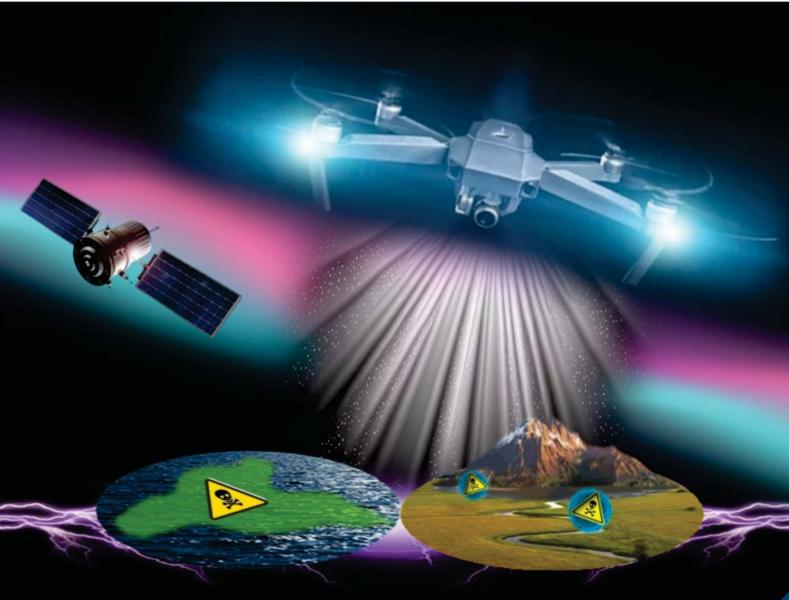
Volume 15 Number 37 7 October 2023 Pages 4789-4988

# Analytical Methods

rsc.li/methods



ISSN 1759-9679



**PAPER** Vagner B. dos Santos *et al.* Lab-on-a-Drone: remote voltammetric analysis of lead in water with real-time data transmission

# Analytical Methods



# PAPER



Cite this: Anal. Methods, 2023, 15, 4827

Received 28th June 2023 Accepted 11th August 2023

DOI: 10.1039/d3ay01088k

rsc.li/methods

# Introduction

Lab-on-a-Drone: remote voltammetric analysis of lead in water with real-time data transmission<sup>†</sup>

João Paulo B. de Almeida,<sup>a</sup> Vinicius de A. Carvalho,<sup>a</sup> Leandro P. da Silva,<sup>a</sup> Maysa L. do Nascimento,<sup>ab</sup> Severino B. de Oliveira, <sup>b</sup> Matheus V. Maia, <sup>c</sup> Willian T. Suarez, <sup>c</sup> Carlos D. Garcia <sup>d</sup> and Vagner B. dos Santos <sup>b</sup> \*<sup>a</sup>

The present work describes a laboratory-on-a-drone (Lab-on-a-Drone) developed to perform in situ detection of contaminants in environmental water samples. Toward this goal, the system was mounted on an unmanned aerial vehicle (UAV) (drone) and remotely controlled via Wi-Fi to acquire a water sample, perform the electrochemical detection step, and then send the voltammetry data to a smartphone. This Lab-on-a-Drone system was also able to recharge its battery using a solar cell, greatly increasing the autonomy of the system, even in the absence of a power line. As a proof of concept, the Lab-on-a-Drone was employed for the detection of Pb<sup>2+</sup> in environmental waters, using a simple electrochemical cell containing a miniaturized screen-printed boron-doped diamond electrode (SP-BDDE) as a working electrode, an Ag/AgCl as a reference electrode, and a graphite ink as a counter electrode. For quantification purposes, analytical curves were constructed covering a concentration range from 1.0  $\mu$ g L<sup>-1</sup> (4.83 nmol L<sup>-1</sup>) to 80.0  $\mu$ g L<sup>-1</sup> (386.10 nmol L<sup>-1</sup>), featuring a detection limit of 0.062  $\mu$ g L<sup>-1</sup> (0.30 nmol L<sup>-1</sup>). The Lab-on-a-Drone was applied to monitor a water reservoir in the Metropolitan Region of Recife, Brazil. To evaluate its performance regarding accuracy and precision, a reference method based on inductively coupled plasma optical emission spectrometry (ICP-OES) was applied, and the results obtained by both methods showed no statistical differences (t-test at 95% confidence level, n = 3). These results represent the first demonstration of the capabilities of an adapted UAV for the quantification of electroactive environmental contaminant using voltammetry, with real-time data transmission. Thus, the Lab-on-a-Drone makes it possible to reach difficult-to-access environmental reserves and to monitor potentially polluting activity in distant water bodies. Thus, this tool can be used by governments and non-profit organizations to monitor environmental waters using fast, low-cost, process autonomy with accurate and precise data useful to decision making.

