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## A Hybrid Screen-Printed Strip for Enhanced Electroanalysis towards Lead and Cadmium in Multi-Matrices

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Although heavy metals represent a major treat for ecosystem and human health, reference methods for their monitoring are characterized by time-consuming procedures, skilled personnel and sophisticated equipment (e.g. ICP-MS, AAS). The development of portable solutions is required, particularly improving interventions and reducing complexity. To this regards, an electrochemical strip for the determination of lead and cadmium in clinical, environmental and food matrices have been developed. The Bismuth film-based flexible device has been optimized and it has been able to detect cadmium and lead, respectively, down to the detection limit of 1.3 and 2 ppb. The use of Whatman No.1 chromatographic paper has allowed to improve the sensitivity towards the detection of heavy metals, because of the porosity that allowed to pre-concentrate species. This led to an improvement in the sensitivity, with a detection limit of 0.3 and 0.5 ppb, respectively, to cadmium and lead, and offers the possibility to tune the sensitivity according to needs, e.g., improving the number of pre-concentration steps. Subsequently, the application of the electrochemical sensor in drinking water, mussel and blood serum was evaluated, demonstrating how these hybrid polyester-paper electrochemical strips can significantly lower the time and costs for on-site measurements, through analytical methods of simple use. The accuracy has been evaluated by comparison with ICP-MS measurements, giving satisfactory results.

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Heavy metals are particularly harmful because of their non-biodegradable nature, long biological half-lives and their potential accumulation in different parts of the body, are extremely toxic due to their solubility in water and have harmful effects on humans and animals as there is no good mechanism for their elimination from the body. They can cause pollution in soil, air and water causing serious toxic effects and health problems.<sup>1</sup> Heavy metals are absorbed by the body by inhalation, ingestion and skin absorption. Among the various toxic effects, irritation, acute or chronic intoxication and carcinogenicity may occur. When they enter biological organisms, they are not excreted easily and accumulate in proteins or fats. The rapid increase in heavy metals in the environment in recent decades is due to the strengthening of industrial and mining activities, also can be discharged through other natural sources, such as rain water, soil, atmospheric agents and erosion, from rock which can increase the release of toxic metals into water intensity.<sup>2</sup> Of the various heavy metals, lead and cadmium are highly toxic, and even small doses of these can lead to a number of human health problems. Both metals are released into the environment by natural or anthropogenic phenomena. The sources of exposure are: ingestion of contaminated food or water, soil, dust, cigarette smoke (for cadmium) and occupational exposure. Lead and cadmium can cause several toxic effects on humans. Studies suggest that cadmium is associated with several clinical complications, mainly kidney dysfunction and bone disease, but also tumours.<sup>3</sup> FAO/WHO (Food and Agriculture Organization of the United Nations/World Health Organization) recommended the provisional tolerable weekly intake (PTWI) of 7 ppb body weight per cadmium (420 g/week for a 60 kg person).<sup>4</sup> Exposure to lead may occur by ingestion of contaminated food or water, via soil, lead-based powder or paint.<sup>5</sup> Occupational exposure is a major source of lead poisoning in adults.<sup>6</sup> People who have been exposed to lead for a long time may suffer from memory deterioration, prolonged reaction times, and reduced comprehension. Acute exposure to lead causes proximal tubular renal damage.<sup>3</sup> Chronic lead toxicity in humans often develops obtuseness, irritability, poor

attention span, constipation, vomiting, seizures, coma and death.<sup>7</sup> FAO/WHO established a provisional tolerable weekly intake (PTWI) for lead of 25 ppb body weight.<sup>8</sup> Due to the high toxicity of cadmium and lead, and heavy metals in general, it was necessary to develop appropriate analytical techniques in order to monitor their concentrations in clinical matrices (such as serum, sweat, etc.), food (such as marine microorganisms, fruits, vegetables, etc.) and environmental (such as water, soil, particulate matter, etc.), so as to allow an early detection of their presence in a body and in an environment and thus prevent its accumulation. The conventional analytical techniques used for the analysis of lead, cadmium and other heavy metals are mainly represented by atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectroscopy (ICP-OES),<sup>8–11</sup> electrothermal atomic absorption spectroscopy (ETAAS). Although these approaches appear highly sensitive and selective, they are characterized by several limitations: require tedious sample preparation, long analysis times, cleaning, pre-concentration procedures, expensive tools, specialized personnel and requirements for heavy and large equipment,<sup>2</sup> and they are not prone to be applied for on-site analysis.<sup>9</sup> The development of portable methods is highly required, in order to allow a preventive monitoring of the presence of these metals in various matrices. Among the existing ones, electrochemical methods are low-cost, easy to use, reliable and suitable for field applications. These methods allow for simple, small-circuit manufacturing procedures in the form of portable devices for in situ contaminated sample monitoring. They are also quicker compared to spectroscopic methods that allow on-line monitoring of water samples.<sup>10</sup> In particular, the use of printed electrochemical strips has been reported to be of high interest for many applications, in particular towards the detection of heavy metals in various matrices. For instance, a work of Rueda-Holgado et al., describes a voltammetric stripping procedure based on commercial screen-printed gold electrodes for on-site determination of soluble Cu (II) in atmospheric deposition samples taken around an industrial complex. Electrode conditioning procedures, chemical and instrumental variables have been optimized to develop a reliable method capable of measuring dissolved copper

