INTRODUCTION

One of the most challenging aspects concerning metal pollution of water sources is field monitoring of environmental samples (Santos et al., 2017; Li et al., 2015; Moraes, Gonçalves, & Pereira, 2018; Wang et al., 2014). Particular interest is developed regarding the pollution caused by lead (Pb), taking into account public concern and medical data about related risks to human health and environment (Wani, Ara, & Usmani, 2015). For instance, lead is known to have diverse negative impacts on children related to cognitive development, hearing function, growth, nerve conduction, haemoglobin synthesis; lead also holds adverse effects in adults like abdominal pain, anaemia, kidney failure, brain disorders, hypertension or male infertility (Mitra, Sharma, Purohit, & Sharma, 2017; Moriarity, Harris, & Cox, 2014). More alarming, blood lead levels above 100 µg L\(^{-1}\) (ppb) can be lethal for both children and adults (Triantafyllidou & Edwards, 2012).

Powerful analytical techniques, like inductively coupled plasma (ICP) or atomic absorption spectrophotometry (AAS), even though being reliable and sensitive are often inconvenient for on-site lead detection due to price and lack of portability. On the other hand, electroanalytical devices are portable and straightforward alternatives (Lu et al., 2018). Indeed, primordial voltammetric techniques, like polarography with its Hg electrode, started precisely by metal determination in aqueous solutions (Barek & Zima, 2003).
Nowadays, detection of metals in water can be achieved with a variety of commercial screen-printed electrodes (Honeychurch & Hart, 2003). Despite all the amazing qualities of these electrodes, they are often too expensive for large-scale use in low-income countries, in particular considering shipping costs. Moreover, it is precisely in these locations where water analysis is most needed in many cases. Although there are many works in the existing literature using electrodes containing graphene (Gan & Hu, 2011), including some applied in the electroanalysis of lead (Zuo et al., 2019), there seem to be no works concerning the electroanalysis of lead making use of laser-scribed graphene. Robust composite electrodes can provide necessary levels of detection varying from ppm to the exceptional ppt range. Despite their good performance, the complexity behind their build-up and the fact that they are not disposable make them difficult for on-site application. Laser-scribed graphene is decade old technology (El-Kady, Strong, Dubin, & Kaner, 2012; Strong et al., 2012) that demonstrates that is possible to in situ produce graphene by relatively low-cost lasers (Lee, Kim, & Yoon, 2018; Zhang et al., 2019). This work aims to show the possibility of employing a low-cost laser-pyrolysed paper electrodes (LPPEs), produced with a commercially available CO₂ laser and cardboard, in the voltammetric determination of Pb.

2 | EXPERIMENTAL

2.1 | Chemicals and samples

All reagents were of analytical grade and were used without further purification. Hydrochloric acid (HCl) solutions were prepared from the concentrated acid (CAQ), and lead(II) and zinc(II) solutions were prepared from salts lead nitrate (Pb(NO₃)₂ (Casa Americana) and zinc sulphate heptahydrate (Zn(SO₄)₂·7H₂O (Sigma Aldrich), respectively. All aqueous solutions were prepared using ultrapure water with resistance not <18.2 MΩ cm at 298 K.

Paper was acquired in a local office retail store, a 594 × 420 mm sheet costed R$3.20 (i.e. ca. US$0.60 or 0.50€).

2.2 | Fabrication of laser-pyrolysed electrodes

The LPPEs used in this study were fabricated using a CO₂ laser cutting system—WS 9060C (WorkSpecial). The optimized scribing parameters were as follows: laser speed of 16.5 mm s⁻¹, laser power on 12%, interval distance between the scribing lines of 0.08 mm, working distance 13 mm. Silver grids were painted on the connection pads of the electrodes to improve their electrical conductivity. Also, the silicone glue barrier was printed perpendicular to electrodes to prevent direct contact between the liquid and the silver grids. Finally, to overpass the common electrochemical reference electrode instability in paper-based devices, silver ink was painted on top of the reference electrode area. Further details can be found in the literature (de Araujo et al., 2017; Martins et al., 2019).