Population growth and industrial development often increase the demand for natural resources.<sup>1</sup> Among other factors, the consumption of drinking water around the world has recently accelerated and according to the United Nations (UN), the world is currently facing a water crisis.<sup>1</sup> The UN estimates that 3.6 billion people have some type of difficulty in accessing drinking water and that by 2050 this problem will grow by up to 30%.<sup>1</sup> In addition, the report noted that about 80% of industrial and wastewater is currently released into the environment without receiving adequate treatment.<sup>1</sup> Even in developed countries, most pollutants are not eliminated in current water or sewage treatment plants.<sup>1,2</sup> This worrying aspect reveals the urgent need for an efficient and continuous monitoring system to detect the contaminants in water.<sup>2</sup>

Pollutants such as heavy metals constitute a serious environmental concern, and their biological consequences are already well established in the literature.<sup>2</sup> Contaminants, such as Pb<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup>, are not only persistent but can also accumulate in fish and crustaceans and propagate *via* the food chain, leading to several health problems, including various forms of cancer and neural disorders.<sup>2,3</sup> According to the World Health Organization (WHO), the United States Environmental Protection Agency (US-EPA) and the Environment National Council from Brazil (CON-AMA) the tolerable levels of Pb<sup>2+</sup> in surface water are 10, 15 and 30  $\mu$ g L<sup>-1</sup>, respectively.<sup>4</sup> In this context, an efficient water monitoring employing a fast, accurate and precise method is critical to warn environmental agencies regarding potential polluting activities. However, in general, analytical methods for quantification of

<sup>&</sup>lt;sup>a</sup>LIA<sup>3</sup>, (Laboratório de Instrumentação e Automação em Analítica Aplicada) da Universidade Federal de Pernambuco, Recife-PE, Brazil. E-mail: vagner.bsantos@ ufpe.br

<sup>&</sup>lt;sup>b</sup>Universidade Federal Rural de Pernambuco, Recife-PE, Brazil

<sup>°</sup>Universidade Federal de Viçosa, MG, Brazil

<sup>&</sup>lt;sup>d</sup>Clemson University, USA

<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d3ay01088k

these contaminants are time-consuming and require expensive, laborious techniques, and highly qualified professionals.5-7 In addition, when collecting environmental samples, researchers are generally exposed to dangerous places, susceptible to accidents, and there is a possibility of exposure to a range of toxic compounds.5 Thus, to overcome these drawbacks, the use of unmanned aerial vehicles (UAV) represents a safe and efficient option. UAVs are fixed-wing aircrafts with sensors (generally used to avoid collisions) and cameras.8-12 Although increasingly accessible, the cost of most commercially-available UAV place them outside the reach of most low-income communities, where the contaminants are typically discharged. Many of these systems can evaluate chlorophyll levels,13 estimate nutrition of plants,14 detect deforestation,<sup>15</sup> compute urbanization<sup>16</sup> or even identify cracks in concrete structures.17 In addition, these sophisticated UAV need greater flight stability, greater autonomy and the possibility of carrying loads, use multiple rotors like the hexacopter,<sup>8,18</sup> leading to substantial cost increases. Aiming to increase their accessibility, low-cost adaptations have been recently reported in the literature.<sup>13-17</sup> For environmental applications, the main applications using UAV are related to measurements of turbidity, pH, alkalinity, ionic conductivity and chlorophyll, using multiparameter probes.13-17 However, many of these measurements employ analytical methods with limited selectivity.5,19 Thus, the miniaturization of additional instrumentation could open additional avenues to monitor specific contaminants.<sup>20,21</sup>

Among other alternatives, Lab-on-a-Chip (LOC) devices can provide some competitive advantages over traditional analytical platforms, such as the possibility to perform sampling, filtration, pre-concentration, separation, and detection in a single device.<sup>20,21</sup> In addition, LOC devices can be fabricated using a variety of substrates including paper,<sup>22,23</sup> glass,<sup>24</sup> polymers,<sup>25</sup> and ceramics<sup>26-28</sup> using various optical<sup>29</sup> or electrochemical means.<sup>30-35</sup> As an extension of this idea, this paper presents a Lab-on-a-Drone, a flying unit capable of performing in situ electrochemical detection. The system uses non-toxic sensors based on screen-printed boron-doped diamond electrodes (SP-BDDE) and is powered using a battery, which was recharged using an integrated solar panel. To the best of our knowledge, this is the first report describing a Lab-on-a-Drone capable of performing remote voltammetric detection of contaminants for environmental applications.

# **Experimental**

#### Chemicals and solutions

The Pb<sup>2+</sup> stock solutions were prepared from Pb(CH<sub>3</sub>COO)<sub>2</sub> (Sigma-Aldrich, Brazil) in acetic acid/acetate buffer solution pH 4.5. A solution of 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> (Dinâmica, Brazil) was used to activate the surface of the boron doped diamond electrodes (BDDE). To check the electrochemical response of the pre-treated BDDE, a solution of 1.0 mmol L<sup>-1</sup> K<sub>4</sub>[Fe(CN)<sub>6</sub>] prepared in 0.1 mol L<sup>-1</sup> KCl was employed. To study possible interferences in the determination of Pb<sup>2+</sup> in water samples, the following chemical compounds were used: BaCl<sub>2</sub>, Na<sub>3</sub>PO<sub>4</sub> (Neon, Brazil), CaCO<sub>3</sub>, KCl, KI, KNO<sub>3</sub> (Dinâmica, Brazil), CaCl<sub>2</sub>, FeCl<sub>2</sub> (Vetec, Brazil). All reagents employed were of analytical grade and used as received.

The 0.1 mol  $L^{-1}$  of stock solution of Pb(CH<sub>3</sub>COO)<sub>2</sub> was standardized employing a titration with 0.1 mol  $L^{-1}$  KI and a correction factor of 1.01 was obtained.