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with a LOD of ca. 4 ppb, useful for pollution monitoring or screening purposes.<sup>11</sup> Bernalte et al. have studied an electrochemical methodology for the rapid and effective simultaneous electrochemical detection of heavy metal ions of concern (Pb, Cu and Hg) in water, with a single screen-printed electrode probe. This methodology showed a very good analytical performance in the optimized conditions with a wide quantification range for each pollutant (5–300 ppb), and detection limits below the Environmental Protection Agency (EPA) maximum contaminant levels for drinking water: 15, 1300 and 2 ppb for Pb, Cu and Hg, respectively.<sup>12</sup> Moreover, a voltammetric method for the determination of arsenic in commercial apple juice has been developed by using gold nanoparticles modified carbon screen printed electrodes. The developed methodology had a sensitivity of 0.1  $\mu\text{A/ppb}$  and a limit of detection of ca. 17 ppb.<sup>13</sup> With regards to the detection of lead and cadmium, bismuth film has been highlighted as an eco-sustainable sensing strategy to be used instead of mercury. Bismuth films are used as an alternative to mercury, because of its low toxicity and its adequate electrochemical properties, such as a wide range of operational negative potentials, low background currents, and the ability to reduce elements on its surface by formation of intermetallic compounds or fused alloy.<sup>14</sup> It also has a high-quality stripping performance and therefore is useful for the substitution of mercury in the determination of heavy metals.<sup>15</sup> In literature some examples have been reported. Lu et al. report a disposable sensor for the differential pulse anodic stripping voltammetric determination of the ions Zn, Pb and Cu. Simultaneous detection is accomplished by using a screen-printed carbon electrode co-modified with an in situ plated bismuth film and gold nanoparticles. The detection limits are 50 ppt for Zn, 20 ppt for Pb, and 30 ppt for Cu. The method was applied to the determination of the 3 ions in spiked lake water samples.<sup>16</sup> Ketafa et al. describe the detection of Cd, Pb and Zn at the low ppb levels by square wave anodic stripping voltammetry on a bismuth-film electrode (BFE) plated in situ. The LOD were 0.2 ppb for Cd and for Pb and 0.7 ppb for Zn at a preconcentration time of 10 min. Finally, BFE's were successfully applied to the determination of Pb and Zn in tap water and human hair and the results were in satisfactory statistical agreement with AAS.<sup>17</sup> A microbial-based support has been applied to screen-print carbon electrodes for the electrochemical detection of Cd and Pb in sweat, with detection limits of 1.01 and 0.43  $\mu\text{M}$ , respectively.<sup>18</sup> The use of paper-based devices is sometimes limited to replacing other typologies of substrates that are often used to print electrodes, mainly plastic.<sup>19</sup> However, in addition to all the features associate to the sustainability of paper, a great possibility is represented by the adoption of paper as an accumulator.<sup>20–22</sup> Some methods have displayed the use of porous papers to detect metals, both colorimetric and electrochemical, i.e. copper ions in sweat and serum, mercury and silver in drinking water, nickel and iron in ash samples.<sup>23–26</sup> In addition, a lateral flow paper-based sensing device has been also proposed to quantify lead and cadmium in aqueous samples, reaching 7 and 11 ppb as the detection limit, respectively.<sup>27</sup> However, a major limitation occurs, especially in the electrochemical architectures: this is purely attributable to the fact that the targets need flowing within the porous structure, with the effect of sensitivity reduction, perhaps in comparison to plastic-based systems (displaying the detection limit lower than 1 ppb).<sup>28</sup> Herein, we exploited the use of a chromatographic paper to be combined with a printed electrochemical strip, with the effect of improving the sensitivity depending on the various steps of pre-concentration. With simple tasks, the sensitivity can be tuned by utilizing more pre-concentration steps (involving the use of microliter of samples). The analytical methodology thus becomes extremely sensitive due to the multi-functionality of the combination of traditional substrates with porous paper-based materials.<sup>29,30</sup> With the optimized configuration the detection of lead and cadmium has been lowered down to 0.5 and 0.3 ppb, respectively to lead and cadmium. Finally, the optimized