2.3 | Electrochemical measurements

All electrochemical experiments were performed with AUT86702 system operated by the software Nova v 2.1.4 (Metrohm). Laser-scribed paper analytical electrodes with the central circular area of 4 mm in diameter were employed for the voltammetric measurements (Figure 1). Measurements were carried out in water containing different concentrations of lead, at room temperature. A preconcentration potential of −1.6 V (vs. the pseudo reference Ag electrode) was applied to the working electrode for 5 minutes under a constant flow of nitrogen in the specially designed chamber. The square-wave anodic stripping voltammograms (SWASV) were recorded from −1.6 to 0 V vs. Ag, with a frequency of 20 Hz, modulation amplitude of 20 mV and step of 1 mV. The electrolyte consisted of hydrochloric acid 0.1 mol L⁻¹, i.e., pH ca. 1.0.

3 | RESULTS AND DISCUSSION

Electroanalytical methods for metals are typically established on anodic stripping voltammetry (ASV) procedures. These include pre-concentration of the metal cations on the surface of the working electrode with their reduction to zero-valent state, and consequent dissolution, during which the potential is swept in such a manner that the metals are oxidized to cations (Lu et al., 2018). This oxidation is characterized by a peak current in the observed potential range, and its position is an inherent property of each metal of interest (Rodrigues et al., 2011).

Square-wave stripping anodic voltammograms (SWASV) for samples containing 10 ppm of Zn, as the internal standard, and different Pb concentrations, ranging from 5 to 40 ppb, are presented in Figure 2. Two major features are observable in diagrams, peak at −1.02 ± 0.01 V vs. Ag, corresponding to Zn, and a peak at −0.46 ± 0.01 V vs. Ag, corresponding to Pb. Zn was chosen as the internal standard because of different peak potential, low-cost and easy handling. It is true that Zn may also be present in the chosen samples; however, the large concentration (10 ppm) diminishes possible issue. The ratio between peak currents for Zn and Pb peaks was used to make the calibration curve, which is presented in Figure 2. The analytical parameters obtained from the calibration curve (Figure 2A) are the following: square of the sample correlation coefficient (r²) of 0.99, ipPb/ipZn = (24 ± 2) × 10⁻⁴ [Pb] − (1 ± 6) × 10⁻³, limit of detection and quantification (LOD and LOQ) of 6.0 and 20 ppb, respectively; linear range up to 50 ppb. LOD and LOQ were calculated as three and ten times the standard deviation of the intercept/slope, respectively. Additionally, a 4% repeatability was attained by performing measurements in solutions with 30 ppb of lead during the same day (n = 4); a reproducibility of 5% was evaluated in the same manner but on different days.

Laser-pyrolysed paper electrodes, also known as laser-scribed paper analytical devices (LSPaDs), have been recently developed (Martins et al., 2019; de Araujo et al., 2017); they are produced during the single-step laser pyrolysis of the cellulosic material, resulting in...
graphene-enriched structures. More details concerning the material characterization can be found in literature (de Arauo et al., 2017). Although there is, indeed, an interesting very recent work (Pungjunun et al., 2020) that uses a bismuth nanoparticle-modified screen-printed graphene electrode (BiNP/SPGE) on a paper-based device for lead determination, presented graphene was not laser-produced. Considering the simple fabrication technique, facile functionalization and low cost (with each paper sheet it can be

**FIGURE 1** (a) The laser creating the LPPEs; (b) Photograph of the LPPEs, a Real Brazilian coin serves as size comparison; (c) LPPEs with the contacts made by silver ink

**FIGURE 2** SWASV curves obtained for different concentrations of Pb, and 10 ppm of Zn as the internal standard (moving average baseline correction was applied to the original voltammograms). Inlay a: the corresponding calibration curve, ratio of peak current Pb/Zn vs. Pb concentration. Inlay b: the applied potential by time
produced up to 200 electrodes), the LPPEs are adequate candidates for swift on-site determination of metals in water, like lead.

4 | CONCLUSIONS

Laser-pyrolysed paper electrodes were fabricated by burning common cardboard using a commercially available CO₂ laser. This process creates small and low-cost electrodes. The produced carbon-based electroactive surface was applied in the electroanalysis of lead in water. Using zinc as an internal standard, analytical parameters obtained for lead determination were 6.0 and 20 ppb, for LOD and LOQ, respectively, as well as 4% of repeatability and 5% of reproducibility.

5 | NOTES

The expression ‘heavy metals’ was avoided in the text due to its dubious definition (Duffus, 2002).

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CONFLICT OF INTEREST

All authors declare no conflicts of interest.

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