#### Instrumentation and apparatus

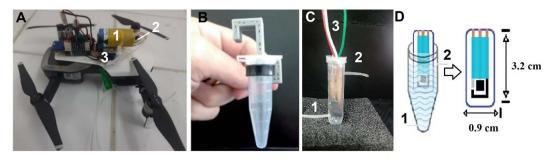
The Milli-Q (Direct-Q) ultrapure water (Merck, Brazil) (resistivity  $\geq$ 18 M $\Omega$  cm) was used to prepare the solutions. A HANNA/HI 2221 pH meter with a combined glass electrode was used to measure the pH of the solutions. A potentiostat/galvanostat (PGSTAT 302N) with NOVA 11.1 software (Metrohm Autolab, Switzerland) was used in the laboratory to perform the chronopotentiometry, cyclic voltammetry (CV), square wave anodic stripping voltammetry (SWASV) and differential pulse anodic stripping voltammetry (DPASV) experiments. The EmsStatPico 1 (PalmSens, USA) miniaturized potentiostat was controlled using PStrace 5.11 software or an algorithm in C language developed to be driven by a MKRZero 1010 (Arduino, Germany) microcontroller. An inductively coupled plasma optical emission spectrometer (Optima 7000 DV model) with a charge coupled device array detection system (PerkinElmer, USA), argon-purged (99.999% purity) (White Martins, Brazil) optics and Echelle optics were also used. For ICP-OES analysis, all water samples were filtered using 0.48 µm PTFE syringe filter and treated with 5.0% HNO3.

#### Lab-on-a-Drone instrumentation

An electronic circuit was developed to control the power supply of the water sampling and the electrochemical system of the Lab-on-a-Drone. The electronic circuit was based on the microcontroller MKRZero 1010 and was designed to provide enough power to drive the micropump (Aliexpress, China, 38 mm  $\times$  21 mm), the microvalve (Filipeflop, Brazil, 18 mm  $\times$ 14 mm), and the electrochemical detection system (see Fig. S1†). To control these peripherals and the miniaturized potentiostat, an algorithm was also developed using C language.<sup>5,7</sup>

During normal operation, a three-way solenoid microvalve directs the water sampled to the lightweight polypropylene bottles (2.0 mL) used as reservoirs for the electrochemical cell (EC). The water samples enter through the base of the sampling bottle and exit through a 1 cm of polypropylene tube (0.8 mm i.d.) inserted in the top of the EC to eliminate few  $\mu$ L of the excess of sample, Fig. 1. After sampling, air is pumping leaving the sampling probe empty for a new sampling. This probe is a polypropylene tube with an internal diameter of 0.8 mm and a length of 1.5 m, connected to a hollow copper tube at the end (30 mm × 5 mm i.d.). This procedure presented no cross-contamination as previously reposted.<sup>5,19</sup> To replace the ECs, a new EC is connected to the polypropylene tube (0.8 mm i.d.) by an opening in its base and the drain is connected in its upper side without any leakage, because the tubes are forced in.

The water sampling flasks were coupled to the UAV using a PLA (polylactic acid) support made using a 3D printer (Ender 3D pro, Creality). To overcome problems associated with low batteries during the *in situ* analysis, a solar cell system was used to recharge them. This solar system consists of solar plates with



**Fig. 1** The sampling system and electrochemical detection were attached to the Mavic air UAV (A). The 9 V battery (1), micropump, at the back of the battery (2), miniaturized solenoid valve (3) (A). The electronic circuit and the Arduino MKR 1010 board are below the micropump, tube and battery. The sample vial is supported by a plastic clip that is attached to the front rods of the aircraft (B). Sample vial as an electrochemical cell with inlet (1) and outlet flow (2), and electric contact between the SP-BDDE and the miniaturized potentiostat (3) (C). Schematic picture of the SP-BDDE is attached to the 2.0 mL electrochemical cell with inlet (1) and outlet flow (2) (D).

60 W, a stationary battery of 12 V 100 A  $h^{-1}$ , a solar charge controller of 12 V, and an inverter module 12 V DAC as a renewable energy system to increase the autonomy of the system. This solar system was able to charge both the sampling system and the UAV batteries during use (Fig. S2†).

#### Voltammetric detection

Conventional three-electrode cells of 10 mL containing a 25 mm<sup>2</sup> BDDE with 6000 ppm of boron (Boromond, China) as a working electrode, Ag/AgCl (KCl 3.0 mol  $L^{-1}$ ) as a reference electrode, and 1 cm<sup>2</sup> platinum as a counter electrode were used for analysis in the laboratory. For *in situ* analysis, the BDDE was soldered onto a copper plate (5.0 mm  $\times$  10.0 mm) and conductive graphite ink (Nilton, Brazil) and Ag paste (Mcn Dj002; Mechanic, China) were employed. This miniaturized 3electrode was inserted into a sampling flask (2.0 mL) to obtain a compact and lightweight electrochemical cell to be coupled to the adapted UAV. The BDDE was electrochemical treated by applying  $\pm 0.5$  mA mm<sup>-2</sup> of density current for 180 s for an anodic and cathodic treatment using a 0.5 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> solution as a supporting electrolyte. To check the electrochemical response of the pre-treated BDDE and to prepare a Ag/ AgCl stable reference electrode, 50 cyclic voltammograms were performed ranging from -1.0 V to +1.0 V vs. Ag/AgCl at a solution of 1.0 mmol  $L^{-1}$  K<sub>4</sub>Fe(CN)<sub>6</sub>. SWASV was performed for Pb<sup>2+</sup> quantification in acetic acid/acetate buffer (pH 4.5), using a deposition potential of -1.4 V for 120 s, followed by SW sweep (50 mV of amplitude, 5 mV of increment and frequency of 10 Hz).6 These voltammetry parameters and optimized supporting electrodes were adapted from previous reports<sup>6,7</sup> to be used in the portable potentiostat. Using these optimized conditions, a calibration curve for Pb<sup>2+</sup> quantification was developed.

