**Graphene Oxide-TiO₂ Composite Solid Phase Extraction Combined
with Graphite Furnace Atomic Absorption Spectrometry for the
Speciation of Inorganic Selenium in Water Samples**

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ABSTRACT: In this paper, a method of graphene oxide (GO)-TiO₂ composite solid phase extraction followed by graphite furnace atomic absorption spectrometry (GFAAS) detection was proposed for the speciation of inorganic selenium in environmental waters. The adsorption behavior of inorganic Se(IV) and Se(VI) on the GO-TiO₂ (1:1) composite was investigated. It was found that Se(IV) was quantitatively retained on the GO-TiO₂ composites within a wide pH range of 0.5-10, while Se(VI) was quantitatively adsorbed on GO-TiO₂(1:1) composite at pH 0.5-2, and no obvious adsorption of Se(VI) within the pH range of 4-10 was found. By selecting pH 6.0, Se(IV) could be easily determined. After reduction of Se(VI), total Se was determined by the proposed method, and Se(VI) was calculated as the difference between the total Se and Se(IV). The factors affecting the separation/preconcentration of Se(IV) and Se(VI) were studied. Under the optimum conditions, the isothermal adsorption of Se(IV) on the GO-TiO₂ (1:1) composite fitted Langmuir model; a linear range over 0.1-12 ng mL⁻¹ was obtained. The limit of detection (LOD) and precision of the method for Se(IV) was 0.04 ng mL⁻¹ and 9.4% (c_{Se(IV)}=0.5 ng mL⁻¹, n=7), respectively. In order to verify the accuracy of the method, a standard water sample (GSBZ50031-94) was analyzed, and the determined value was in a good agreement to the certified value. The established method was applied to inorganic Se speciation in environmental water samples and the recovery of 87.4%-102% was obtained for the spiked samples.

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Keywords: Se(IV)/Se(VI) speciation, GO-TiO₂ composite, solid phase extraction, graphite furnace atomic absorption spectrometry, environmental water

1. Introduction

Selenium (Se) is an essential element for human body whilst it has potential toxicity, which is related to its concentration and existing forms [1]. Low level of Se exhibits antioxidant activity which is beneficial to health [2], while Se is toxic at concentrations of three to five times higher than the essential level [3]. The recommended daily intake of Se for adults is 55 µg, and the tolerable upper limit is 400 µg [4]. Selenosis may occur when the daily intake amount exceeds the tolerance limit, leading to gastrointestinal disorders, sloughing of nails, hair loss, fatigue, irritability, arrhythmia or nerve damage as well as myocardial depression or pulmonary edema in very acute cases [5]. Among various Se species, the inorganic forms are more toxic than organic forms, and the toxicity of inorganic forms follows the order of Se(IV)<Se(VI)<H₂Se [6]. Se exists in natural water mainly as selenite, Se(IV), and selenate, Se(VI) [7], which can directly or indirectly enter human body. Therefore, it is necessary to develop appropriate methods for the speciation of inorganic Se in natural water.

At present, the speciation of selenium is mostly realized by hyphenated techniques involving separation techniques and elemental specific detection techniques. Highly sensitive and element-specific detection techniques such as inductively coupled plasma optical emission spectrometry/mass spectrometry (ICP-OES/MS) [8-10], graphite furnace atomic absorption spectrometry (GFAAS) [11-13], hydride generation atomic fluorescence spectrometry (HG-AFS) [14-16] are generally employed for selenium detection. Among these techniques, GFAAS is the most widely employed because of its highest analytical sensitivity and low cost. For the separation of different Se species, high performance liquid chromatography and capillary electrophoresis are efficient techniques, and some non-chromatographic schemes have been proved to be simple and low cost for selenium speciation without