system has been challenged towards the heavy metals detection in drinking water, mussels and human serum, and it opens to a generalizable approach for other (bio)systems.

## Experimental

**Reagents and equipment.**—Conductive inks (Ag/AgCl and graphite) purchased from Acheson (Italy), sodium acetate, potassium chloride, hydrochloric acid, nitric acid, bismuth, lead, arsenic, copper and magnesium (ICP-MS standards, 1000 ppm) have been purchased from Sigma Aldrich (Italy). Real matrices, including drinking water, Acqua Monte Rosa, Acqua San Benedetto, Acqua Lauretana have been purchased in the local market, as well for mussels. Human serum has been purchased from Sigma Aldrich. All the measurements have been carried out with the use of a portable potentiostat, EmStat3 (PalmSens, Netherlands) connected to a laptop.

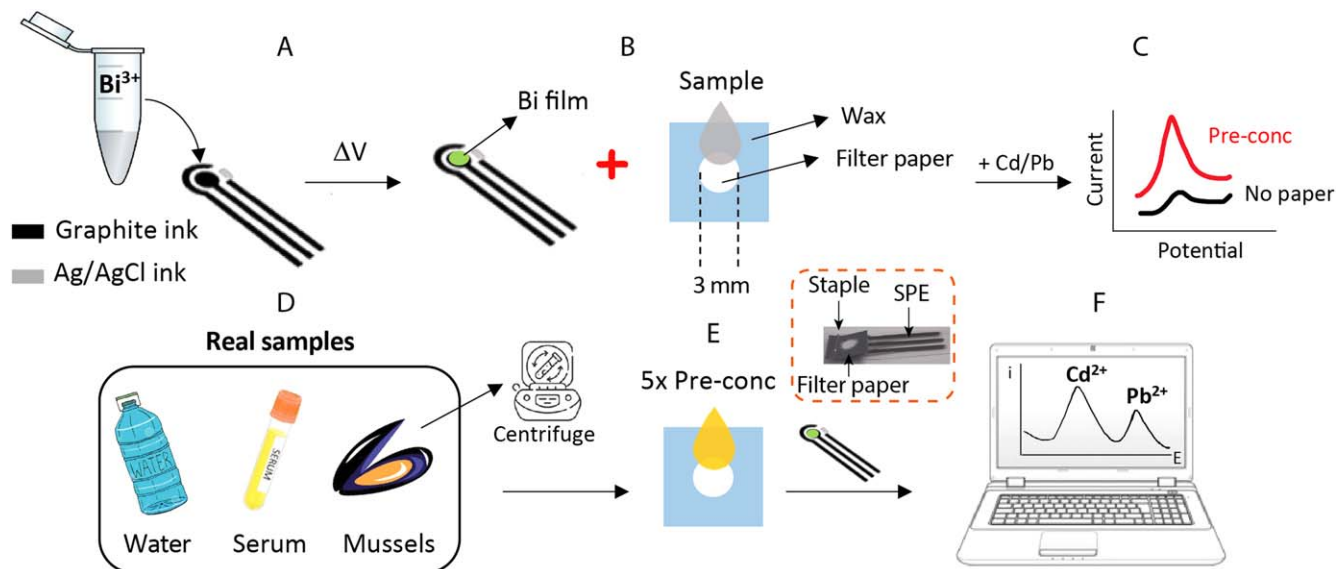
**Electrochemical strips' manufacture.**—Screen-printed electrodes were produced through manual screen-printing onto a flexible polyester-based support, using graphite-based conductive ink (Elettrodag 421) for working and counter electrode and Ag/AgCl (Elettrodag 477 SS) for reference electrode. Each of the two steps has been followed by an 80 °C curing in the oven for 20 min. An adhesive tape (commercially available, in this case was "Scotch" adhesive tape) has been used to insulate the printed electrodes. The diameter of the working electrode was 0.4 cm, and the electrochemical strips are ca. 2.5 cm × 1 cm.