#### Lab-on-a-Drone application

Procedures involving UAVs begin with updating the aircraft's firmware, and then compass calibration through communication<sup>36,37</sup> with at least 7 satellites using the DJI Go 4 procedures, as defined by the manufacturer DJI (USA). The samples were collected at Duas Una Dam, in Jaboatão dos Guararapes, a metropolitan region of Recife-PE-Brazil. The quantification of Pb<sup>2+</sup> ions by SWASV was used as a proof of concept of the Lab-ona-Drone with electrochemical detection. No pretreatment of the water samples was necessary, just a simple on-line filtration performed using a 0.45 µm PTFE filter connected at the end of the sampling probe.<sup>19</sup> During the water sampling, the filter was not clogged because the surface water collected did not present solid materials. Just one filter was used for each water sampled to avoid cross-contamination.<sup>5,19</sup> For voltammetric detection the SP-BDDE was employed, *via* a miniaturized bipotentiostat attached to the UAV. For this, an algorithm in C language was recorded in the memory of the microcontroller to perform CV and SWASV to obtain data on applied potential and sampled current. Moreover, in this algorithm, the potential and current peak are shown also the concentration in µg L<sup>-1</sup> of Pb<sup>2+</sup> using the linear equation of the analytical curve.

The basic algorithms loaded on the microcontroller were able to execute the CV, SWASV and DPASV analysis, code that is available from the manufacturer by METHOD SCRIPT. However, several modifications were performed in the source code, to enable Wi-Fi transmission, optimize the amount of data transmitted, and to trigger both the water sampling system and the start of the electrochemical analysis. In addition, the code enabled the identification of the peak current, peak potential, and the calculation of the Pb<sup>2+</sup> concentration. Relevant sections of the algorithm, developed to perform the water sampling, are available in the ESI (Scheme S1<sup>†</sup>). The algorithms for CV and SWASV are also presented in schemes from S2 to S5.† The DPASV also was developed as another possible voltammetric method, with optimized data transmission (Scheme S6<sup>†</sup>). Due to its higher sensitivity, only the data collected via SWASV were used for quantitative purposes.6,7 However, to show the advantages of the Lab-on-a-Drone over recent publications,38 its high versatility, and functionally, it was able to perform the CV and DPASV.7 Thus, the CV was used to check the BDD performance and DPASV was developed due to being widely used in electroanalytical analysis.7

#### Validation of the electrochemical detection used in the Labon-a-Drone

The *in situ* quantification of  $Pb^{2+}$  using the Lab-on-a-Drone was validated in the laboratory using an ICP-OES method. Results

were compared using a paired *t*-test, at a 95% confidence level. The interference test employing ions commonly found in environmental waters was performed employing a concentration of 30 µg L<sup>-1</sup> of Pb<sup>2+</sup> ions for 1 : 100 (analyte : interference) ratio.<sup>6,7</sup> The level of interference was analyzed considering the relative variation of the  $I_p$  (obtained with 30 µg L<sup>-1</sup> of Pb<sup>2+</sup>) with/ without the corresponding species. The recovery tests were performed at levels of 10, 20 and 30 µg L<sup>-1</sup>, using diluted spiked samples. The limit of detection (LD) and the limit of quantification (LQ) were calculated for the SWASV using the following equations: LD = 3s/m and LQ = 10s/m, where *s* is the standard deviation of the blank solution and *m* is the slope of the analytical curve.

#### Fortification of samples and SWASV and ICP-OES method

After performing the sampling and voltammetric analysis, the aircraft returns to home, and the electrochemical cell (EC) with the samples were sealed with paraffin film and stored in Styrofoam with ice to be analyzed in the laboratory by ICP-OES or spiked using micropipette. If the Pb<sup>2+</sup> concentration is lower than the LD for SWASV, the sample is spiked with a concentration near to 30  $\mu$ g L<sup>-1</sup> and the SWASV is again performed. An on-line spike automated method could be performed as reported,6 however, the manual procedure was performed. The same waters were again spiked to obtain the concentrations of  $\ensuremath{\text{Pb}}^{2+}$  to be measured by ICP-OES and the SWASV method for comparison purposes. For this purpose, each sample was spiked to obtain a Pb<sup>2+</sup> concentration fitting into linear from 0.1 to 10.0 mg  $L^{-1}$  for the ICP-OES method. After adequate dilution using acid/acetic buffer solution pH 4.5, the analyses were performed using SWASV to obtain concentrations of Pb<sup>2+</sup> in spiked water samples, and thus, concentrations fitting into the linear range from 1.0 to 80  $\mu$ g L<sup>-1</sup>.<sup>19,39</sup>

# **Results and discussion**

#### Electronic circuit of the Lab-on-a-Drone

The electronic circuit developed to carry out surface water sampling is represented in Fig. S1,† it is composed of a microcontroller (Arduino MKRZERO 1010, US\$ 20), which is responsible for controlling the activation of a three-way solenoid microvalve (S) and a micropump diaphragm (M), powered by a ULN2003 integrated circuit used to increase the power transferred by the microcontroller. All electronic circuits are controlled by a 9 V rechargeable battery (4500 mA h<sup>-1</sup>).

