 mm diameter well where water samples were placed for analysis. This design ensured secure

**Fig. 1** **a** Schematic representation of the PCB with the matrix of gold interdigitated electrodes where the functional thin films were deposited; **b** Scheme of the mounting of the system for heavy metal detection; **c** Scheme of the impedance spectroscopy measurements



containment of the samples within the device during the testing process.

### Electrical characterization and sensing tests

For the sensing tests, water solutions containing cobalt ( $\text{Co}^{2+}$ ) and manganese ( $\text{Mn}^{2+}$ ) ions were placed into the well of the sample holder. The concentration of the solutions varied from 10 up to 100 ppm. Impedance measurements were then conducted for each pair of functionalized electrodes within a sensing unit.

The impedance measurements were performed using a Solartron gain/phase analyzer model 1260A, as shown in Fig. 1c. The measurements utilized a  $50 \text{ mV}_{\text{RMS}}$  excitation signal and swept across the frequency range from 10 MHz down to 0.1 Hz. This frequency range was chosen to capture the impedance response of the sensing device accurately. All measurements were carried out in triplicate, with the samples washed in ultrapure water during 2 h before new exposure to the analyte solutions. For the data analysis, the impedance measured for each analyte and concentration ( $Z_{\text{an}}$ ) was divided by the impedance measured after each washing procedure ( $Z_0$ ), resulting in a impedance ratio ( $Z_{\text{an}}/Z_0$ ) dataset.

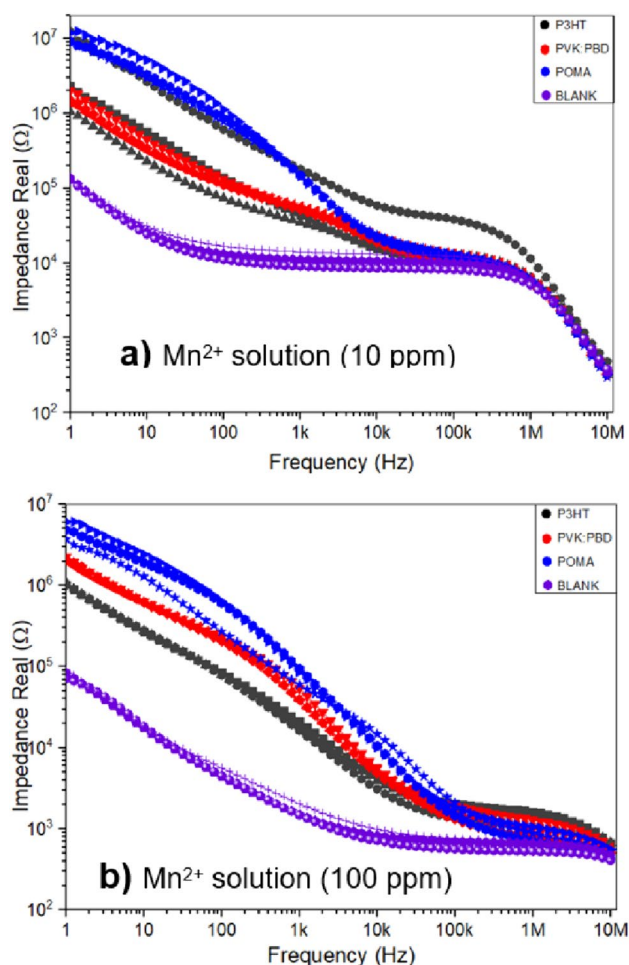
### Data treatment and analysis

The analysis a large number of impedance data can be quite difficult to be performed and we have chosen principal component analysis (PCA) to reduce the dimensionality of the data and facilitate the data observation. Moreover, the direct

use of PCA on impedance data can hinder the analyte discrimination since some frequencies do not contribute significantly to the analysis. Therefore, we used parallel coordinates analysis [17] to filter and select the data used in the PCA analysis. The parallel coordinates technique is used to display multidimensional data into a bidimensional space and to show the correlation of a data distribution with each dimension. The parallel coordinates plots for each unit of the electrode matrix are shown in the supplementary information (SI). The plots show the frequencies which contribute less for the data discrimination, allowing the selection of the most significant data for data discrimination. The initial dataset comprised by 164 components (41 frequencies times 4 electrode units) and was reduced to 57 after parallel coordinates analysis using PEx-Sensors [18, 19]. After the data selection using parallel coordinates analysis, direct PCA analysis was performed on the data, allowing a total dimensionality reduction from 164 to 2 components.

### Results and discussion

The impedance responses of each sensing unit, obtained from the real component of the complex impedance as a function of frequency, are depicted in Fig. 1. Each sensing unit exhibits a unique impedance spectrum when exposed to the analyte ( $\text{Mn}^{2+}$ ). By comparing the spectra shown in Fig. 2a with b, a noticeable difference can be observed when the concentration of the heavy metal is changed from 10 to 100 ppm. This variation in the impedance spectra reflects the



**Fig. 2** Impedance spectra (real component) for the 4-sensor matrix in aqueous solution of  $\text{Mn}^{2+}$  at the concentrations of 10 ppm (a) and 100 ppm (b)

sensitivity of the sensing device to different concentrations of the analyte.