special separation instruments [17, 18]. A series sample pretreatment techniques are involved, including magnetic solid phase extraction (MSPE) [14, 19], capillary microextraction (CME) [20], solid phase extraction (SPE) [9, 13, 21, 22], cloud point extraction (CPE) [23, 24], dispersive liquid-liquid microextraction (DLLME) [25] and dispersive solid-phase microextraction (DSPME) [26, 27]. Among them, SPE is the most employed alternative due to its simple operation, high enrichment factor, low consumption of organic solvent, low cost and on/off-line operation available. The SPE adsorbents determine the analytical performance of the SPE-based system to a great extent, in terms of selectivity, enrichment factor and adsorption capacity [28]. Modified silica [8], resins [13, 29], metal oxide materials [21, 22] and carbon-based materials [9, 30] are the representative SPE adsorbents for the analysis of inorganic Se speciation.

Carbon-based nanomaterials have been widely applied as the adsorbents in sample pretreatment due to their good chemical stability, high adsorption capacity, various shapes (spherical shell, tube, layer, etc.), tunable surface properties and large surface areas. Wang et al. [14] prepared the magnetic carbon nanotubes (MCNTs) for the adsorption of trace Se(IV) in tap water and lake water. Skorek et al. [26] used multiwalled carbon nanotubes (MWCNTs) as the solid adsorbent and ammonium pyrrolidinedithiocarbamate (APDC) as the chelating agent to extract Se(IV) from mineral water and biological samples. Kocot et al. [27] reported the application of graphene along with APDC for inorganic Se speciation in water and biological samples. Peng et al. [9] applied the amino modified MWCNTs as a SPE micro-column packing material for the speciation of inorganic As, Cr and Se in the environmental water samples. Graphene oxide (GO) is a novel two-dimensional carbon-based nanomaterial, possessing oxygen-containing groups and large surface area which makes it ideal for retention of interest analytes compared to carbon nanotubes.

The surface of GO can be easily modified, and the GO-based composites obtained through modification of other inorganic materials [31-34] have widen the application of GO in removal of pollutants, separation/pre-concentration of trace metal ions and

analysis of organic compounds. Fu et al. [33] synthesized a kind of water-dispersible magnetic nanoparticle-graphene oxide (MGO) composite for removal of Se(IV) and Se(VI) in water. Nanometer-sized TiO₂ featured with high surface area was used for the selective adsorption of Se(IV) at pH < 8, probably due to the electrostatic attraction between metal ions and surface charges of TiO₂ nanoparticles [16]. In our previous work [34], a GO-TiO₂ composite was prepared by hydrolysis of Ti(BuO)₄ to TiO₂ on GO nanosheets, and it exhibited good extraction performance for heavy metals and rare earth ions. Herein, the synthesized GO-TiO₂ composite was applied as the micro-column packing material for selective adsorption of Se(IV). Se(VI) was calculated as the difference between the total Se and Se(IV). A method of SPE-GF-AAS for the speciation analysis of Se(IV) and Se(VI) in water samples was established.

2. Experimental

2.1. Apparatus

GF-AAS (Z-2000, Shimadzu, Japan) was used for the determination of Se(IV) and the main operation parameters were shown in Table S1. ICP-OES (Intrepid XSP Radial, Thermo, USA) was employed in investigation of the adsorption capacity of materials and isothermal adsorption model and its operation conditions were presented in Table S2. The pH values were adjusted with a pH meter (320-S, Mettler Toledo Instruments Co. Ltd., Shanghai, China) supplied with a combined electrode. High purity water (18.2 MΩ·cm) was obtained from Milli-Q Element system (Millipore, Molsheim, France). HL-2 peristaltic pumps (Shanghai Qingpu Huxi Instrument Factory, Shanghai, China) and self-made PTFE micro-columns (20 mm × 2.0 mm i.d.) were used in the SPE pre-concentration process.