**Paper-based booster.**—A circle pattern was designed with Adobe Illustrator and it has been printed onto a chromatographic paper (Whatman No. 1) with a solid-ink printer (Xerox 8580). The wax-printed paper has been cured in the oven for 2 min at a temperature of 100 °C. The process is essential to facilitate the permeation of wax-based ink through the paper, creating a completely insulated hydrophilic area where the samples can be added.<sup>31</sup> The diameter of the hydrophilic area is 0.3 cm.

**Bismuth film.**—A bismuth film has been electrodeposited onto the working electrode surface, in order to be sensitive in presence of lead and cadmium, forming Bi-Pb and Bi-Cd alloys. The film has been obtained by applying a potential difference of  $-1.6\text{ V}$  (vs Ag/AgCl) for 200 s in presence of 50 ppm bismuth dissolved in 50 mM acetate buffer (pH = 4.6) containing 50 mM potassium chloride.<sup>32</sup>

**Lead and cadmium determination.**—The two heavy metals have been detected following two strategies. Determination onto flexible strips: samples have been added directly on top of the electrodes, and they have been quantified in a 100-microliter drop composed by buffer and bismuth. Determination with paper-based: all the reagents and samples have been added within the waxed paper. Successively they have been released and analyzed at the printed strips. Depending on the sensitivity need, different amount of drops containing samples might be added to the paper-based substrate. It should be taken into account that each drop is added when the solvent contained in the previous is evaporated. All the measurements have been performed with Square Wave Anodic Stripping Voltammetry (SW—ASV) under the optimized conditions described in the text. In particular, the flexible electrochemical strip and the chromatographic paper disk have been coupled by the use of a common metallic staples, as indicated in the inset of Fig. 1.

As showed in panel 1C, the presence of pre-concentration (using flexible-based electrode coupled with chromatographic paper, red line) allows to increase the sensitivity of the platform in presence of the metal of interest: in fact, the black line is relative to the measurement of a metal (Cd or Pb) using the flexible electrode without the pre-concentration disk (without paper). Panel 1F, is relative to the recorded current following the simultaneous measure



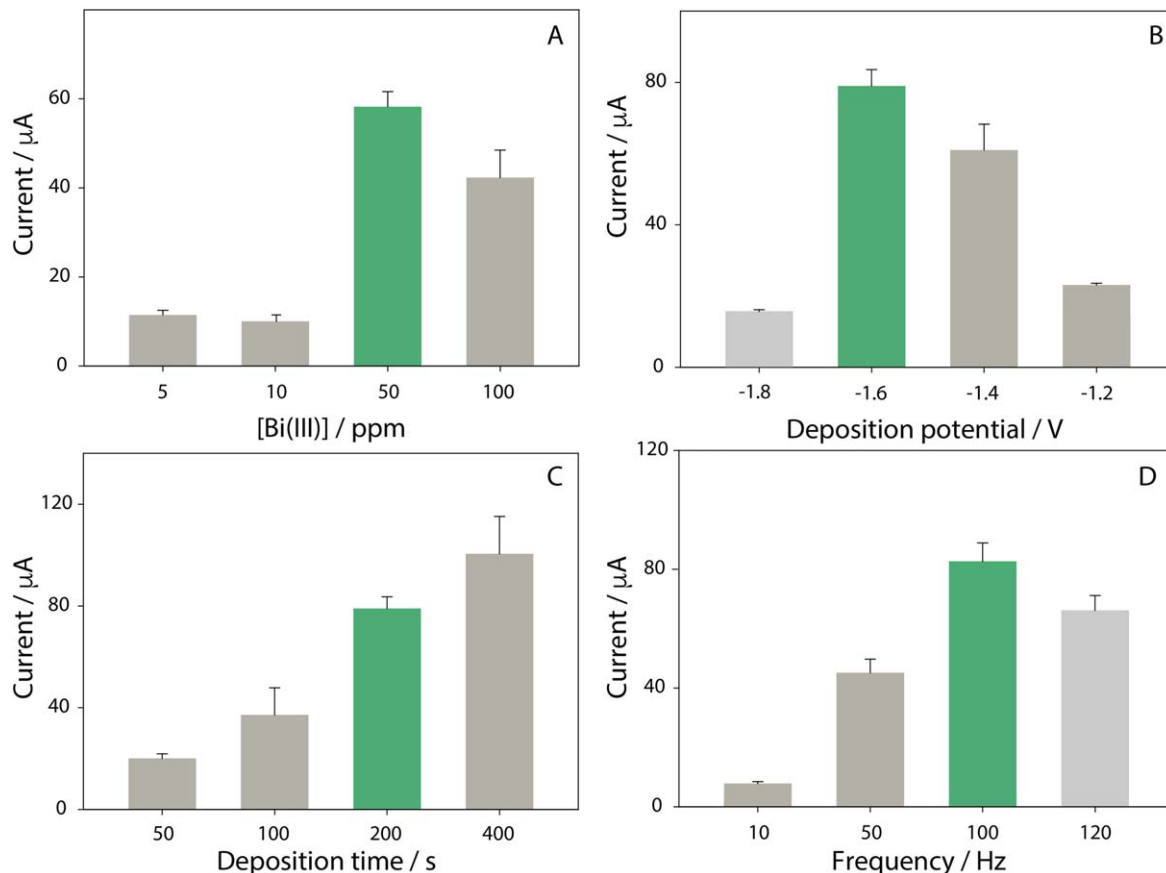
**Figure 1.** Schematic representation for the development of the hybrid polyester-paper platform to detect cadmium and lead in three different matrices: drinking water, human serum and mussels. Highlight of the pre-concentration effect on the sensitivity of heavy metals detection.