An LM 7805 voltage regulator was used to supply 5 V to the electronic circuit, except the ULN20003 device powered by 9 V from battery. The water sampling system had a cost of (US\$ 30). To perform *in situ* electrochemical measurements, the EmStat-Pico1 bipotentiostat (18 mm  $\times$  30 mm  $\times$  2.6 mm) with only 5 g was used (US\$ 1000). This potentiostat was controlled by the microcontroller using an embedded Wi-Fi transmission module. The module was also responsible for the data transmission to a smartphone using the same IP and a web page (Fig. S1†). It is important to mention that while the electrochemical system represents a significant fraction of the overall

cost of the system, it could be replaced by other systems with lower cost reported in the literature.<sup>7,35</sup>

The sampling system allows a flow rate of 30.0 mL min<sup>-1</sup>, enough to require only 7 s to fill the sampling probe (3 mL) and the 0.5 mL of the sample flask employed as electrochemical cell (Eppendorf®). The power consumption of the complete system was approximately 0.3 A, being activated only during the water sampling, greatly reducing the energy consumption of the prototype. All adaptations on the UAV added only 110 g.

# Adaptation of the sampling and detection system to the commercial UAV

To carry out the surface water sampling, an UAV (Mavic Air manufactured by DJI) was purchased. It is a quadcopter with  $168 \times 184 \times 64$  mm and 430 g (shown in Fig. 1). The aircraft can reach a speed of 68.4 km h<sup>-1</sup> with an autonomy of 21 min of flight time and has a cost of US\$ 1000. After integrating the analytical systems, the Lab-on-a-Drone was tested and the aircraft did not present stability issues during at least 20 min of flight. A battery charging system was made using solar-type renewable energy (Sollaris Engenharia, Brazil). This solar system charged the batteries of the UAV and the collection/ detection system, with this, energy autonomy was guaranteed in the UAV's flight conditions. At only 15 min the UAV battery was changed on a sunny day (25–33 °C), Fig. 2 and S2.† The cost of all systems described was around US\$ 2870.

# Programming the Lab-on-a-Drone to perform water sampling, electrochemical detection, and data transmission for *in situ* analysis

The C language was chosen to develop open-source code.<sup>6,35</sup> All commands to activate the M and S to collect the water sample were carried out using Wi-Fi of a smartphone only when the aircraft reached the first sampling point. After 7 s, the sampling probe is filled with the sampling flask bottle with 0.5 mL of sample and the automated voltammetry is performed employing CV, SWASV, DPASV with the data transmitted in real-time to the smartphone used to control the aircraft. Next, the sampling system is switched ON to pump the first sample collected to the electrochemical cell, leaving the aircraft ready to move to the next sampling point. At this point, operators have the option to collect other water sample and dispense it to electrochemical cell-2, containing other SP-BDDE. However, for this sequential sampling (without bringing back the UAV), no filter was used, thus minimizing cross-contamination. However, for applications such as near to the beach, the corals, the filter could clogged because of the presence of particles in suspension with diameter higher than the polypropylene tube (0.8 mm i.d.). To overcame this drawback, a simple solution could be a tube with a high internal diameter, as previously reported.<sup>5,19</sup> Hence, the current values generated upon application of potential were transmitted via Wi-Fi by the microcontroller to a smartphone for real-time decision making.7 The Wi-Fi communication between the Lab-on-a-Drone and the smartphone was adequate within approximately 30 m, enabling the control of the sampling system, analysis and data collection without

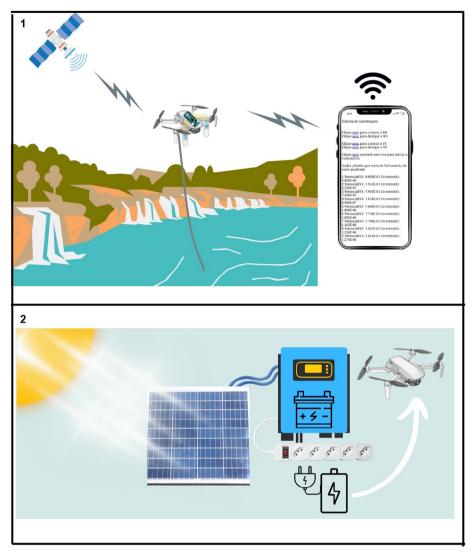


Fig. 2 The Lab-on-a-Drone for in situ electrochemical analysis. Wireless communication (1). Solar system (2).

interruption. Other possibilities are to save the data using a memory card or to save the data in cloud, or starting the data transmission only near to the Wi-Fi signal, *i.e.* 30 m.