2.2. Standard solutions and reagents

The stock standard solutions (1.000 g L⁻¹) of Se(IV) and Se(VI) were prepared by

115 dissolving certain amounts of Na_2SeO_3 (97%, Wako, Japan) and Na_2SeO_4 (97%,
116 Wako, Japan) in 2% HNO_3 , respectively. Working standard solutions were prepared
117 daily by stepwise dilution of the stock standard solutions. Other reagents employed in
118 the experimental process were at least analytical grade and high purity water was used
119 throughout the experiments.

120 2.3. Column preparation

121 Thirty milligrams of $\text{GO-TiO}_2(1:1)$ composite was filled into a PTFE micro-column.
122 Some cotton wool was used on both ends to prevent packing losses. Before use, 0.5
123 mol L^{-1} HNO_3 and 0.1 mol L^{-1} $\text{CH}_3\text{COONH}_4$ were passed sequentially through the
124 micro-column in order to clean and condition the packed material. The self-prepared
125 GO-TiO_2 composites with varying GO/TiO_2 ratios [34] were treated with the same
126 procedures.

127 2.4. General procedure

128 Sample solutions containing Se(IV) were adjusted to pH 6.0 with 0.1 mol L^{-1}
129 NaOH and 0.1 mol L^{-1} HNO_3 . 25 mL of Se(IV) solution was pumped through the
130 micro-column at a flow rate of 2 mL min^{-1} . The adsorbed Se(IV) was eluted with 0.9
131 mL of 3.0 mol L^{-1} HNO_3 at a flow rate of 2 mL min^{-1} from the opposite direction.
132 Then, 4 mL 0.1 mol L^{-1} $\text{CH}_3\text{COONH}_4$ was used to balance the material. Finally, the
133 eluted Se(IV) was detected by GF-AAS. Ultrapure water was employed as the blank
134 and subjected to the same procedure.

135 2.5. Sample pretreatment

136 Spring water 1 and Spring water 2 (Enshi, China) were collected and filtered
137 through the $0.45 \mu\text{m}$ membrane filter. The water samples were kept at 4°C . The
138 concentration of Se(IV) in water samples was determined according to the procedures
139 specified in section 2.4. For determination of total Se, reduction Se(VI) to Se(IV) was
140 performed in the reference material and water samples as follows [35, 36]: the sample

141 solution was mixed with concentrated HCl and KBr, and the final concentration of
142 HCl and KBr were 6 mol L⁻¹ and 0.05 mol L⁻¹, respectively. The solution was boiled
143 for 40 min in water bath, and evaporated in an open system (almost to dry). Then, the
144 solution was diluted with ultrapure water to a constant volume and analyzed for total
145 Se immediately according to the general procedure. The content of Se(VI) in the
146 samples was obtained by subtracting Se(IV) from the total Se.

147 **3. Results and discussion**

148 *3.1. Selectivity of GO-TiO₂(1:1) composite to Se(IV)*

149 The adsorption behavior of inorganic Se(IV) and Se(VI) on the GO-TiO₂(1:1)
150 composite and TiO₂ were investigated and compared under different pH conditions
151 using the micro-column operation. Fig. 1 shows the effect of pH on the adsorption of
152 inorganic Se species on GO-TiO₂(1:1) composite and TiO₂ material. It could be seen
153 that Se(IV) was quantitatively retained on both adsorbents within a wide pH range of
154 0.5-10. While the adsorption behavior of Se(VI) on the two adsorbents was different.
155 As shown in Fig. 1 (A), the quantitative adsorption of Se(VI) on GO-TiO₂(1:1)
156 composite was achieved at pH 0.5-2, and Se(VI) was not retained on the composite
157 within the pH range of 4-10. As can be seen in Fig. 1 (B), Se(VI) could be adsorbed
158 quantitatively on TiO₂ at pH 0.5-3, and it could not be retained at pH 6-10. A wider
159 span of pH for selective adsorption of Se(IV) from Se(VI) on GO-TiO₂(1:1)
160 composite was achieved than that on TiO₂ material.

