A Functionalised Carbon Fiber for Flexible Extraction and Determination of Hg(II) Using Au(NP)-Thiol-CF Inductively Coupled Plasma Mass Spectrometry

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Abstract: This work illustrates the improvement in ultra-trace Hg(II) determination in water based on a novel flexible extraction and preconcentration technique (FEPT). This method focuses on the covalent functionalisation of carbon fibre (CF) based on (3-mercaptopropyl)trimethoxysilane. The functionalisation of CF is carried out in two steps: functionalising the surface of CF using acid treatment to obtain hydroxy and carboxyl groups on the surface, followed by a condensation reaction between the carboxyl or hydroxy groups on the carbon (CF-OH) and (3-mercaptopropyl)trimethoxysilane to form mercapto-CF (CF-SH). FTIR, EDX, SEM, XRD and UV-Vis were utilised to confirm the modification. ICP-MS is utilised to determine the Hg(II) and to assess the influence of the memory effect on the results using Au3+ solution and suspended Au nanoparticles (Au-NPs). The result shows that the Au-NPs improve Hg(II) detection and eliminate the memory effect. This study also includes appropriate parameters for contact time, eluent solution, pH, and the foreign metal and ions preconcentration factor. As a result, thiol-CF shows high Hg(II) uptake, flexibility, and stability during the analysis process, with a recovery of 98.96% ± 0.41% for 10 preconcentration factors. These features make FEPT a valuable method for extracting pollutants and overcoming the problems associated with the analysis of such samples.

Keywords: thiol; carbon fibres; mercury; ICP-MS; Hg2+; memory effect

1. Introduction

Mercury has many uses in various industrial applications. For example, it is used in batteries, dental amalgams, the paper industry, measuring equipment, switches, communication, chlor-alkali production, chemical intermediates, and catalysts; it has other miscellaneous uses, such as in gold production. The total consumption of mercury in 2015 was around 4900 tonnes [1]. The combustion of fossil fuels, natural degassing of the earth's crust, and other industrial releases are also contaminant sources of mercury in water [2–4].

A United States governmental agency classified Hg as the third most toxic substance on the planet, and the problem of mercury stems from its bioaccumulation in the body [5]. In 1956, the Japanese discovered that many inhabitants of Minamata, Japan, were suffering from severe neurological diseases. The cause of these diseases was later identified after investigative operations: the contamination of the water supply due to the dumping of mercury [6].

Mercury is classified as a global pollutant as it can be quickly absorbed into gastrointestinal tissues, the respiratory tract, and human skin [7]. Mercury is a contaminant...
of water, and it presents in water as mercuric Hg\(^{2+}\), metallic mercury (Hg), and methyl mercury [8–10].

Several techniques have been utilised to determine the presence of mercury, such as atomic absorption spectroscopy (AAS) and inductively coupled plasma (ICP) [11]. The ICP analyser includes ICP-optical emission spectrometry (ICP-OES), utilised for trace metal detection in petroleum and chemical samples, and ICP-mass spectrometry (ICP-MS), which is applied in cases of ultra-trace high sensitivity for which quantification is needed [12–14]. Previous works have used the ICP-MS for low-concentration-mercury detection because it presents most of the major features required for an idealistic reagent for hybrid chromatography techniques [15]. The Environmental Protection Agency’s (EPAs) method for determining Hg is based on the cooling steam technique (i.e., reducing the mercury ions to Hg\(^0\) and purifying the Hg steam from the solution into the absorption cell) [16,17].

The memory effect of Hg is a problem caused by its accumulation within the instrument, which is then increasingly released over time to produce rising response signals of mercury concentration [16,18]. Gold has been used to eliminate the memory effect, as it mitigates the problems of mercury uptake within the system and negatively contributes to mercury measurement [19]. Mercury contamination of devices may be attributed to their adsorption in the conveyor tube, nebuliser apparatus, and spray chamber, which are often used to quantify mercury in solutions when combined with atomic fluorescence spectroscopy (AFS) or atomic absorption spectroscopy (AAS) [16]. The disadvantage of this technique is that Hg vapor production requires additional equipment to be generated and measured [16].