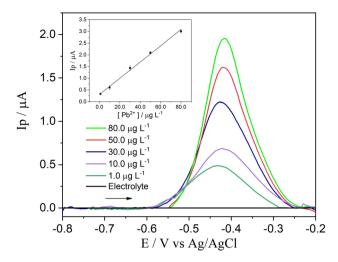
#### Voltammetric data obtained employing the Lab-on-a-Drone

Prior to the *in situ* detection of Pb<sup>2+</sup>, the voltammetric response of the system was evaluated using 1.0 mmol  $L^{-1}$  K<sub>4</sub>Fe(CN)<sub>6</sub> in KCl 0.1 mol  $L^{-1}$ . In these cases, the electric current in  $\mu$ A and potential data in V were sent *via* Wi-Fi in real-time to the smartphone, showing well-defined peaks and reversible behavior (Fig. S3 and Table S1†).

The SWASV technique was selected to perform the electrochemical quantification for Pb<sup>2+</sup> ions using the Lab-on-a-Drone (Fig. S4<sup>†</sup>). The environmental waters were collected in Duas Una Dam, in Jaboatão dos Guararapes-PE-Brazil (Fig. S5<sup>†</sup>). The UAV was employed based on the visual line of sight to be a secure UAV flight according to the ANAC (National Civil Aviation Agency) from Brazil.<sup>5</sup> Thus, a probe with 1.5 m with a copper tube in the end was used to collect the surface sample, and the sampling depth ranged from 0.5 to 1.0 m for a secure procedure.

As previously noted, preliminary experiments performed on site allowed demonstrating the functionality of the device but the Pb<sup>2+</sup> was not detected or the concentration was above the LD. Thus, water samples were fortified with a standard solution (7 mg L<sup>-1</sup>) to obtain Pb<sup>2+</sup> concentrations in the 0.1 to 10.0 mg L<sup>-1</sup> range (suitable for the ICP-OES method). Spiked samples in the 1.0 to 80.0 µg L<sup>-1</sup> range were also prepared in acetate buffer (pH 4.5, used as support electrolyte) to measure them *via* SWASV. This procedure was needed due to the different sensitivity of the methods.<sup>39</sup> The voltammogram from this analysis can be seen in Fig. 3 with the concentrations of the spiked samples presented in Table S2.<sup>†</sup>

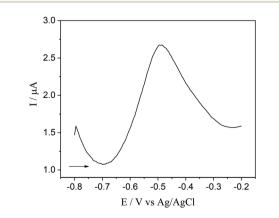
Before sending the Lab-on-a-Drone, the analytical curve was developed in the laboratory, and only the water samples were analyzed *in situ*. Thus, the calibration curve was saved in the memory of the microcontroller, and the current measured at potential of -0.49 V (peak potential) *vs.* Ag/AgCl was converted



**Fig. 3** Analytical curve to detect Pb<sup>2+</sup> in environmental water samples in the range from 1.0 to 80.0 µg L<sup>-1</sup> employing acetic acetate/acid acetic buffer solution 0.5 mol L<sup>-1</sup> pH 4.5 using SWASV at SP-BDDE embedded in the Lab-on-a-Drone. SWASV parameters: deposition potential = -1.4 V, time of deposition = 120 s, f = 10 Hz, a = 50 mV,  $\Delta E_s = 5$  mV.  $I_p/(\mu A) = 0.302 \pm 0.033 + 0.035 \pm 0.001 \times [Pb^{2+}]/(\mu g L^{-1})$ ,  $R^2 = 0.9979$ . All voltammograms were baseline corrected.

to concentration of  $Pb^{2+}$ , using the calibration curve presented in Fig. 3 (inset). This procedure was automatically performed using the Lab-on-a-Drone, employing the algorithm presented in Schemes S2 and S3† and leading to the SWASV data presented in Fig. 4 and in Table S3.† As it was expected, a welldefined peak corresponding to the oxidation of the Pb<sup>2+</sup> electrodeposited on the electrode was always observed.

The results shown in Table S2<sup>†</sup> and Fig. 4 not only demonstrated the capacity of the Lab-on-a-Drone to perform remote analysis but also presented a satisfactory accuracy and precision, with respect to the data acquired using the ICP-OES method.



**Fig. 4** Voltammogram of SWASV regards the data transmitted by the Lab-on-a-Drone presented in Table S3<sup>+</sup> for analysis of a spiked water sample; the peak potential of ( $E_p = -0.4987$  V), peak current ( $I_p = -2.68 \mu$ A) were selected using the algorithm developed and the concentration 30 µg L<sup>-1</sup> of Pb<sup>2+</sup> was obtained in real time. SWASV parameters: deposition potential = -1.4 V, time of deposition = 120 s, *f* = 10 Hz, *a* = 50 mV,  $\Delta E_s = 5$  mV. Data without baseline correction.