161 The different adsorption behaviors of Se(IV) and Se(VI) on the GO-TiO₂(1:1)
162 composite and TiO₂ material demonstrate possible different adsorption mechanisms
163 of Se species on them. The pK₁ and pK₂ of H₂SeO₃ are 2.46 and 7.31, respectively and
164 the pK₂ of H₂SeO₄ (a strong acid) is 1.92 [37]. Thus, Se(IV) exists mainly as H₂SeO₃
165 at pH < 3 and HSeO₃⁻ at pH 3-7 as well as SeO₃²⁻ at pH > 7, while Se(VI) is mainly
166 in the form of HSeO₄⁻ at pH < 2 and SeO₄²⁻ at pH > 2. The pH_{pzc} (point of zero
167 charge) values of GO and TiO₂ are ~3.9 [38] and 5.9 [39], respectively. For TiO₂, the
168 surface covered with OH groups appears negatively charged under conditions of pH

169 higher than the pH_{pzc} of TiO_2 , and positively charged cations would be adsorbed
 170 through electrostatic attraction. On the contrary, if the surface is positively charged it
 171 will capture anions when the solution pH is lower than the pH_{pzc} of TiO_2 [16]. For
 172 GO- TiO_2 (1:1) composite, it contains hydroxyl binding sites located on GO sheets ($\equiv$
 173 C—OH, X-OH) and on TiO_2 ($\equiv$ Ti—OH, X-OH), respectively.

178 At $\text{pH} < 3$, H_2SeO_3 can be adsorbed on both GO- TiO_2 (1:1) composite and TiO_2
 179 probably through H-bonds. At $\text{pH} > 3$, Se(IV), a strongly binding anion, may form
 180 two types of inner-sphere complexes on the aforementioned two SPE adsorbents via
 181 ligand exchange mechanism (Eq.(1) and (2)), while Se(VI) is a relatively weak
 182 binding anion and could be retained on the surface of GO- TiO_2 (1:1) and TiO_2 mainly
 183 through electrostatic attraction to form outer-sphere complexes (Eq.(3) and (4)) [33,
 184 40, 41]. Eq.(3) and (4) indicate that lower pH facilitates the adsorption of Se(VI) on
 185 the adsorbents. At pH higher than pH_{PZC} , the surfaces of GO- TiO_2 (1:1) and TiO_2 are
 186 negatively charged, increasing the electrostatic repulsion between Se(VI) and the
 187 adsorbents and resulting in the reduced adsorption percentage of Se(VI). The different
 188 pH_{PZC} between GO- TiO_2 (1:1) composite and TiO_2 is most likely responsible for the
 189 different adsorption behaviors of Se(VI) on GO- TiO_2 (1:1) and TiO_2 adsorbents, and
 190 GO in the GO- TiO_2 (1:1) composite changed the pH_{PZC} of the prepared materials,
 191 which plays a critical role for the separation of the two Se species in a wider pH
 192 range.

193 3.2. Dynamic adsorption capacities of the GO- TiO_2 composites

194 It was found in our previous work [34] that high pressure occurred in the SPE
 195 column packed with GO- TiO_2 (3:1) or GO- TiO_2 (9:1) material. Therefore, the
 196 adsorption performance of TiO_2 , GO- TiO_2 (1:9), GO- TiO_2 (1:3) and GO- TiO_2 (1:1) for

