**Electronic Supplementary Material**

**SENSITIVE DETERMINATION OF MERCURY BY A NEW MAGNETIC DISPERSIVE SOLID PHASE EXTRACTION COMBINED WITH FLOW-INJECTION-COLD VAPOR-GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY**

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**Synthesis of MGO ferrofluid**

The synthesis of MNPs was optimized previously by us. [1] 11.68 g of $FeCl_3$ $6H_2O$ were dissolved in 200 mL, 4.30 g of $FeCl_2$ $4H_2O$ was added under a nitrogen atmosphere and vigorous stirring at 85 ºC. After that, 50 mL of 30% (vol/vol) ammonia were added and maintained for 70 min. The suspension was cooled down to room temperature and the nanoparticles were washed with deionized water, 0.02 mol $L^{-1}$ sodium chloride and ethanol several times.

GO was prepared according to the Hummers method modified [2] by chemical exfoliation of natural flake graphite followed by repeated purification cycles using centrifugation.

The coupling of MNPs with GO was carried out mixing 300 mg of GO suspended in 300 mL of deionized water, 1.5 g of sodium hydroxide and 1.5 g of sodium acetate chlorine and stirred for 2 h. After that, the mixture was centrifuged. The solid was washed twice with ethanol 96%. The obtained solid was mixed with 0.1 g of DCC and 6–8 mL of Ethanol 96% and ten drops of glacial acetic acid. After was stirred for 2 h at room temperature, 1.5 g of MNPs were added and refluxing for 48 h at 50 ºC. The MGO suspension was cooled to room temperature and separated using an external permanent magnet and washed with ethanol. Finally, the solid was dried at 80 °C for 24 h.[3]

In order to obtain the ferrofluid, 20 mg of the synthesized MGO were mixed with 100 µL of acetic acid, as stabilizing agent. The mixture was heated at 50°C for 10 min under continuous stirring to allow acetic acid adsorption. Then, acetic acid-coated magnetic nanospheres were dispersed in 120 µL [Bmim][BF4]. This suspension was sonicated for 10 min.

**Characterization of MGO**

The synthesized MGO was characterized by TEM, XPS and nitrogen adsorption isotherms. In the TEM image (Fig. ESM1) can be observed that $Fe_3O_4$ nanoparticles are disorderly coupled over the GO sheets.

The results of the XPS elemental analysis showed the presence of C (34.7%) and Fe (15.0%), confirming the MNP-GO-coupling.

The nitrogen adsorption-desorption experiments showed the isotherms were similar to those type IV, a typical of mesoporous materials and presented a high surface area ($57.23 \, m^2g^{-1}$).

**Optimizing operating parameters**

The optimized furnace programs for Hg can be seen in Table ESM1.

**Optimization of the MDSPE/CV-GFAAS procedure**

**(a) Study of the concentration of MTS**

The influence of the MTS concentration on the extraction of Hg(II) was evaluated in the concentration range of 0.0 – 0.01 % (wt/vol). As can be seen in Figure ESM2, the extraction recovery of Hg increased when MTS concentration increases of up to 0.0025 %, and after that point the absorbance signal remained constant. In order to have an excess of chelating reagent a concentration of 0.007 % was chosen for subsequent experiments.

**(b) Effect of ionic strength**

Ionic strength is an important factor in any extraction mechanism because it affects the rates at which ions react with each other and thus, the equilibrium and the extent to which the reaction occurs. Due to this important fact, the behaviour of the Hg extraction must be studied considering the ionic strength.

The addition of salt to water samples usually decreases the solubility of Hg-MTS complex in aqueous phase and therefore improve its extraction because of salting-out effect. However, a very high ionic strength decreased the sorption of mercury. This effect could be explained due to the competition of chloride ions in the formation of mercury complex with MTS. Thus, different concentrations of NaCl between 0.0 to 15.0

% (wt/vol) were tested to evaluate the effect of the ionic strength of the sample on the extraction of Hg(II). The results (Figure ESM3) showed a significant effect on the extraction recoveries of Hg(II), the absorbance signal increase up to approximately 10 % of NaCl. In order to adjust the ionic strength, a concentration of NaCl of 10.0 % was selected. Thus, the ionic strength in real samples and standards must be adjusted at 10.0 % of NaCl.