of both cadmium and lead in the same solution, following five pre-concentration steps. In this case, we report only the results on the laptop obtained with pre-concentration settings.

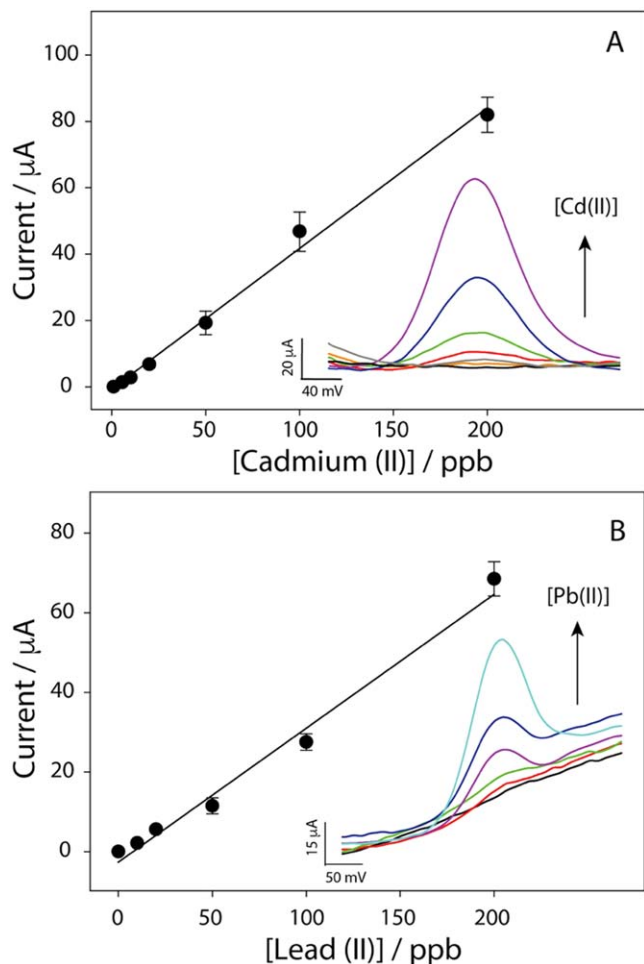
**Treatment of real samples.**—Drinking water and serum have been analysed without treatments. Mussels were homogenized with

water (through simple mixing) and successively the solid content has been removed.

**ICP-MS measurements.**—Samples have been mineralized: 250 microliters were transferred into a 7 ml Pyrex. Hydrochloric acid and nitric acid were added to each sample (3:1 v/v). The reaction was



**Figure 2.** (A) Evaluation of the Bi(III) concentration (5, 10, 50, 100 ppm), (B) Optimization of the deposition potential ( $-1.8$ ,  $-1.6$ ,  $-1.4$ ,  $-1.2$  V), (C) Choice of the deposition time between 50 and 400 s, (D) Optimization of the frequency of the square wave (10, 50, 100, 120 Hz). All measurements have been carried out in 50 mM acetate buffer ( $\text{pH} = 4.6$ ) containing 50 mM potassium chloride and all the points are the results of three replicates.



