

# **Novel strategy for sequential analysis of gold nanoparticles and gold ions in water samples by combining magnetic solid phase extraction with inductively coupled plasma mass spectrometry**

Shaowei Su, Beibei Chen, Man He, Zuowei Xiao, Bin Hu\*

Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education),  
Department of Chemistry, Wuhan University, Wuhan 430072, P R China

\*Corresponding author: Dr. Bin Hu, E-mail: binhu @ whu.edu.cn, Fax: 86-27-68754067, Tel:  
0086-27-68752162

## Supplementary Information

The present document provides further information on the paper mentioned above.

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**Table S1**

### Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@IDA

3.5 g IDA was dissolved in 50 mL high purity water and then the solution was adjusted to pH 11 with 10 mol L<sup>-1</sup> NaOH. After magnetic stirring for 10 min in an ice-bath, 1.5 mL GLYMO was dropwise added with magnetic stirring for about 0.5 h. The reaction system was then heated to 65 °C, maintained for 6 h and cooled down to ambient temperature. Finally, the obtained IDA-derived silane coupling agent solution GLYMO-IDA was adjusted to pH 6 with concentrated HCl.

The Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared by the conventional co-precipitation method<sup>35</sup>. 2 g of prepared Fe<sub>3</sub>O<sub>4</sub> nanoparticles were homogeneously dispersed in the mixture of ethanol (160 mL) and deionized water (40 mL) under ultrasonic vibration for 30 min. Then 5 mL concentrated ammonia aqueous solution was added into the dispersion under vigorous stirring at ambient temperature. After stirring for 1 h, 4 mL TEOS was added into the above prepared dispersion and the mixture was stirred for 12 h at room temperature. After the obtained Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> microspheres were separated from the solution and washed with ethanol and water sequentially, they were redispersed in a mixed solution containing 150 mL high purity deionized water, 1.0 mL concentrated ammonia aqueous solution and 50 mL ethanol. The mixture was homogenized for 0.5 h to form a uniform dispersion. Then, 50 mL of GLYMO-IDA solution was added dropwise to the dispersion with continuous stirring. After reaction for 12 h, the product of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@IDA was collected with a magnet, washed repeatedly with ethanol and water and finally dried in vacuum at 60 °C.

### Effect of elution volume and elution time

The elution volume and time affect the elution efficiency significantly. To study the effect of elution volume on the desorption, three portions of 0.5 mL 10 mmol L<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> or 0.15 mol L<sup>-1</sup> NH<sub>3</sub>·H<sub>2</sub>O were used as eluent to elute Au ions or AuNPs from the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@IDA-Al<sup>3+</sup>, respectively. The results in Fig. S2 indicate that 0.5 mL of elution solution was sufficient to elute quantitatively Au ions or AuNPs, respectively. The influence of elution time on the recovery of the Au ions and AuNPs was also investigated, respectively. The results in Fig. S3a and S3b show that the Au ions could be quantitatively recovered when the elution time was above 10 min and AuNPs could be quantitatively recovered when the elution time was in 1 min, which indicates the prepared Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@IDA-Al<sup>3+</sup> has fast desorption kinetics for AuNPs and Au ions. In this

work, the elution time of 15 min for MSA-Au ions and 2 min for MSA-AuNPs was selected for quantitative and sequential desorption. Finally, 0.5 mL 10 mmol L<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> with elution time of 15 min for Au ions and 0.5 mL 0.15 mol L<sup>-1</sup> NH<sub>3</sub>·H<sub>2</sub>O with elution time of 2 min for AuNPs was employed as the optimized elution conditions.

### Effect of adsorption time and Sedimentation Time

The adsorption time should be optimized to ensure quantitative retention along with minimal time required for sample processing. To study the effect of adsorption time, 25 mL of sample solution containing 2 ng mL<sup>-1</sup> AuNPs and Au ions was ultrasonicated for several minutes and eluted sequentially. The experimental results in Fig. S4 show that quantitative recoveries could be obtained for the AuNPs and Au ions in 2 min, which indicates the prepared Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@IDA-Al<sup>3+</sup> had fast adsorption kinetics for AuNPs and Au ions. In this work, 5 min was selected for quantitative adsorption.

In this study, the adsorbent could be separated rapidly from the sample solution using an external magnetic field instead of filtration or centrifugation, due to the superparamagnetism of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@IDA-Al<sup>3+</sup>. Therefore, the effect of sedimentation time on the recovery was investigated in the range of 2-20 min. It can be found from Fig. S5 that the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@IDA-Al<sup>3+</sup> could be completely sedimented with a recovery for AuNPs and Au ions higher than 92% in the whole tested time range. In subsequent experiments, a sedimentation time of 2 min was employed.