**(c) Extraction time**

This parameter expresses the contact time between the ferrofluid and the aqueous phase. The extraction time was studied between 1 and 10 min, Fig. ESM4. The best signals were reported for 1 min of extraction time between MGO and MTS-Hg complex. At higher time, signals decrease until a constant value, this fact might be explained due to the influence of the ultrasonic bath which could degrade the non-covalent interactions ($\pi$-$\pi$ stacking) between graphene nanosheets and the mercury complex. [43] Thus, 1 min was selected as the extraction time for further experiments.

**(d) Elution conditions and CV generation**.

To find the best eluent for the retained mercury ions, different eluent solutions based on our previous works [7, 11-13] were studied: $HNO_3$, HCl, thiourea, and the mixtures thiourea-$HNO_3$ and thiourea HCl (5% in all cases). As can be seen in Figure ESM5, the best signal was obtained with the mix of $HNO_3$ 5 % and Thiourea 5 %. The following step was to study the optimum concentration of both reagents. A response surfaces design was performed for this purpose, which was also used to optimize the reductant ($NaBH_4$) concentration for the CV generation. A total of 17 experiments were performed in order to determine the optimal conditions. In Fig. ESM6 the principal effects diagram is shown. The optima conditions calculated were: 0.5 % Thiourea, 0.5 % $HNO_3$, and 0.5 % $NaBH_4$. The reductant was stabilized with NaOH 0.1 %. Considering a 500 µL sample loop in the FI system, a volume of 2 mL of eluent was used in all experiments, thus, the eluent could be measured at least three times.

With the eluent concentration optimized, the elution time necessary to separate the analyte from the solid phase was studied. This parameter was studied between 1 and 5 min. No significant variations on the mercury signals were observed and 1 min was selected as elution time.

Once the elution conditions and the reductant concentration were optimized, the reductant flow rate in
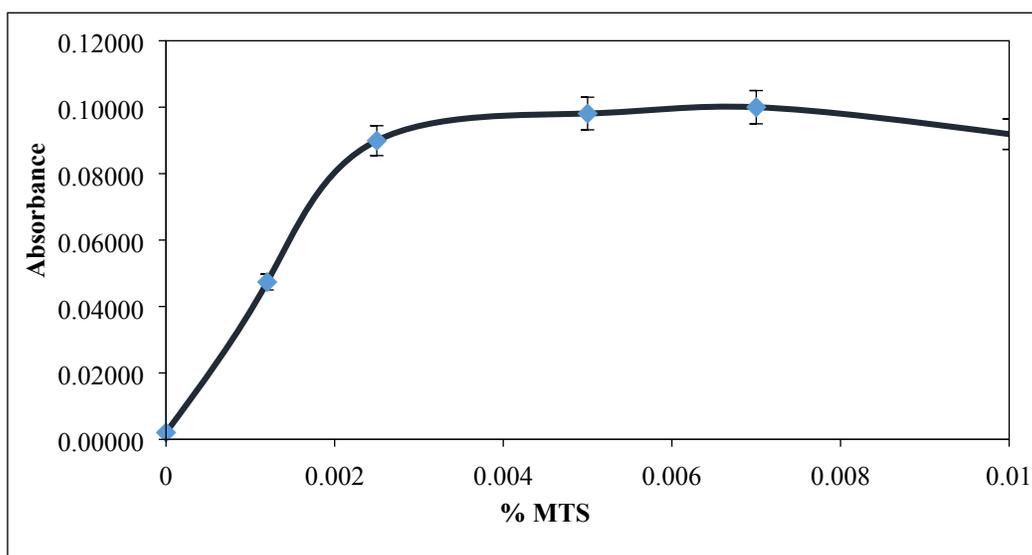
the FI system was optimized by changing the parameter between 0.6 and 6.4 mL min$^{-1}$. As can be seen in Figure ESM7, the optimum value was 0.6 mL min$^{-1}$.