**Figure 3.** (A) Calibration curve in the linear range from 5 to 200 ppb of Cd (II) standard solution in presence of 50 ppm bismuth dissolved in 50 mM acetate buffer (pH = 4.6) containing 50 mM potassium chloride. (B) Calibration curve in the linear range from 10 to 200 ppb of Pb (II) standard solution in presence of 50 ppm bismuth dissolved in 50 mM acetate buffer (pH = 4.6) containing 50 mM potassium chloride. The voltammetric curves relating to the measured concentrations for Cd (II) and Pb (II) are also reported. Experimental parameters:  $E_{\text{dep}} = -1.6$  V;  $t_{\text{dep}} = 200$  s;  $E_{\text{begin}} = 1.0$  V;  $E_{\text{end}} = 0.4$  V;  $E_{\text{step}} = 0.01$  V;  $\text{Freq} = 100$  Hz. All the points are the results of three replicates.

conducted for 16 h at 90 °C, and after digestion samples have been diluted to 15 ml in ultrapure water. Measurement have been performed with an Agilent 7700 ICP-MS instrument (Agilent Technologies) equipped with a frequency-matching radio frequency (RF) generator and 3rd generation Octopole Reaction System (ORS3) operating with helium gas in ORF. The following parameters were used: RF power: 1550 W, plasma gas flow: 14 L min<sup>-1</sup>; carrier gas flow: 0.99 L min<sup>-1</sup>; He gas flow: 4.3 ml min<sup>-1</sup>. <sup>103</sup>Rh was used as an internal standard. Lead and cadmium concentrations have been measured with three replicates.

## Results and Discussion

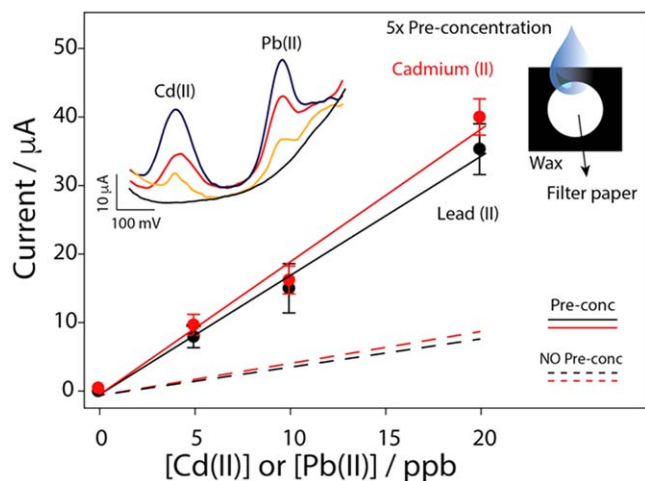
**Optimization of the experimental parameters.**—Being the electroanalytical method developed on the deposition of heavy metals onto a bismuth layer, the first step of manufacture has been characterized by the choice of substrate. Office paper (80 g m<sup>-2</sup>, Fabriano, Italy) and polyester have been chosen to conduct this evaluation. Experimentally, the bismuth layer is formed simultaneously to heavy metal detection, by dropping onto the working area all the required species. The performance at various substrates have been evaluated the SW-ASV signal by measuring a 100 ppb

cadmium solution in presence of 50 ppm bismuth in acetate buffer. The same optimization has been conducted using lead solutions as well, obtaining same trend for each parameter that has been taken into account (not shown). The signal measured with office paper appears obviously lower than that one obtained using polyester (Supplementary Material, Fig. S1 (available online at [stacks.iop.org/JES/169/037516/mmedia](https://stacks.iop.org/JES/169/037516/mmedia))). This could be ascribable to the porosity of office paper that leads to a decrease of the availability of bismuth ions on the working electrode to form the sensitive layer. Although the porosity of office paper is not high as the chromatographic one, during the time for deposition of heavy metals is possible that part of the bismuth is being adsorbed out from the working electrode. After having selected the flexible polyester-based substrate, the experimental setup has been optimized, by investigating the effect of bismuth concentration, deposition potential, deposition time and frequency of square wave, as reported in Fig. 2.