Due to the bio-accumulation of mercury, the focus on determining and extracting very low concentrations of mercury has been increasing [20–23]. Thus, this requires the development of materials with high selectivity and high surface areas to remove mercury from environmental samples at the ultra-trace concentration within the presence of many interfering substances. ICP-MS is a well-established technique for analysing metal ions at low concentration [24]. Two factors should be considered when analysing Hg: the vapor pressure of mercury, as it is very low; and the memory effect [25], which is the most considered factor. Adding an appropriate amount of gold to eliminate the memory effect was investigated [19]; however, the oxidation state of Au required to eliminate the memory effect also needs to be considered. In this study, we present a new novel flexible extraction and preconcentration technique (FEPT) by introducing the thiol groups to the high surface area and flexible carbon fibres (CFs) using (3-mercaptopropyl)trimethoxysilane to increase the selectivity and extraction process for Hg(II) and to take advantage of CF for its high surface area, flexibility, stability, and reusability. We also report the effect of Au\(^{3+}\) and Au nanoparticles (NPs) on the elimination of the memory effect. This FEPT will open new frontiers in the field of extracting heavy metals.

2. Experimental Work
2.1. Chemical and Solutions

Hydrochloric acid (38.0%), nitric acid (70%), and glacial acetic acid (99%) were obtained from Alfa Aesar (Massachusetts, MA, USA); mercury(II) chloride was obtained from BDH (Poole, UK); and toluene (99%) from Fisher Scientific (Leicestershire, UK). Gold(III) chloride hydrate and 3-mercaptopropyl)trimethoxysilane (95%) were purchased from Sigma-Aldrich (Gillingham, UK). The carbon fibres (ACC-5092-20) were obtained from Kynol (Hamburg, Germany) and featured a thickness of 0.55 mm and a surface area of 1800 m\(^2\)g\(^{-1}\). NaBH\(_4\) was bought from Avocado Research Chemical Ltd. (London, UK).

The mercuric chloride stock solution (100 ppm) was prepared by dissolving 0.01355 g of HgCl\(_2\) in 100 mL of ultra-pure deionised water, and the solution was stored at 4 °C. The working solutions were prepared by making appropriate dilutions of the stock solution. Ultrapure water (resistivity > 14 MΩ cm) was obtained from the MilliQ water purification
system in Millipore, MA, USA. The glassware was cleaned by soaking overnight in 10% (v/v) hydrochloric acid and then rinsing with deionised water.

2.2. Characterisation

The absorbencies of the CF, carbon fibre-mercapto (CF-SH), and carbon fibre-mercapto bound to Hg (CF-SH-Hg) samples were measured using UV-3600 from Shimadzu. The samples were ground, and the resulting carbon particles were taken and suspended in methanol, sonicated, and transferred to a 3 mL UV quartz cuvette. The Fourier transform infrared spectroscopy (FT-IR) measurement was recorded using a VERTEX 70v BRUKER spectrophotometer with a resolution of 4 cm\(^{-1}\) and 64 scans. Thermogravimetric analysis was achieved using SDT Q600 under helium, and the analysis was recorded at 10 \(\degree C\) min\(^{-1}\) from 25 to 750 \(\degree C\). Energy-dispersive X-ray spectroscopy (EDS) was conducted using an X-ray detector integrated into the scanning electron microscope (SEM), (JEOL, JSM-7800F). An aluminium holder was used as deep scratches were created on the surface of the stand, and the fibres were then pressed into the scratches instead of using carbon tape, the use of which leads to an overlap in the proportion of carbon. Phase characterisation was carried out using a Bruker D8 Advance. The source of the X-ray was a 2.2 kW Cu anode, and the running conditions were 40 kV and 40 mA. The Hg concentration was determined using PerkinElmer NexION 300× (plasma gas flow 18 L min\(^{-1}\), auxiliary gas flow 1.2 L min\(^{-1}\), and RF power 1600 W). To ensure that all internal parts were immaculate, all quartz parts, including the nebuliser, torch, and spray chamber, were removed and immersed in 3% nitric acid for 24 h, removed and washed with ultrapure deionised water, and then re-installed.