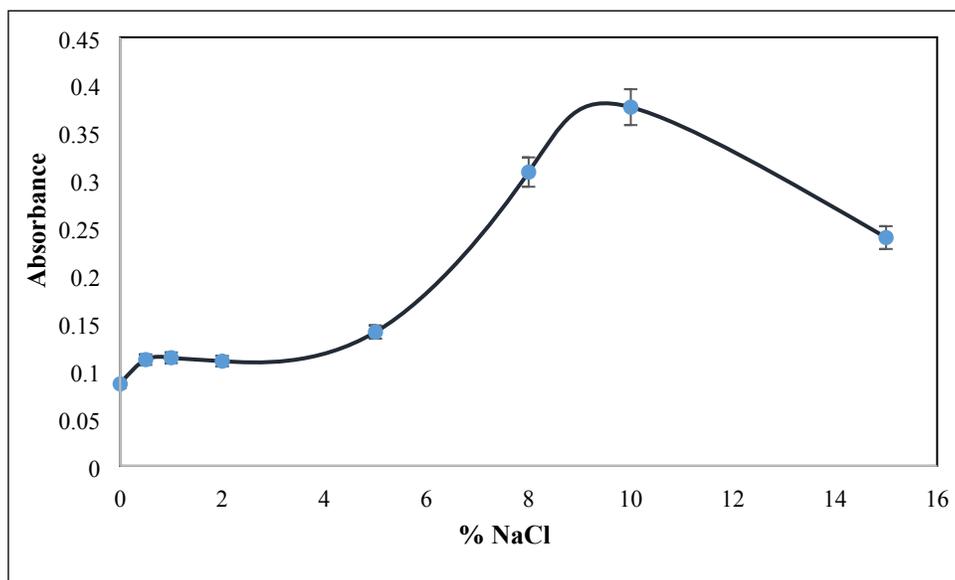**Table ESM1†.** Optimized heating program for Hg.

| Step | Temperature (°C) | Ramp (°C s$^{-1}$) | Hold time (s) | Ar flow rate (mL min$^{-1}$) |
|---|---|---|---|---|
| Drying | 20 | 1 | 3 | 250 |
| Atomization | 1200 | 0 | 5 | 0 |
| Cleaning | 2300 | 1 | 3 | 250 |
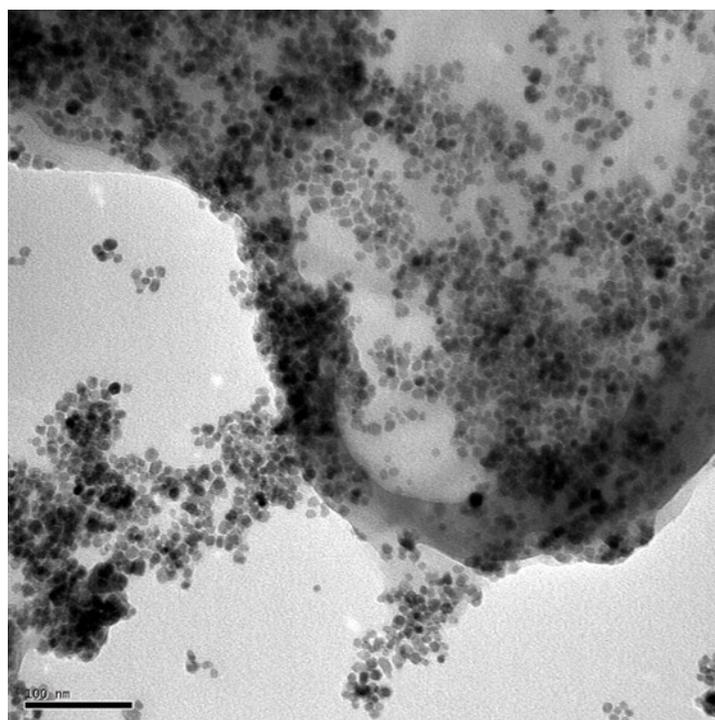


**Fig. ESM1**. TEM images of MGO (scale 100 nm).

**Fig. ESM2.** Influence of MTS concentration on the extraction of 10 μg L$^{-1}$ of Hg(II), prepared with different concentrations % (v/v) of ligand, 0.5 % (wt/v) NaCl, and 1M HCl until pH = 1.0.