Table 1 Recovery test using the Lab-on-a-Drone with electrochemical detection of  $Pb^{2+}$  in environmental water samples

$[Pb^{2+}]$ added (µg L <sup>-1</sup> )	$[\mathrm{Pb}^{2\text{+}}]$ found (µg $\mathrm{L}^{-1}$ )	Recovery (%)
10.00	$10.66 \pm 1.01$	106.6
20.00	$19.10 \pm 1.56$	95.5
30.00	$31.71 \pm 1.28$	105.7
10.00	$9.57 \pm 1.43$	95.7
20.00	$20.04 \pm 1.17$	100.2
30.00	$27.65 \pm 2.19$	92.2
10.00	$9.52\pm0.08$	95.2
20.00	$21.00 \pm 2.65$	105.0
30.00	$32.96 \pm 0.83$	109.9
	10.00 20.00 30.00 10.00 20.00 30.00 10.00 20.00	

The linear range of 1.0 to 80.0  $\mu$ g L<sup>-1</sup> and a LD of 0.062  $\mu$ g  $L^{-1}$  allow to quantifying low concentrations of  $Pb^{2+}$  ions in environmental waters at levels above the accepted by environmental protection agencies such as US-EPA (15  $\mu$ g L<sup>-1</sup>) and CONAMA (10  $\mu$ g L<sup>-1</sup> for classes I and 30  $\mu$ g L<sup>-1</sup> for classes II). Moreover, the accuracy of the system was evaluated by performing recovery tests, for additions of 10  $\mu$ g L<sup>-1</sup>, 20.0  $\mu$ g L<sup>-1</sup> and 30  $\mu$ g L<sup>-1</sup> (see results in Table 1). These results showed recovery values in the 92% to 110% range, which were considered acceptable for the proposed application. In addition, it is worth mentioning that no interference from any of the selected metal ions was observed, including K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Fe<sup>2+</sup>,  $Cu^{2+}$ ,  $SO_4^{2-}$ ,  $PO_4^{3-}$ ,  $CO_3^{2-}$ ,  $Cl^-$  and  $NO_3^-$ , Table S4.<sup>†</sup> Moreover, DPASV data presented in Table S5 and Fig. S6<sup>†</sup> referred to a spiked water sample with 65  $\mu$ g L<sup>-1</sup> of Pb<sup>2+</sup> measured and transmitted using the Lab-on-a-Drone to a smartphone was obtained to show the versatility of the Lab-on-a-Drone.

### Conclusions

The methodology developed using a microcontroller to control the potentiostat allows in-flight detection with the (UAV), with a spatial and temporal analysis for monitoring environmental waters. This Lab-on-a-Drone allows acquiring fast, low cost, accurate and precise information regarding potentially toxic elements in environmental water. The stability of the signal transmitted was observed, and information of voltammetry data and information of Pb<sup>2+</sup> concentration as fast as to make a decision about environmental contamination.

The total cost of the water sampling and electrochemical system and is a very attractive feature for professionals involved in water sampling. The results obtained show an environmental tool with a high degree of innovation and technology in terms of monitoring water resources, with the possibility of large-scale production. The Lab-on-a-Drone with electrochemical detection was developed as a platform that could be used to couple additional sensors in the near future.

### Author contributions

João Paulo B. de Almeida – data curation, formal analysis, methodology, validation, and writing – original. Vinícius de A.

#### Paper

Carvalho – data curation, formal analysis, methodology, validation. Leandro Paulo – data curation, formal analysis, methodology. Maysa Nascimento – investigation, visualization, and writing – review & editing. Severino Carlos-investigation, project, resources, visualization, and writing – review & editing. Willian T Suarez – investigation, project, resources, visualization, and writing – review & editing. Carlos D. Garcia – resources, visualization, and writing – review & editing. Vagner B. dos Santos – conceptualization, data curation, funding acquisition, investigation, project, administration, resources, supervision, and writing – original and review & editing.

# Conflicts of interest

There are no conflicts to declare.

# Acknowledgements

This work was supported by CNPq (grant number: 421147/2018-0), FACEPE (APQ-0942-1.06/22 and APQ-0413-1.06/21), and FAPEMIG (APQ-01889-21). The authors are grateful to CNPq, FACEPE and CAPES for the fellowships provided in support of this research.

## References

- 1 ONU NEWS, https://unric.org/pt/agua/, accessed April 2023.
- M. Bonsignore, D. S. Manta, S. Mirto, E. M. Quinci, F. Ape, V. Montalto, M. Gristina, A. Traina and M. Sprovieri, *Ecotoxicol. Environ. Saf.*, 2018, 162, 554.
- 3 M. Wahiduzzaman, M. M. Islam, A. H. F. Sikder and Z. Parveen, *Biol. Trace Elem. Res.*, 2022, **200**, 3854.
- 4 CONAMA, https://www.gov.br/icmbio/pt-br, accessed April 2023.
- 5 J. Neto, I. Resque, R. Avelino, V. Santos, L. Leite, L. Cesar, P. da S. Belo, J. Albuquerque and J. de L. Filho, *Quim. Nova*, 2022, **45**, 734.
- 6 V. B. Santos, E. L. Fava, O. D. P. Neto, S. R. Bianchi, R. C. Faria and O. F. Filho, *Anal. Methods*, 2014, **6**, 8526.
- 7 V. B. Santos, E. L. Fava, N. S. de M. Curi, R. C. Faria, T. B. Guerreiro and O. F. Filho, *Anal. Methods*, 2015, 7, 3105.
- 8 J. P. Ore, S. Elbaum, A. Burgin, B. Zhao and C. Detweiler, *Field and Service Robotics*, 2015, p. 137.
- 9 B. P. Banerjee, S. Raval, T. J. Maslin and W. Timms, *Int. J. Min., Reclam. Environ.*, 2020, **34**, 385.
- 10 H. Doi, Y. Akamatsu, Y. Watanabe, M. Goto, R. Inui, I. Katano, M. Nagano, T. Takahara and T. Minamoto, *Limnol. Oceanogr.: Methods*, 2017, 15, 939.
- 11 C. Koparan, A. Koc, C. Privette and C. Sawyer, *Water*, 2019, **11**, 604.
- 12 T. Villa, F. Gonzalez, B. Miljievic, Z. Ristovski and L. Morawska, *Sensors*, 2016, **16**, 1072.
- 13 X. Zhao, Y. Li, Y. Chen, X. Qiao and W. Qian, *Drones*, 2022, 7, 2.
- 14 K. Montgomery, J. Henry, M. Vann, B. E. Whipker, A. Huseth and H. Mitasova, *Drones*, 2020, 4, 36.