2.3. Experimental Procedures

2.3.1. CF Modification

The CF was first functionalised with a hydroxy group by acid treatment. Then, 60 mL of acetic acid was placed in a round-bottomed flask connected to a condenser, and the adequate weight of the CF was transferred to the acidic solution and left for 12 h at 70 \(\degree C\). The CF was removed from the acidic solution and rinsed with deionised water three times until the pH level of the flushed water reached around seven; it was then transferred to an oven and kept overnight at 90 \(\degree C\). This batch was named CF-OH.

The functionalisation of the CF-OH with thiol groups was achieved using (3-mercapto propyl)trimethoxysilane, where 50 mL of toluene was transferred to a 250 mL round-bottomed flask; CF-OH was introduced to the flask when the temperature was steady at 80 \(\degree C\). Then, 3 mL of 3-mercaptopropyl)trimethoxysilane was injected into the flask. The reaction was carried out under nitrogen for 6 h. The modified product was removed and rinsed three times with toluene and finally with methanol and left to dry under a vacuum in a desiccator; the product was named CF-SH.

2.3.2. Adsorption Capacity of Hg(II) and Preconcentration

The adsorption capacity and preconcentration of Hg(II) for CF, CF-OH, and CF-SH were assessed by taking an accurate weight of CF, CF-OH, and CF-SH and then transferring them to 50 mL polypropylene tubes. Then, 40 mL of 100 ppm Hg(II) solution was added to each tube. The tubes were left on the checker for an appropriate time, were centrifuged, and the discarded water layer was removed. Then, the fibres were rinsed extensively with deionised water. A suitable eluent (with or without gold solution) was then added to the tubes. The tubes were checked for 30 min, and the solution was transferred using a 0.4 \(\mu\)m filter syringe to a 10 mL plastic tube, which was then ready for ICP-MS analysis. For the preconcentration work, different concentrations were evaluated based on the volume of samples, and the process was carried out as previously explained.

2.3.3. The pH Effect Experiment

The aliquot weight of CF-SH was transferred to a 10 mL tube, then 10 mL of mercury solution (100 ppb) was transferred into the tube. The pH level was adjusted to pH 2.2,
4.0, 7.0, and 8.7 using an HCl or NaOH solution. Then, the tube was centrifuged, and the solution was discarded and the fibre was rinsed with deionised water. Afterward, 2 mL of an eluent solution was added, the tube was shaken, and the solution was transferred to the vial, ready for ICP-MS analysis.

2.3.4. Eluent Effect Experiment

A stock solution of Au(III) (0.01 M) and Au(NP) (0.01 M) were prepared, and the appropriate dilutions were created using 2% HNO\textsubscript{3} to obtain 200 ppb for the Au(NP) and Au(III). Three eluent solutions were assessed: HNO\textsubscript{3} 2% \((v/v)\), Au(III) 200 ppb in 2% HNO\textsubscript{3}, and Au(NP) 200 ppb in 2% \((v/v)\) HNO\textsubscript{3}. The appropriate contact time was also assessed at 5, 15, 30, 45, and 60 min, and the effect of pH on recovery percentage was evaluated.

3. Results and Discussion

3.1. Surface Modification

The schematic of the modification process is illustrated in Figure 1. The functionalisation of CF surfaces, where in the first stage the fibre is treated with acid and where hydroxyl groups are formed, was followed by reacting the hydroxyl groups with a silane coupling agent (3-mercaptopropyl)triethoxysilane), so that the mercapto groups could be obtained on the CF surface. This process is characterised by the high selectivity of mercury ions.