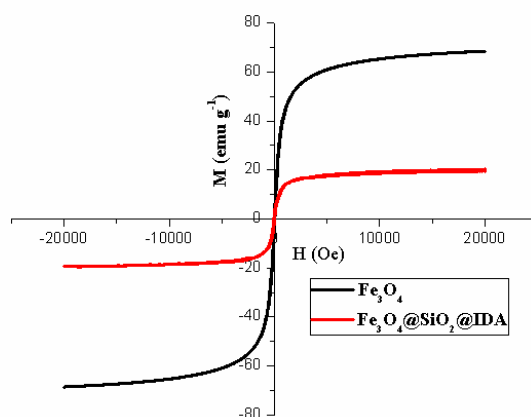
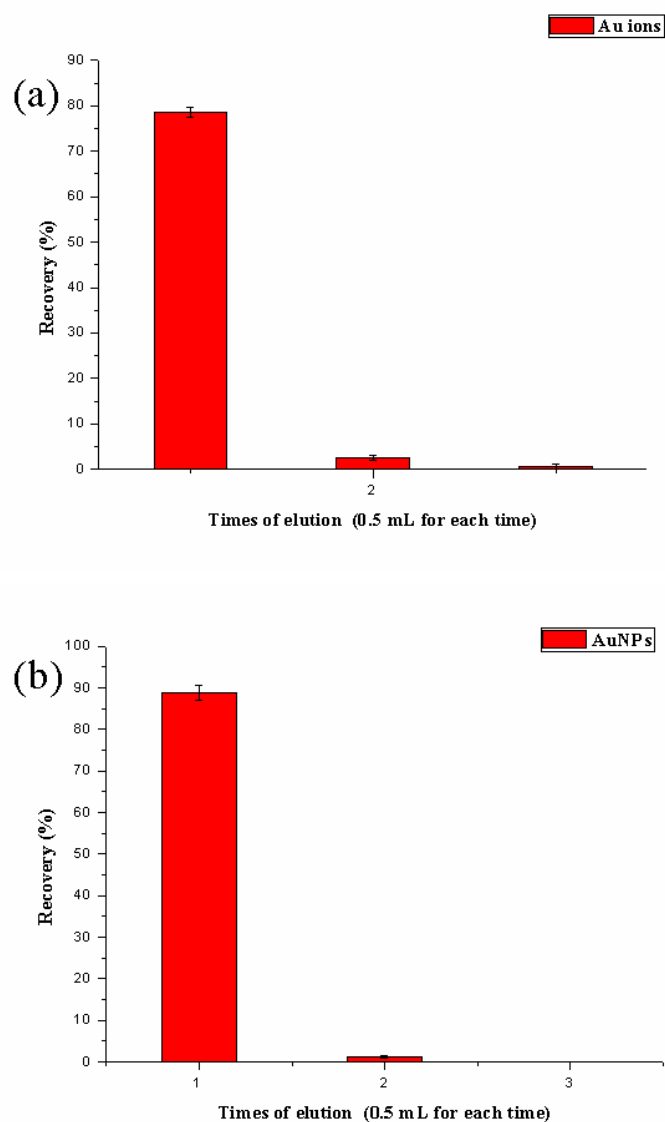
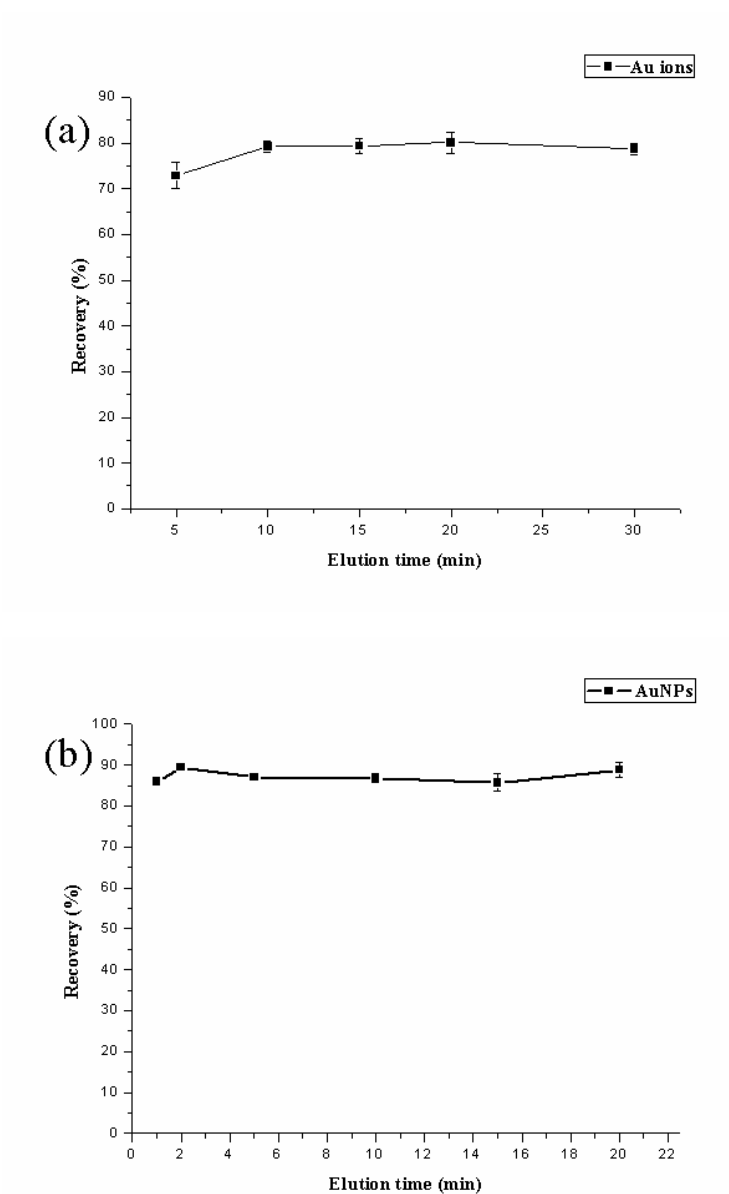