The impedance spectra data obtained from the triplicated measurements for both analytes ( $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$ ) at three different concentrations (10 ppm, 50 ppm, and 100 ppm) were subjected to parallel coordinates analysis followed by PCA using the procedure described in “Data treatment and analysis” section. This procedure allowed us to reduce the multidimensional data into a two-dimensional plot, specifically the principal component 1 (PC1) versus the principal

component 2 (PC2), as illustrated in Fig. 3. By visualizing the data in this manner, we aim to enhance data visualization and facilitate interpretation, enabling clearer differentiation between the analytes and their respective concentrations.

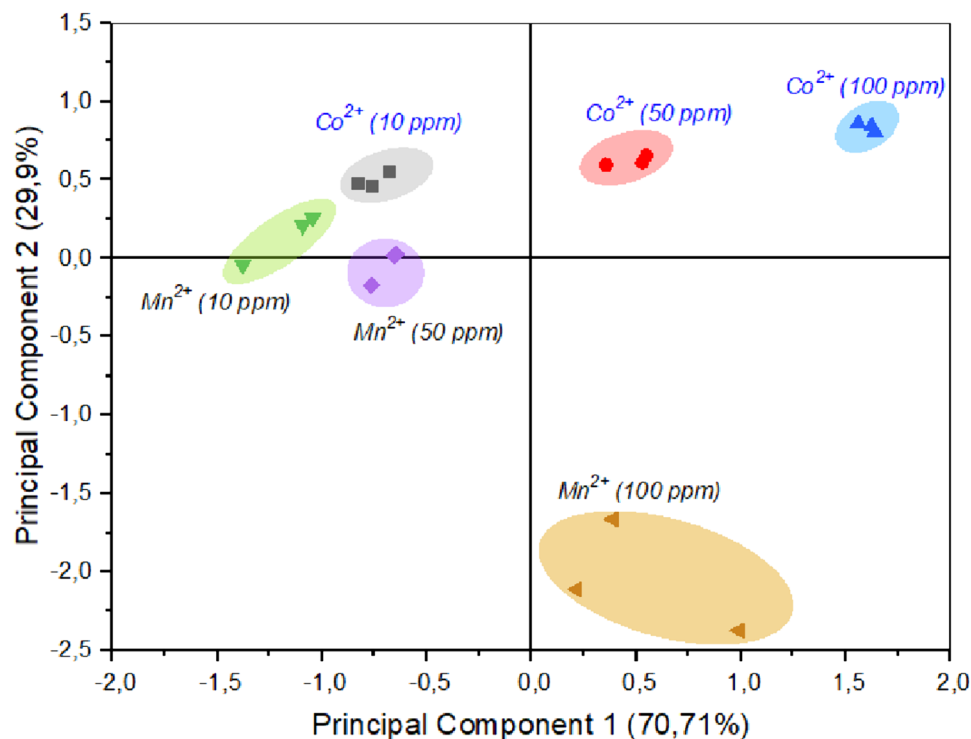
The PCA plot provides valuable insights into the discrimination capabilities of the sensing device. It reveals that the triplicated measurements for each analyte are tightly clustered together in a distinct region, which is noticeably different from the regions occupied by measurements from other analytes and different heavy metal concentrations. This observation suggests that it is indeed possible to discriminate between water samples contaminated with  $\text{Mn}^{2+}$  or  $\text{Co}^{2+}$  ions, even at relatively low concentrations such as 10 ppm. The clear separation of the clusters in the PCA plot indicates the potential of the sensor matrix to accurately identify and differentiate between different analytes and their respective concentrations.

## Conclusions

The present study provides compelling evidence for the feasibility of constructing devices that combine the principles of diffusive gradient thin-film devices with a sensing matrix of functionalized electrodes. These devices have the potential to discriminate and quantify the concentration of heavy metals in water environments. The advancements in the Internet of Things and instrumentation have reached a stage where these devices can be seamlessly integrated with low-cost instruments. These instruments are capable of measuring the impedance response of each sensing unit, performing real-time analysis, wirelessly transmitting the data, and storing it in cloud servers for further analysis.

While it is acknowledged that such systems may not achieve the same level of precision and accuracy as traditional laboratory analysis, they can still serve as powerful tools for sample screening, real-time monitoring, and early alert systems. The ability to quickly screen samples, monitor water environments in real time, and provide early warnings about the presence of heavy metals can greatly enhance environmental monitoring efforts and facilitate prompt actions to mitigate potential risks.

**Fig. 3** Principal component analysis of the impedance spectroscopy results for aqueous solutions of  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$  at different concentrations. Each measurement was taken in triplicate, with washing procedure carried out in between



**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1557/s43580-024-00847-8>.

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**Author contributions** J. B. Cantuária: Investigation, Formal analysis, Writing—original draft. J.V. Mendes: Investigation, Conceptualization. L. Fugikawa-Santos: Writing—review & editing, Writing—original draft, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization.

**Data availability** The data from this study will be immediately available upon reasonable request.

## Declarations

**Conflict of interest** The authors declare no conflict of interests.

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