![Figure 1. Schematic diagram of modification and functionalisation processes for CF.](image_url)

The occurrence of modification and the presence of the thiol group were confirmed using FT-IR. The IR spectra of CF-OH, CF-SH, and CF-S-Hg are illustrated in Figure 2. The CF-OH shows a band at 606 cm\(^{-1}\), which is due to the C-C ring bending, and bands at 1400, 1528, and 1615 cm\(^{-1}\) were ascribed to the C=O stretching in the aromatic plane of the CF. The band at 1687 cm\(^{-1}\) was attributed to C-O and C=O [26]. The band at 3427 cm\(^{-1}\) was assigned to the OH band of the hydroxy group at 3427 cm\(^{-1}\) was almost dispersed from the CF-SH batch, confirming that the functionalisation process was accrued by the condensation of the methoxy group on the silane coupling agent and the hydroxy groups on the carbon surface [27]. The other associated bands for CF-SH that appeared at 1090 cm\(^{-1}\) were ascribed to Si-O, and the bands at 687, 721, and 835 cm\(^{-1}\) were attributed to C-H. The band at 1076 was for C-O stretching, and the band at 1119 cm\(^{-1}\) was assigned to Si-O. The bands at 1457 and 1553 cm\(^{-1}\) were ascribed to asymmetric CH\textsubscript{2}. The weak band at 2622 cm\(^{-1}\) was attributed to SH stretching, as shown in Figure 2. The stretching of the CH\textsubscript{2}
bands appeared at 2849 and 2917 cm\(^{-1}\) \[29\]. After Hg(II) attached to the CF-SH, almost all bands appeared, such as the two bands at 2850 and 2918 cm\(^{-1}\), which are assigned for the symmetric and asymmetric C-H stretching band at 3620 cm\(^{-1}\) attributed to the stretching vibrations of OH. However, the thiol band at around 2622 cm\(^{-1}\) disappeared due to the hindering effect \[30\], which was caused by the binding of the thiol group to Hg(II). This can be confirmed by using micro Raman spectroscopy \[31\]. Hence, these results confirm the binding of Hg (II) with the SH group.

Figure 2. IR spectra of (a) CF-OH, (b) CF-SH, and (c) CF-SH-Hg.

The UV-Vis spectra of the CF batches showed absorbance from 280–780 nm for all three batches, as illustrated in Figure 3. It is interesting to note that the surface of CF after modification with the SH group, as well as its attachment to mercury, led to a clear cut-off at 565.6 nm, as shown in Figure 3, for both CF-SH and CF-SH-Hg. However, this phenomenon was not noticed in CF-OH, which confirms the surface modification and Hg loading \[32,33\].

Figure 3. UV-vis absorption spectra of (a) CF-OH, (b) CF-SH, and (c) CF-SH-Hg.
The scanning electron microscopy images are shown in Figure 4. As illustrated in Figure 4a,b, the carbon fibre (CF) before and after modification did not show noticeable damage. The average diameter of the tube was around 10 µm, as shown in Figure 4c. The energy-dispersive X-ray (EDX) spectra of the CF-Si-SH-Hg, illustrated in Figure 4d, confirm the occurrence of functionalisation with the thiol group. The thiol shows 2.30 Kev, and Hg shows a close peak to thiol at 2.12 Kev that belongs to Si from the silane agent. The carbon Kα peak appears at 0.27 Kev, and the Kα peak for oxygen appears at 0.53 Kev. The weight percentage of the elements is illustrated in Table 1. The presence of these elements confirms the chemical attachment of the silane coupling agent and the ability of the CF-Si-SH to attract mercury (II).

![Figure 4. SEM images of (a) CF before modification, (b) CF-SH-Hg, (c) color intensity of CF-SH-Hg, and (d) EDX spectra of CF-SH-Hg.](image)

Table 1. Elements analysis of CF-SH-Hg.

| Element | Weight % | Atomic % |
|---------|----------|----------|
| C K     | 61.63    | 72.05    |
| O K     | 25.93    | 22.76    |
| Si k    | 5.31     | 2.66     |
| S K     | 5.52     | 2.42     |
| Hg M    | 1.61     | 0.11     |