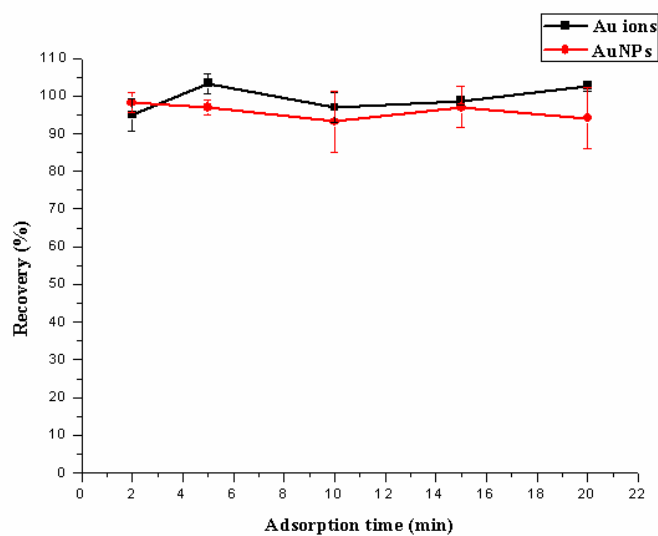
Fig. S1 Magnetic hysteresis loops of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@IDA



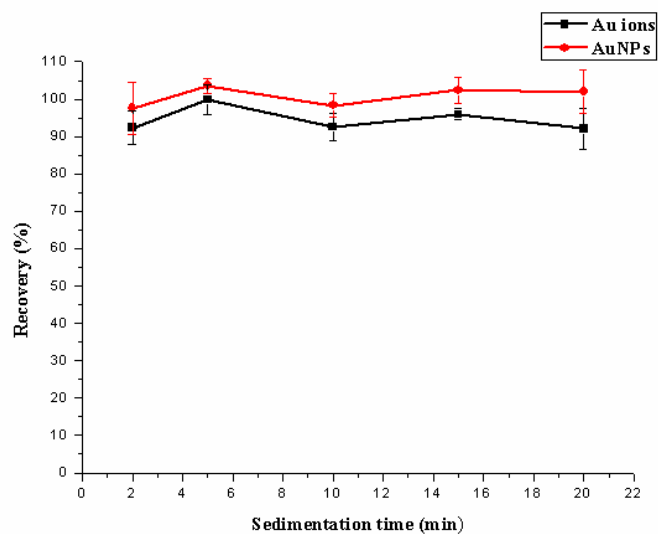
**Fig. S2** Effect of the elution volume on the recovery of the Au ions (a) and AuNPs (b) ( $10 \text{ ng mL}^{-1}$ ). Conditions: sample volume:  $5 \text{ mL}$ ; adsorption time:  $20 \text{ min}$ ; eluent for Au ions:  $10 \text{ mmol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3$ ; eluent for Au NPs:  $0.15 \text{ mmol L}^{-1} \text{ NH}_3 \cdot \text{H}_2\text{O}$ .



