Electronic Supplementary Information

Merging office/filter paper-based tools for pre-concentring and detecting heavy metals in drinking water

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Choice of the substrate for detecting mercury ions

As indicated in the main text (Figure 1), the choice of using office paper instead of chromatographic paper is due to their different porosities. Office paper is not porous and it is capable of being covered with a solution in direct contact with the AuNPs, while in the case of chromatographic paper (pore size of ca. 10 μ m), the working solution readily diffuses within paper and the contact with AuNPs is minimized.



Figure S1. Determination of 100 ppb mercury ions in 0.1 M hydrochloric acid using electrodes that have been screenprinted onto office paper, plastic and porous paper (Whatman No.1), modified with 2 μ L AuNPs, using the optimized experimental conditions as reported in the caption of Figure 3 (main text).

SEM images of paper-based substrates

SEM images highlight the difference between chromatographic and office paper. Chromatographic paper displays the presence of pores that are not present in the office paper structure. Prior to imaging samples were coated with ~ 10 nm - layer of gold. Imaging was carried out using a ULTRA Plus Zeiss field emission gun (FEG) Scanning Electron Microscopy (SEM), fixing the voltage acceleration in the range of 5-20 kV and a working distance of 8-30 mm. Micrographs were acquired in secondary and backscattered electrons modes.



Figure S2. Scanning Electron Microscopy (SEM) images relatively to A,B,C) chromatographic and D,E,F) office paper, using different magnification.

SEM images of AuNPs onto paper-based substrates

AuNPs have been synthesized following this procedure. The first step is focused on glassware cleaning with aqua regia (HCl/HNO₃ 3:1 v/v) and piranha solution (H₂SO₄/H₂O₂ 7:3 v/v). After each step all the glassware is rinsed with distilled water. To conduct synthesis, 9 mL of distilled water were mixed with 1 mL of 25 mM HAuCl₄ and 2 mL of 35 mM sodium citrate. Then, 500 μ L of 20 mM sodium borohydride were added, and the solution turned red. The solution was left under stirring and in dark conditions for 24 h. Scanning Electron Microscopy (SEM) and energy dispersive X-ray (EDS, Detector x-act Oxford) measurements were carried out attaching the Au-NP-paper substrates and the blank sample (paper without synthesis of Au-NPs) on an aluminum stub covered by a carbon tape. Chromium sputter –coating (7 nm, è hr 208, Cressington) was required for the samples and the samples were then placed in a Field Emission Scanning Electron Microscope SEM (FESEM, ultraplus zeiss) and imaged using 10–20 kV accelerating voltage1-7. EDS deconvolution spectra were obtained by Aztec software, Oxford.



Figure S3. A) SEM images of blank paper-based substrate, B) EDS analysis of blank paper-based substrate, C) EDS layered images showing signal from i) C, ii) O and iii) Au, D) SEM microscopies of AuNPs on paper-based substrate and E) EDS analysis of AuNPs on paper-based substrate.

Optimization of the experimental parameters

After having selected the substrates where screen-printing the electrodes, the experimental parameters have been optimized. Response varies in presence of different amount of AuNPs, and it seems 2 microliters of AuNPs provide the highest sensitivity, perhaps due to the fact the higher amount of AuNPs produces thicker surface (less conductive). Hydrochloric acid has been used both for stabilizing mercury ions in its oxidized form and also as the supporting electrolyte. 0.1 M gave the highest sensitivity and a possible explanation is that 0.01 M produces a low concentration of supporting electrolyte while 1 M HCl probably has a great chloride-stabilization effect on Hg ions. The accumulation potential and the time of accumulation have been optimized. Accumulation potential is essential for reducing mercury ions and 0.2 V allowed to obtain the highest signal, while a time of 100 s was chosen due to no apparent difference in the average peak current in the range from 100 and 300 s. The other optimized electrochemical parameters were relative to the stripping wave utilized (square wave): amplitude potential (height of pulse), frequency and step potential (step height of the staircase), and the optimal sensitivity has been obtained by selecting 0.1 V, 60 Hz and 0.01 V, respectively.

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Figure S4. A) Optimization of AuNPs drop cast onto paper-based SPE, B) HCl concentration, C) accumulation potential, D) accumulation time for stripping of mercury ions, E) amplitude of square wave, F) frequency of square wave and F) step potential of square wave. All measurements have been carried out in presence of 100 ppb Hg(II).

Selectivity studies

The selectivity has been tested in presence of As^{3+} , Pb^{2+} , Cd^{2+} and Cu^{2+} (20 ppb). All the measurements have been carried out in absence and in presence of 20 ppb Hg²⁺.



Figure S5. Voltammetric curves obtained in absence of metals (blank) and in presence of 20 ppb of the reported metals. In the inset, the curves have been obtained by analyzing mixed solutions containing 20 ppb mercury ions and another metal. The color legend is the same for the two set of experiments. The experiments have been performed using the optimized experimental parameters.