The X-ray powder diffraction (XRD) was utilised to characterise CF-SH and CF-SH-Hg, and the XRD patterns are presented in Figure 5. The first broad diffraction peak at 23° (002 C plane of an aromatic layer) and the other weak diffraction peak at 42° (100 C plane of an aromatic layer) appeared, which confirmed that the CF was in an amorphous phase. After the Hg ions attached to the thiol group (CF-SH-Hg), the XRD showed a shift toward low theta values; this may have contributed to the effect of Hg binding to the thiol group, which led to this shift due to interaction with the structure via the introduction of a small portion of metal phase [34,35].
The thermogravimetric analysis (TGA) is illustrated in Figure 6 for three samples: CF-OH, CF-SH, and CF-SH-Hg. As we can see, the total weight loss for CF-OH was around 17.57%. The primary weight loss was due to the physically adsorbed water molecules and residual material utilised in the synthesis processes [36]. The CF-SH shows a total weight loss of 32.4% in the three main steps, the first of which moved from 30–210 °C and was attributed to water and solvent that physically and chemically adsorbed [37]. The second step was from 210–380 °C (7.1%), which was attributed to the organic degradation of the organic silane coupling agent [38]. The high weight loss in the third step (from 380–750 °C) was possibly due to degradation of the multilayered silane coupling agents [39]. The CF-SH-Hg shows many steps for weight loss, and the total weight loss was 44.7%. The weight loss of the silane coupling agent was around 8.2% (190–350 °C), which is close to the result obtained from CF-SH. The difference in weight loss between the CF-SH and CF-SH-Hg batches may be due to the attachment of Hg to the silane coupling agent and to degradation [40]. Thus, these results confirm the process of binding the silane coupling agent to the CF. The weight loss percentage of the coupling agent is close to the result obtained by EDX.
3.2. Hg CF-SH Extraction and Parameters Effect

3.2.1. Memory Effect

The optimum conditions for the preconcentration process were investigated, including the eluent, pH, and contact time. As shown in Figure 7, three eluent solutions were inspected: 2% (v/v) HNO₃; 2% (v/v) HNO₃, 200 µg L⁻¹, Au(III); and HNO₃, 200 µg L⁻¹, Au(NP). Au(III) and Au(NP) were investigated as additives to 2% HNO₃. The result, as illustrated in Table 2, demonstrates that adding Au(III) or Au(NP) is essential for Hg recovery, and without adding them, hazy results would be obtained. In the same context, the use of Au(NP) shows 99% better recovery compared to Au(III) 76%. Therefore, Au(NP) is more reliable for obtaining high recovery and reproducibility results. This outcome is consistent with results gained from previous research, where it was reported that adding a gold solution to HNO₃ can preserve Hg as free ions. Thus, adding 200 µg L⁻¹ of Au(NP) is recommended when using ICP-MS for Hg analysis to avoid the memory effect [13,41,42].

Table 2. Effect of eluent solutions.

| SDT (n = 3) | Average Recovery (%) | Eluent |
|------------|----------------------|--------|
| 1.54       | 12.47                | 2% HNO₃ |
| 1.42       | 76.12                | 2% HNO₃-Au(III) |
| 0.75       | 99.27                | 2% HNO₃-Au(NP) |

3.2.2. The Efficiency of CF for Mercury Uptake

The calibration points are in line up to 1000 ng L⁻¹, as shown in Figure 8, and the coefficient of determination is $R^2 = 0.9997$, which was acquired from six points at various Hg(II) concentrations: 0.0, 100, 250, 500, 750, and 1000 ng L⁻¹. The limit of detection (LOD) was determined using Equation (1)

$$\text{LOD} = \frac{3s\bar{y}}{m}$$

where $s\bar{y}$ is the standard deviation of the zero concentration for 10 readings and $m$ is the slope of a calibration curve. The $s\bar{y}$ is calculated based on the y intercepts of the calibration curve. Therefore, as $m = 1.4$ and $s\bar{y} = 1.005$, the LOD = $\frac{3(1.005)}{1.4} = 2.15$ ng L⁻¹.
1.42 76.12 74.87 2% HNO\textsubscript{3}-Au(III) 
77.66 
75.83 
0.75 99.27 99.84 2% HNO\textsubscript{3}-Au(NP) 
98.42 
99.55 
3.2.2. The Efficiency of CF for Mercury Uptake