Bismuth concentration is a crucial factor for the efficiency of lead and cadmium detection. It determines the thickness of the film that covers the working electrode. It is necessary to choose the most appropriate level in order to avoid the formation of thick films that would limit the electronic transfer between the electrode and the analyte in solution. It should be noted that all these measurements have been carried out in the drop, without any stirring of the working solution. It means that the concentration of bismuth is required to be high, because the layer will be formed with the diffusion only (instead of convection). Among the tested value of bismuth, from 1 to 100 ppm, 50 ppm allowed the optimal sensitivity (Fig. 2A). It has been observed a decrease of the signal by using 100 ppm, probably due to the excessive thickness of the bismuth film that was formed on top of the working electrode. Successively, deposition potential and time have been considered as shown in Figs. 2B and 2C. These parameters are fundamental to have selectivity and sensitivity, respectively, by choosing the optimal potential difference for reducing the metal of interest and the time for having a high amount of metal deposited. Of course, a good balance among the time of experiment and sensitivity needs to be evaluated, in order to obtain a quick method. In this case the optimal compromise has been reached by applying a  $-1.6$  V for 200 s. In particular, it should be observed that even if a deposition of 400 s has allowed to reach a superior sensitivity of the platform, doubling the time has not been consistent with a double sensitivity. The last parameters to be evaluated has been the frequency of the square wave that is correlated with the scan rate by the following relation,  $\text{frequency} \times \text{step potential}$ .<sup>33</sup> The effect of the step potential has not been reflected in a significative change of the sensitivity. As shown in Fig. 2C, the intensity of current relating to the stripping of 200 ppb cadmium is optimal when a 100 Hz frequency is used, and it is characterized by a satisfactory repeatability of 10% calculated on different measurements.

**Calibration curve for cadmium and lead.**—Subsequently to the optimization of the experimental parameters, both the heavy metals have been detected in a wide range of concentrations within the ppb level. Calibration curves have been obtained by investigating concentrations in the range between 5 and 200 ppb, and 10 and 200 ppb, respectively, for cadmium (Fig. 3A) and lead (Fig. 3B).

As reported in Fig. 3, linear correlation has been obtained between the height of the current peaks and the concentration of both cadmium and lead ions. The relationship is described by the following equations,  $y = 0.42 (\pm 0.03) x - 0.69 (\pm 0.08)$ ,  $R^2 = 0.983$ , and  $y = 0.34 (\pm 0.02) x - 2.66 (\pm 0.11)$ ,  $R^2 = 0.977$ , respectively, for cadmium and lead ions (where y represents the current difference between metal and the blank, and x represents the metal level expressed in ppb). The detection limits, calculated as  $S/N = 3$  (is the value of the signal that is three times higher the signal of blank), have been calculated equal to 1.3 and 2 ppb, and the limits of quantification have been calculated as 4.3 and 6.5 ppb, respectively to cadmium and lead (the limit of quantification has been calculated equal to signal-to-noise ratio of 10). For both the systems a good repeatability of ca. 10% has been obtained (calculated on five



**Figure 4.** Calibration curve for Cd (II) and Pb (II) in standards solution at concentrations up to 20 ppb with 5x pre-concentration (solid lines). Dashed lines represent calibration curve for Cd (II) and Pb (II) detection without pre-concentration steps. Inset: SW-ASV recordings of simultaneously measured solutions containing cadmium and lead at increasing concentrations. All the points are the results of three replicates.

replicates). In addition, the signal due to interfering species has been evaluated using the same experimental conditions. In particular, SW-ASV measurements of samples containing 100 ppb of Copper, Arsenic, Mercury and Magnesium did not produce significant interferences.

**Paper-based boosting.**—The effectiveness of paper-based substrates has been demonstrated in various approaches, however, in this work we evaluated and highlighted the relevance of a tiny piece of waxed filter paper to improve the practicability and sensitivity of heavy metals monitoring. This opens to a new concept in electroanalysis because, depending on the necessity, the end user is capable to obtain an improvement of the sensitivity of the platform just by adding samples onto an external paper-based pad. The adoption of wax printing allows designing the most appropriate platform to be coupled with printed strip. In addition, the porosity of disk is capable to store all the reagents included bismuth and acetate buffer, that can be released just by dropping water. As reported in Fig. 4, a clear

improvement in the sensitivity has been obtained by using multi-drop additions.