Se(IV) were investigated (Fig. 2). The dynamic adsorption capacities of GO-TiO₂ composites with varying GO/TiO₂ ratios and TiO₂ for Se(IV) were measured according to the reported method [42] by passing 9 mL sample solutions of 5, 10, 20, 30, 40 and 50 µg mL⁻¹ Se(IV) at a constant flow rate of 2.0 mL min⁻¹, respectively. ICP-OES was used to detect the concentration of Se(IV) in the effluent. Q_e (mg g⁻¹) and C_e (mg L⁻¹) represent the adsorption amount at equilibrium and the corresponding Se(IV) content in the effluent. The dynamic adsorption capacities of TiO₂, GO-TiO₂(1:9), GO-TiO₂(1:3) and GO-TiO₂(1:1) for Se(IV) were calculated to be 2.45, 2.92, 3.25, 3.77 mg g⁻¹, respectively. An increasing adsorption capacity for Se(IV) was obtained by increasing the percentage of GO in the material. While, high pressure occurred in the SPE column packed with GO-TiO₂(3:1) or GO-TiO₂(9:1) material [34]. Accordingly, the GO-TiO₂(1:1) adsorbent was used as the adsorbent for subsequent experiment and the sample solution was adjusted to pH 6 for the selective adsorption of Se(IV).

The dynamic adsorption capacities of some reported SPE materials for Se(IV) were listed in Table 2. The adsorption capacity (3.77 mg g⁻¹) of GO-TiO₂(1:1) composite was comparable to most of the cited SPE adsorbents, e.g. magnetic MWCNTs (2.5 mg g⁻¹) [14] and Mg-FeCO₃ layered double hydroxides loaded cellulose fibre (3.84 mg g⁻¹) [15], while lower than that obtained by chemically modified mesoporous silica (SBA-15) [10] probably due to the porous structure of mesoporous silica.

3.3. Optimization of the SPE procedure

3.3.1. Elution conditions

The effect of HNO₃ concentrations on the elution was investigated in the range of 1-4 mol L⁻¹ by using 2 mL eluent. The results in Fig. S1 showed that quantitative recovery for Se(IV) was obtained when the concentration of HNO₃ was higher than 2 mol L⁻¹. Therefore, 3 mol L⁻¹ HNO₃ was applied for elution of the retained Se(IV) in subsequent experiments. Then the effect of HNO₃ volume on the elution was studied in the range of 0.6-2.0 mL. As can be seen in Fig. S2, quantitative recovery was

225 achieved when the volume of HNO_3 was above 0.8 mL. Finally, 0.9 mL of 3 mol L^{-1}
226 HNO_3 was applied for elution of the retained Se(IV).

227 The influence of elution flow rate on the recovery of Se(IV) was further
228 investigated in the range of 0.5-2.5 mL min^{-1} . The results in Fig. S3 indicate that the
229 analyte could be recovered quantitatively with the tested elution flow rate range. And
230 a flow rate of 2.0 mL min^{-1} was used for elution in subsequent experiments.

231 3.3.2. *Effect of sample flow rate and sample volume*

232 The influence of sample flow rate on the adsorption of Se(IV) was studied by
233 passing the solution through the micro-column at flow rate range of 0.5-2.5 mL min^{-1} .
234 Quantitative recovery was obtained for Se(IV) in the whole tested range (Fig. S4).
235 Hence, a flow rate of 2 mL min^{-1} was selected as the optimum condition.

236 In order to obtain a high enrichment factor, a large volume of sample solution is
237 preferred. The effect of sample volume on retention of Se(IV) was investigated by
238 passing 5, 10, 20, 25, 30, 40 and 50 mL sample solutions containing 2 μg of Se(IV)
239 through the micro-column, respectively. As shown in Fig. S5, the analyte on the
240 adsorbent could be quantitatively desorbed when the sample volume was less than 30
241 mL, resulting in a theoretical enrichment factor of 33.3. In real sample analysis, 25
242 mL solution was employed along with the elution volume of 0.9 mL, and a theoretical
243 enrichment factor of 27.8 was obtained in this work.

244 3.4. *Effect of Se(IV)/Se(VI) ratio*

245 The effect of Se(IV)/Se(VI) ratio on the separation and pre-concentration of Se(IV)
246 has been evaluated under optimum conditions. Various solutions with different
247 concentration ratios of Se(IV)/Se(VI) were employed. And the results shown in Fig.
248 S6 indicate that Se(IV) could be recovered quantitatively with Se(IV)/Se(VI) ratio
249 varying from 10:1 to 1:10, indicating a good application potential of the established
250 method in environmental water samples.