The calibration points are in line up to 1000 ng L\textsuperscript{-1}, as shown in Figure 8, and the coefficient of determination is $R^2 = 0.9997$, which was acquired from six points at various Hg(II) concentrations: 0.0, 100, 250, 500, 750, and 1000 ng L\textsuperscript{-1}. The limit of detection (LOD) was determined using Equation (1)

$$\text{LOD} = \frac{3\sigma}{m}$$  

where $\sigma$ is the standard deviation of the zero concentration for 10 readings and $m$ is the slope of a calibration curve. The $\sigma$ is calculated based on the y intercepts of the calibration curve. Therefore, as $m = 1.4$ and $\sigma = 1.005$, the LOD = $\frac{3(1.005)}{1.4} = 2.15$ ng L\textsuperscript{-1}.

The calculation of the quantitation limit (LOQ) is based on Equation (2) as follows:

$$\text{LOQ} = \frac{10\sigma}{m}$$

Therefore, the LOD = $\frac{10(1.005)}{1.4} = 7.17$ ng L\textsuperscript{-1}.

3.2.3. pH Effect

The efficiency of CF-SH to extract and preconcentrate Hg(II) at various pH levels, 2.2, 4.0, 7.2, and 8.7, was evaluated. The results in Figure 9 show that the pH level influences preconcentration recovery. Furthermore, it is apparent from Figure 9 that there is an effect of the pH level, as the curve begins to increase at pH 2 and continues until it reaches the highest point of extraction at pH 4, and then begins to gradually decline with increasing the pH level until it reaches to the lowest capacity at pH 9. This is due to the ionisation property of the thiol group. Therefore, the appropriate pH level needed to extract Hg(II) using CF-SH from the solution was pH 4, so pH 4 was chosen as a proper point for the extraction and preconcentration process.

Figure 8. The calibration curve of Hg(II). The standard solutions were prepared using a solution of 2% HNO\textsubscript{3} containing 200 ppb Au(NP).

Figure 9. Uptake of Hg(II) based on pH level.
3.2.4. Equilibrium Time Effect

The soft–soft interaction between the thiol group and Hg is clear, as shown in Figure 10. When the fibre (CF-SH) is dipped in the mercury solution, the mercury ions start to covalently bond to the thiol groups. The correlation begins with the start of the reaction and reaches its climax after 20 min.

3.2.5. Capacity of CF

The maximum mercury uptake by CFs was estimated using Equation (3). Three batches of unmodified CF, CF-OH, and after functionalisation with thiol groups. Table 3 reveals that all CFs have the ability to uptake mercury. However, CF-SH showed a superior uptake, five times better than CF, which can be attributed to the high surface area of the CF (1800 m$^2$ g$^{-1}$) and the functionalisation of CF with the thiol groups, which increase the ability of the CF to attract mercury ions from the solution.

\[
\text{Capacity (Ct mg/g)} = \frac{\text{Hg uptake by CF in mg} \times 1000}{\text{weight of dry CF utilized in mg}}
\]

(3)

Table 3. Capacity of CFs (mg Hg/g CF or CF-OH or CF-SH).

| SDT       | Average (n = 3) | mg/g | Capacity |
|-----------|----------------|------|----------|
| ±2.50     | 77.17          | 76.8 | CF       |
|           |                 | 80.4 |          |
|           |                 | 74.3 |          |
|           |                 | 127.2|          |
| ±3.42     | 130.8           | 135.41| CF-OH    |
|           |                 | 129.8|          |
|           |                 | 414.61|          |
| ±5.63     | 422.55          | 425.98| CF-SH    |
|           |                 | 427.05|          |