To carry out the evaluation, we tested the sensitivity of the platforms by adding 5 samples drops onto the waxed filter paper. Each 2-microliter drop has been added after the solvent of the previous added drop was evaporated. The choice of 2 microliters has been chosen in accordance with the dimension of the paper-based disk, in order to avoid accumulation of the sample on the border of the paper. After the pre-concentration has been carried out, all the measurements have been carried out by measuring in presence of re-dissolved bismuth, acetate buffer, cadmium, and lead. It is interesting how the use of 5x pre-concentration steps led to improvement in the sensitivity for both metals. Regarding the linear correlation of cadmium and lead ions, the following equations have been obtained respectively:  $y = 1.98 (\pm 0.09) x - 0.89 (\pm 0.11)$ ,  $R^2 = 0.978$ , and  $y = 1.77 (\pm 0.10) x - 0.89 (\pm 0.10)$ ,  $R^2 = 0.960$ . The five pre-concentration steps led to an improvement of the detection limits of ca. 5-fold, calculated equal to 0.3 and 0.5 ppb for cadmium and lead.

**Real samples.**—To demonstrate the wide applicability of the developed device, three different matrices have been taken into account, representing model examples of clinical, environmental and food samples. In particular, the electroanalytical device has been applied in commercial drinking waters (Monte Rosa, Lauretana and San Benedetto), serum and mussels. After having evaluated the absence of cadmium and lead in these matrices, in comparison to the calculated detection limits, the samples have been spiked and recoveries have been calculated. In addition, ICP-MS experiments have been carried out to evaluate the accuracy. All the samples of drinking waters have been spiked with 10 ppb of cadmium and lead, and the current recorded in comparison with that one obtained in standard solution was not significantly different (Supplementary Material, Fig. S2), and all the calculated recoveries produced satisfactory value (Table I). In the case of mussels, 20 ppb spiking of cadmium and lead have been utilized to evaluate the recovery using the standard addition methods. Due to the complexity of the matrix, the sensitivity was different in comparison with measurements carried out in standard solution, but the use of paper-based platform for filtering gross impurities and the adoption of standard addition method, produced ca. 90% recoveries (Supplementary Material, Fig. S3). The same approach has been adopted to analyze commercial serum, with satisfactory recoveries of 92% and 90%, respectively, for serum spiked with 10 ppb of cadmium and 20 ppb of lead (Supplementary Material, Fig. S4). All the recoveries and the

**Table I. Recoveries and comparison with analysis performed at ICP-MS.**

Sample	Heavy metal	Spiked level (ppb)	Recovery
Acqua Monte Rosa	Cadmium	10	89%
Acqua San Benedetto	Cadmium	10	115%
Acqua Lauretana	Cadmium	10	102%
Acqua Monte Rosa	Lead	10	110%
Acqua San Benedetto	Lead	10	89%
Acqua Lauretana	Lead	10	105%
Mussels	Cadmium	20	91%
Mussels	Lead	20	94%
Serum	Cadmium	10	92%
Serum	Lead	20	90%
Sample	Heavy metal	ICP-MS (ppb)	SPE (ppb)
Acqua Monte Rosa	Cadmium	9.0	8.9
Acqua Monte Rosa	Lead	12.3	11.0
Mussels	Cadmium	18.4	18.2
Mussels	Lead	24.2	18.7
Serum	Cadmium	11.3	9.2
Serum	Lead	25.6	19.0

validation results obtained with ICP-MS measurements have been included in following Table I.

### Conclusions

In this work a facile combination among flexible screen-printed electrode and external waxed filter paper has been highlighted to improve practicability towards the detection of cadmium and lead in different matrices. In particular, it has been demonstrated how the use of a small and low-cost paper-based disk is capable to reduce the tasks for end-user measurements. It has been highlighted how the combination between low-cost materials with different properties has been consistent with a net enhancement of the analytical performance of a portable electroanalytical tool. The detection limits associated to the detection of cadmium and lead have been lowered down to 0.1 and 0.3 ppb, starting from 1.3 and 2 ppb respectively. The result has been attributable to an easy strategy that involved pre-concentration onto waxed printed paper disk with the use of five steps. Depending on the need, this procedure can be applied and customized to reach the desired sensitivity. The effect of porous substrate has been also exploited for storing reagents and treat in gross impurities in real samples, including drinking waters, mussels, and serum. Electroanalysis continuously demonstrates how the adoption of functional materials can be an added point. The use of paper-based substrates, as the platform for screen-printing electrodes or as “booster” can be coupled towards numerous analysis and user-friendly architectures. Additionally, future studies would be focused on the use of biodegradable/compostable substrates for improving the biocompatibility of printed strips, e.g. microbial cellulose.

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