251 3.5. Co-existing ions interference

252 Various coexisting ions were added individually to the sample solutions containing
253 10 ng mL⁻¹ Se(IV), and their effects on the recovery of the analyte were investigated
254 under the optimized conditions. The tolerance limit of the coexisting ions is defined as
255 the largest amount in the presence of which the recovery of Se(IV) remained as
256 90-110%. The results summarized in Table 1 show that the developed method has a
257 good tolerance to common co-existing ions in environmental water samples.

258 3.6. Regeneration of the GO-TiO₂(1:1) composite

259 The regeneration of the prepared GO-TiO₂(1:1) composite for Se(IV) was
260 investigated by pumping 25 mL solution of the analyte through the micro-column,
261 followed by passing through 0.9 mL of 3 mol L⁻¹ HNO₃ and 4 mL of 0.1 mol L⁻¹
262 CH₃COONH₄, repeatedly and continuously. Results demonstrated that the
263 GO-TiO₂(1:1) composite packed micro-column could be reused more than 95 runs,
264 indicating a good acid-resistant ability and long lifetime of the adsorbent.

265 3.7. Isothermal adsorption model

266 Under the optimized conditions, 5, 10, 20, 30, 40, 50, 60 and 70 µg mL⁻¹ Se(IV)
267 solutions were pumped through the GO-TiO₂(1:1) packed micro-column, respectively.
268 The concentration of Se(IV) in the effluent was measured by ICP-OES. The data were
269 fitted with Langmuir adsorption model (Eq. (5)) and Freundlich adsorption model (Eq.
270 (6)), respectively, where Q_{max} (mg g⁻¹) is the maximum adsorption capacity, Q_e (mg
271 g⁻¹) represents the adsorption amount at equilibrium and C_e (mg L⁻¹) is the
272 corresponding Se(IV) content in the effluent, K_L (L⁻¹ mg) is the Langmuir adsorption
273 constant, 1/n and K_F (L mg⁻¹) are the Freundlich adsorption constants [42].

$$274 \quad Q_e = (Q_{\max} K_L C_e) / (1 + K_L C_e) \quad (5)$$

$$275 \quad Q_e = K_F C_e^{1/n} \quad (6)$$

276 As shown in Fig. 3 (A) and (B), the experimental data were fitted well with the

Langmuir adsorption model, which was concluded to be a monolayer adsorption. And $Q_{\max}$ was calculated to be 3.69 mg g^{-1} , which is in agreement with the experimental value (3.77 mg g^{-1}).

3.8. Analytical performance

The analytical performance of the method was evaluated under the optimized conditions. The linear equation for Se(IV) was $Y=0.033x+0.002$ ($R^2=0.999$) with the linear range of $0.1\text{-}12 \text{ ng mL}^{-1}$. The limit of detection (LOD), defined as three times the standard deviation of the blank solution signal ($n=11$), was found to be 0.04 ng mL^{-1} for Se(IV). The relative standard deviation (RSD) of the method for Se(IV) was 9.4% ($c_{\text{Se(IV)}}=0.5 \text{ ng mL}^{-1}$, $n=7$), respectively.

Table 2 is the comparison of the analytical performance data of the present method with some other methods reported in the literatures. As can be seen, the LOD of this method is much lower than Ref. [10] and comparable to that reported in Ref. [12], [20], [21], [22], [26] and [27]. Compared with Ref. [13], [14], [29] and [30] which provided satisfied LOD for Se(IV), the proposed method exhibited much faster adsorption/desorption dynamics and lower consumption of adsorbents with long lifetime.

In order to validate the accuracy of the proposed method, GSBZ50031-94 (water sample) was analyzed, and the results are given in Table 3. As can be seen, a good agreement between the determined value and the certified value was obtained.