- 15 T. A. Ouattara, V. C. J. Sokeng, I. C. Z. Bi, K. F. Kouamé, C. Grinand and R. Vaudry, *Drones*, 2022, **6**, 83.
- 16 C. Gevaert, R. Sliuzas, C. Persello and G. Vosselman, *ISPRS Int. J. Geoinf.*, 2018, 7, 91.
- 17 H. Kim, J. Lee, E. Ahn, S. Cho, M. Shin and S. H. Sim, *Sensors*, 2017, **17**, 2052.
- 18 J. Benson, R. Hanlon, T. Seifried, P. Baloh, C. Powers, H. Grothe and D. Schmale, *Water*, 2019, 11, 157.
- 19 J. C. D. Neto, V. B. Santos, S. C. Bezerra de Oliveira, W. T. Suarez and J. L. de Oliveira, *Anal. Methods*, 2022, 14, 1311.
- 20 S. C. Terry, J. H. Jerman and J. B. Angell, *IEEE Trans. Electron Devices*, 1979, **26**, 1880.
- 21 A. Manz, N. Graber and H. M. Widmer, *Sens. Actuators, B*, 1990, **1**, 244.
- 22 R. Monošík, V. B. dos Santos and L. Angnes, *Anal. Methods*, 2015, 7, 8177.
- 23 A. Economou, C. Kokkinos and M. Prodromidis, *Lab Chip*, 2018, **18**, 1812.
- 24 A. Schaap, T. Rohrlack and Y. Bellouard, *Lab Chip*, 2012, **12**, 1527.
- 25 J. C. G. Moreno, I. C. Barral, S. Ibeas, J. M. García, D. Granès, N. Marchet and S. Vallejos, *ACS Appl. Mater. Interfaces*, 2023, 15, 16055.
- 26 D. S. Dkhar, R. Kumari, S. J. Malode, N. P. Shetti and P. Chandra, *J. Pharm. Biomed. Anal.*, 2023, **223**, 115120.
- 27 A. Priye, S. Wong, Y. Bi, M. Carpio, J. Chang, M. Coen, D. Cope, J. Harris, J. Johnson, A. Keller, R. Lim, S. Lu, A. Millard, A. Pangelinan, N. Patel, L. Smith, K. Chan and V. M. Ugaz, *Anal. Chem.*, 2016, **88**, 4651.
- 28 W. T. Suarez, O. D. P. Neto, V. B. Santos, A. R. de A. Nogueira, R. C. Faria, O. F. Filho, M. Puyol and J. Alonso, *Anal. Bioanal. Chem.*, 2010, **398**, 1525.
- 29 L. A. García-Hernández, E. Martínez-Martínez, D. Pazos-Solís, J. Aguado-Preciado, A. Dutt, A. U. Chávez-Ramírez, B. Korgel, A. Sharma and G. Oza, *Biosensors*, 2023, 13, 439.
- 30 S. Srikanth, U. S. Jayapiriya, S. K. Dubey, A. Javed and S. Goel, *iScience*, 2022, **25**, 105388.
- 31 D. Desagani, S. Kleiman, T. Zagardan and H. Ben-Yoav, *Chemosensors*, 2023, **11**, 283.
- 32 N. Azizipour, R. Avazpour, D. H. Rosenzweig, M. Sawan and A. Ajji, *Micromachines*, 2020, **11**, 599.
- 33 A. I. Muñoz-Martínez, O. I. G. Peña, J. Colomer-Farrarons, J. M. Rodríguez-Delgado, A. Ávila-Ortega and G. Dieck-Assad, *Sensors*, 2018, 18, 4490.
- 34 S. Nantaphol, R. B. Channon, T. Kondo, W. Siangproh, O. Chailapakul and C. S. Henry, *Anal. Chem.*, 2017, 89, 4100.
- 35 C. Koparan, A. Koc, C. Privette and C. Sawyer, *Water*, 2018, **10**, 264.
- 36 H. T. Lally, I. O'Connor, O. P. Jensen and C. T. Graham, *Sci. Total Environ.*, 2019, 670, 569.
- 37 J. I. L. da Silva, V. B. Santos, C. A. Neves and J. P. I. de Souza, *Chem. Pap.*, 2021, 75, 1055.
- 38 L. Ayres, J. Brooks, K. Whitehead and C. D. Garcia, Anal. Chem., 2022, 94, 16847.
- 39 C. Koparan, A. B. Koc, C. V. Privette and C. B. Sawyer, *Drones*, 2020, **4**, 5.