3.2.6. Preconcentration Factor (PCF)

Due to the bio-accumulation of Hg and the need to determine the ultra-trace levels of mercury, a preconcentration process was applied using CF-SH. In this experiment, four levels of preconcentration were assessed (5, 10, 25, and 100 folds), the eluent was HNO$_3$ 200 µg L$^{-1}$ Au(NP), and pH was 4. The preconcentration process was carried out as illustrated in Figure 11. As can be seen from the diagram, after collecting the water sample, the CF-SH was transferred into the vessel so the extraction process could occur. After a suitable time, the fibres can be easily removed. As shown in Table 4, the modified CF (CF-SH) showed remarkable recovery across all four levels, and the average recovery was over 97%.
Table 3. Capacity of CFs (mg Hg/g CF or CF-OH or CF-SH).

| Substance  | SDT Average (n = 3) mg/g Capacity |
|------------|---------------------------------|
| CF         | ±2.50                           |
| CF-OH      | ±3.42                           |
| CF-SH      | ±5.63                           |

3.2.6. Preconcentration Factor (PCF)

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Table 4. The recovery percentage of Hg at different PCFs.

| PCF | Substance  | Average (n = 3) |
|-----|------------|----------------|
| 10  | CF-SH      | 98.96 ± 0.41   |
| 50  | CF-SH      | 95.63 ± 1.09   |
| 100 | CF-SH      | 94.62 ± 1.87   |
| 50  | CF-OH      | 38.49 ± 3.47   |
| 50  | CF         | 17.85 ± 0.61   |

3.2.7. Interferences with Other Cations

The interference of a matrix of ions was evaluated as a percentage of a known Hg concentration (150 ppb). The results, shown in Table 5, confirmed that the interference from other cations was neglected. In addition, the ionic strength was calculated based on Equation (4); the result indicated that the ionic strength had no considerable impact on the extraction and preconcentration processes when a concentration of up to 1 molar of NaCl was utilised.

\[
(Ionic\ Strength)\ I = \frac{1}{2}n \sum i(CiZi) \tag{4}
\]

Here, \( n \) is the sum of ions in the solution, \( i \) is the specific ion in the solution, \( Ci \) is the molar concentration, and \( Zi \) represents the charge number of electrolytes.

Table 5. Recovery of Hg in the presence of metal ions.

| Recovery Percent of Hg | Concentration (mg L⁻¹) | Cations |
|------------------------|------------------------|---------|
| 76.4 ± 1.2             | Na                     |
| 0.7 ± 0.10             | K                      |
| 91.7 ± 1.4             | Mg                     |
| 3.7 ± 1.3              | Ca                     |
| 47.7 ± 1.3             | Ba                     |
| 447.5 ± 2.2            | Cr                     |
| 19.9 ± 3.8             | Fe                     |
| 257.2 ± 2.4            | Co                     |
| 3650.2 ± 3.4           | Ni                     |
| 69.8 ± 2.2             | Cu                     |
| 1.76 ± 2.0             | Zn                     |
| 17.7 ± 1.3             | As                     |
| 1198.8 ± 2.6           | Mo                     |
4. Conclusions

High-surface-area CF was modified using (3-mercaptopropyl)triethoxysilane. The fabrication of CF-SH was conducted by first producing CF-OH using acid treatment. Then, CF-OH was functionalised with 3-mercaptopropyl)trimethoxysilane to obtain CF-SH. FT-IR and EDX analyses confirmed the presence of the sulphur group (SH). UV-vis showed a cut-off of 565.6 nm for CF-S-Hg, and XRD showed a shift toward low theta values. The TGA analysis weight loss was 44.7% of CF-S-Hg.

The FEPT using the CF-SH exhibited excellent capacity for Hg(II)(422.55 mg/g) compared to unmodified CF (77.17 mg/g). Furthermore, the use of Au(NP) as additives to the HNO$_3$ eradicated the memory effect and enhanced the recovery percentage of Hg(II), and showed high selectivity and stability during the analysis process, with recovery of up to 98.9% for 10 PCF. Thus, this technique opens the door to a new frontier in the extraction of heavy metals.

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