3.9. Sample analysis

The method was applied to the analysis of Se(IV) and Se(VI) in natural water samples. The analytical data of the spring water samples along with recoveries of the spiked samples are shown in Table 3. It could be found that (a) the concentration of high oxidation state species (Se(VI)) in these water samples was higher than that of low oxidation state species (Se(IV)); (b) the total inorganic Se in the water samples was at the level of ng mL^{-1} . The precision (RSD, $n=3$) for the natural water analysis

304 ranged from 6.5 to 10.9% for Se species.

305 Since the certified value in GSBZ50031-94 is for total Se instead of Se(IV) or
306 Se(VI), the accuracy validation for the speciation result was further demonstrated by
307 recovery test for real water samples. The recoveries of target analytes were in the
308 range of 87.4%-102%, demonstrating the accuracy of the proposed SPE-GF-AAS
309 method for inorganic Se speciation.

310 **4. Conclusion**

311 The adsorption behavior of inorganic Se was investigated on the prepared
312 GO-TiO₂(1:1) composite and it was found that Se(IV) could be quantitatively retained
313 within a wide pH range of 0.5-10, while Se(VI) could be quantitatively adsorbed at
314 pH 0.5-2. Based on it, the separation of inorganic Se species was achieved by
315 GO-TiO₂(1:1) composite packed micro-column and the reason for their adsorption
316 difference was preliminarily discussed. The isothermal adsorption of Se(IV) on the
317 GO-TiO₂(1:1) composite exhibits as monolayer adsorption, with the adsorption
318 capacity of 3.77 mg g⁻¹. Subsequently, a method of SPE-GF-AAS for inorganic Se
319 speciation was established for analysis of Se (IV) and Se (VI) in environmental water
320 samples, providing an efficient, effective, simple and low-cost strategy for inorganic
321 Se speciation.

322 **Acknowledgements**

323 The authors would like to thank the National Science Foundation of China (No.
324 21075095) and Science Fund for Creative Research Groups of NSFC (Nos 20621502,
325 20921062) for their financial supports.

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387 **Fig. 1** Effect of pH on the adsorption percentage (%) of Se(IV) and Se(VI) on
388 GO-TiO₂(1:1) (A) and TiO₂ (B), respectively. Flow rate: 0.5 mL min⁻¹

389 **Fig. 2** Breakthrough curves of Se(IV) on TiO₂ (A), GO-TiO₂(1:9) (B), GO-TiO₂(1:3)
390 (C), and GO-TiO₂(1:1) (D), respectively

391 **Fig. 3** Langmuir adsorption isotherm (A) and Freundlich adsorption isotherm (B) for
392 Se(IV) on GO-TiO₂(1:1)

393 **Table 1** The influence of common coexisting ions

394 **Table 2** Comparison of the method with those reported in the literature for Se(IV)
395 (E.F.=Enrichment factors)

396 **Table 3** Analytical results of inorganic selenium in certified material of
397 GSBZ50031-94 and environmental water samples (mean ± S.D., n=3)

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Fig. 1

Fig. 2

Fig. 3

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Table 1 The influence of common coexisting ions

Co-existing ions	Tolerance limit (mg L ⁻¹) for Se(IV)
K ⁺	5000
Na ⁺	6000
Ca ²⁺	2000
Mg ²⁺	2000
Cu ²⁺	1000
Zn ²⁺	1000
Co ²⁺	50
Ni ²⁺	100
Mn ²⁺	40
Cd ²⁺	25
Cr ³⁺	5
Al ³⁺	5
Fe ³⁺	10
Cl ⁻	9000
Br ⁻	10000
NO ₃ ⁻	7500
SO ₄ ²⁻	500

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455 **Table 2** Comparison of the method with those reported in the literature for Se(IV)

456 (E.F.=Enrichment factors)