**Fig. ESM3.** Effect of ionic strength for 10 μg L$^{-1}$ of Hg(II), prepared with 0.007 % (v/v) MTS, different concentrations % (wt/v) of NaCl, and 1M HCl until pH = 1.0.
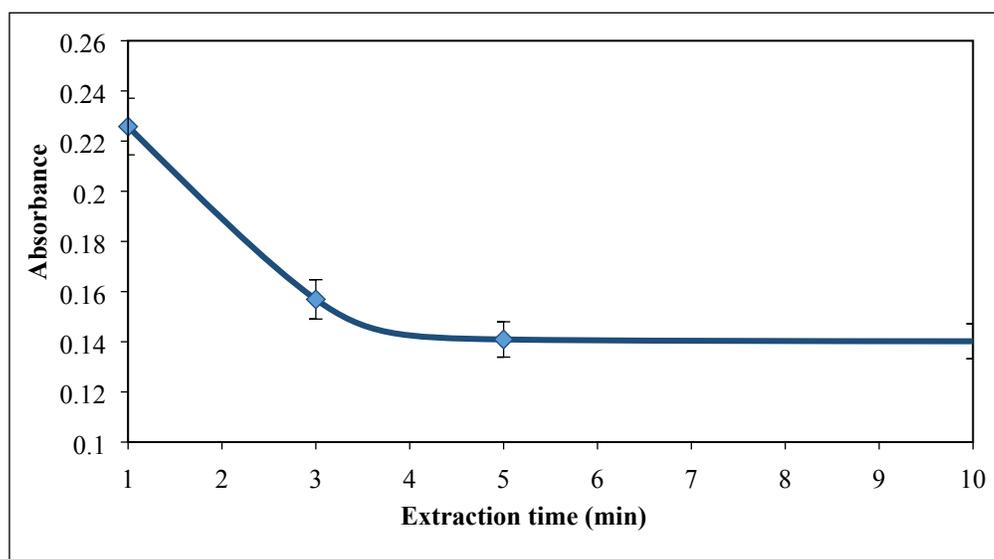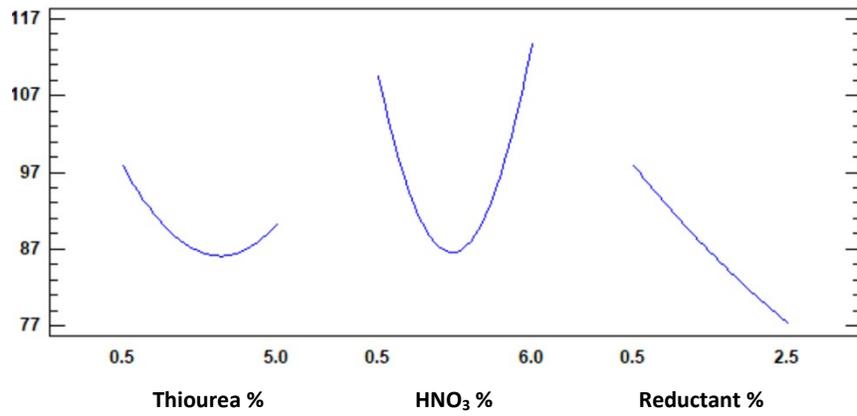
**Fig. ESM4.** Extraction time. 10 µg $L^{-1}$ of Hg(II), prepared with 0.007 % (v/v) MTS, 10 % (wt/v) of NaCl, and 1M HCl until pH = 1.0.
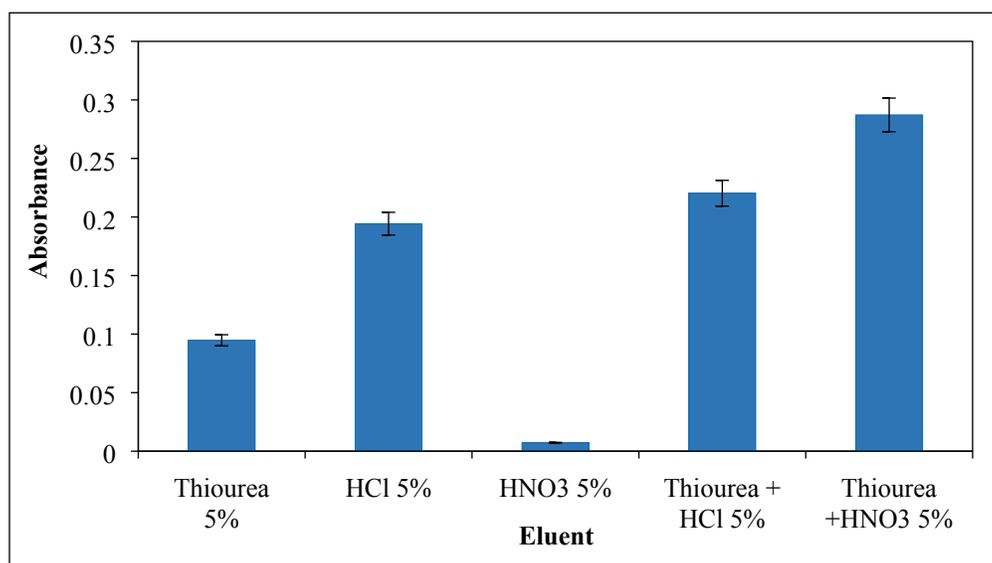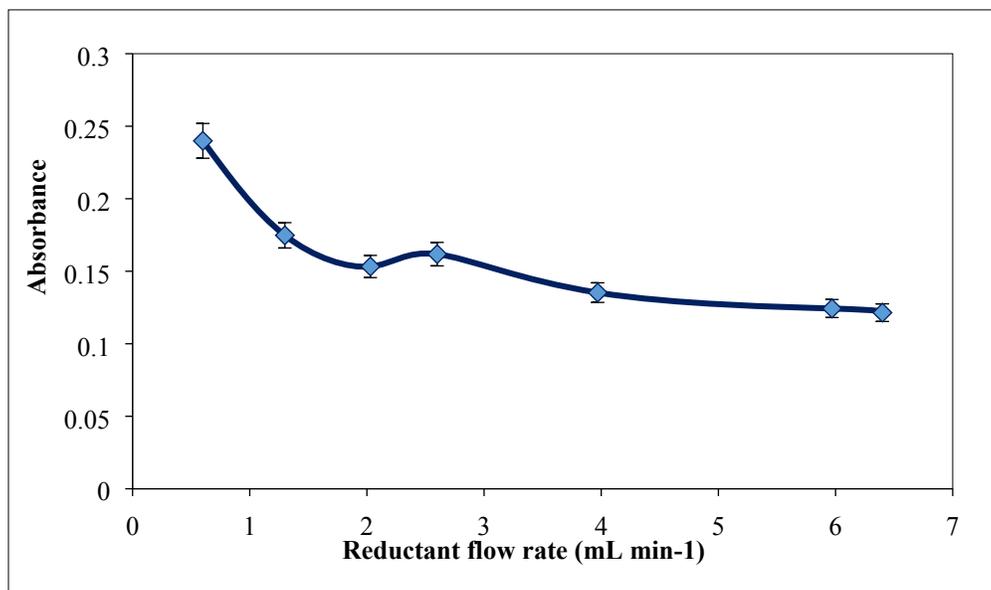
**Fig. ESM5.** Study of eluents, thiourea, HCl, HNO$_3$, mixed of Thiourea and HCl, and Thiourea andHNO$_3$. 10 μg L$^{-1}$ of Hg(II), prepared with 0.007 % (v/v) MTS, 10 % (wt/v) of NaCl and pH = 1.0.

**Fig. ESM6.** Principal effects diagram. 10 µg L$^{-1}$ of Hg(II), prepared with 0.007 % (v/v) MTS, 10 % (wt/v) of NaCl and pH = 1.0.

**Fig. ESM7.** Study of reductant flow rate. 10 μg $L^{-1}$ of Hg(II), prepared with 0.007 % (v/v) MTS, 10 % (wt/v) of NaCl and pH = 1.0.

## References

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2        P. N. Diagboya, B. Y. Olu-Owolabi, D. Zhou and B. H. Han, *Carbon*, 2014, **79**, 174.

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