Adsorbents	Methods	Adsorption capacity (mg g ⁻¹)	E.F.	LODs (ng mL ⁻¹)	Ref.
MPTMS-SBA-15	SPE-ICP-OES	15	20	2.56	[10]
nanometer-sized TiO ₂ (APDC)	SPE-GF-AAS	-	20	0.06	[12]
Dowex 1X8	FI-SPE-ETAAS	-	82	0.01	[13]
Magnetic MWCNTs	MSPE-HG-AFS	2.5	100	0.013	[14]
Mg-FeCO ₃ LDHs-cellulose	SPE-HG-AFS	3.84	13.3	0.011	[15]
MPTS/AAPTS-silica monolith	CME-ICP-MS	-	37.5	0.0311	[20]
nanometer-sized Al ₂ O ₃	SPE-FASS-CE-UV	-	200	0.057	[21]
nanometer-sized Al ₂ O ₃ , DMSA-mesoporous TiO ₂	FI-SPE-ICP-MS	Al ₂ O ₃ :5.1 DMSA-TiO ₂ :4.8	5	0.05	[22]
MWCNTs (APDC)	DSPME-XRF	-	-	0.06	[26]
Graphene (APDC)	DSPME-EDXRF	-	1013	0.032	[27]
Diaion HP-2MG (APDC)	SPE-GF-AAS	5.20	100	0.01	[29]
TBAH-activated carbon	SPE-LC-ICP-DRC- MS	-	76	0.0022	[30]
GO-TiO ₂ (1:1) composite	SPE-GF-AAS	3.77	27.8	0.04	This work

457 TBAH-activated carbon=tetrabutylammonium hydroxide-modified activated carbon

458 DMSA=dimercaptosuccinic acid

459 MPTS=3-mercaptopropyltrimethoxysilane

460 AAPTS=N-(2-aminoethyl)-3-aminopropyltrimethoxysilane

461 MPTMS-SBA-15=3-mercaptopropyl-trimethoxysilane modified mesoporous silica

462 Diaion HP-2MG=methacrylate resin

463 Dowex 1X8=an anionic resin

464 Mg-FeCO₃ LDHs-cellulose=Mg-FeCO₃ layered double hydroxides loaded cellulose fibre
465 SPE-LC-ICP-DRC-MS=solid phase extraction-liquid chromatography-inductively coupled
466 plasma-Dynamic reaction cell-mass spectrometry
467 XRF=X-ray fluorescence spectrometry
468 EDXRF=energy-dispersive X-ray fluorescence spectrometry
469 FASS=field-amplified sample stacking
470 FI=flow injection
471 ETAAS=electrothermal atomic absorption spectrometer

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Table 3 Analytical results of inorganic selenium in certified material of

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GSBZ50031-94 and environmental water samples

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(mean $\pm$ S.D., n=3)

Samples	Species	Added (ng mL ⁻¹)	Found (ng mL ⁻¹)	Certified (ng mL ⁻¹)	Recovery (%)	t test*
GSBZ50031-94	Se(IV)	-	4.73 $\pm$ 0.42	-	-	-
	Se(VI)	-	2.24 $\pm$ 0.28	-	-	-
	Total	-	6.97 $\pm$ 0.49	7.64 $\pm$ 0.82	-	1.93
Spring water 1	Se(IV)	0	0.57 $\pm$ 0.06	-	-	-
		1	1.52 $\pm$ 0.12	-	95	-
Spring water 2	Se(VI)	0	2.62 $\pm$ 0.17	-	-	-
		5	6.99 $\pm$ 0.81	-	87.4	-
	Se(IV)	0	0.92 $\pm$ 0.10	-	-	-
		1	1.92 $\pm$ 0.11	-	100	-
	Se(VI)	0	4.80 $\pm$ 0.50	-	-	-
		5	9.88 $\pm$ 1.41	-	102	-

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* $t_{0.05,2} = 4.31$

Graphic Abstract