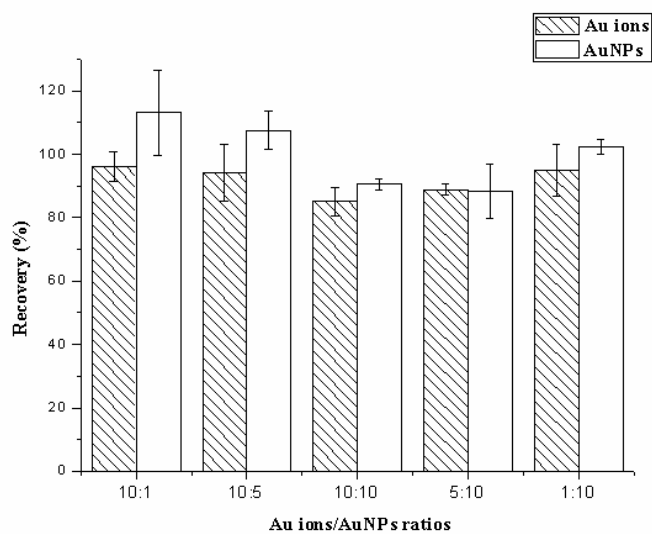
**Fig. S3** Effect of the elution time on the recovery of the Au ions (a) and AuNPs (b) ( $10 \text{ ng mL}^{-1}$ ).  
Conditions: sample volume: 5 mL; adsorption time: 20 min; elution volume: 0.5 mL; eluent for Au ions:  $10 \text{ mmol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3$ ; eluent for Au NPs:  $0.15 \text{ mmol L}^{-1} \text{ NH}_3 \cdot \text{H}_2\text{O}$ .



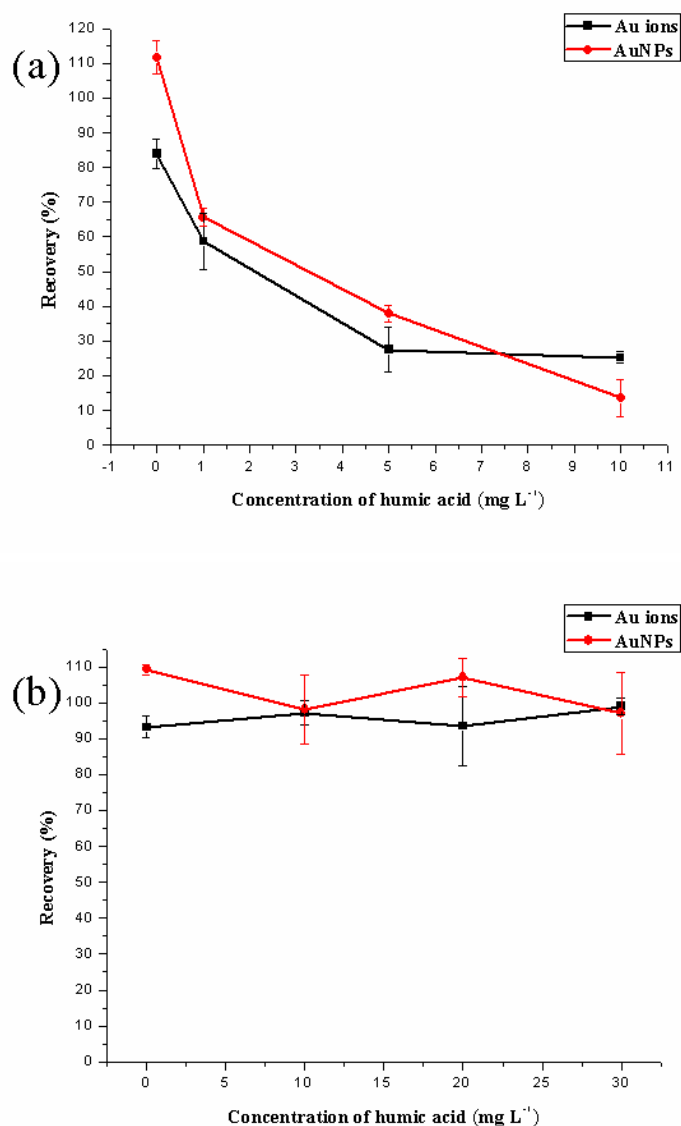
**Fig. S4** Effect of the adsorption time on the recovery of the AuNPs and Au ions. Conditions: sample volume: 25 mL; concentration: 2 ng mL<sup>-1</sup>; elution volume: 0.5 mL; eluent for Au ions: 10 mmol L<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>; eluent for Au NPs: 0.15 mmol L<sup>-1</sup> NH<sub>3</sub>·H<sub>2</sub>O.



**Fig. S5** Effect of the sedimentation time on the recovery of the AuNPs and Au ions. Conditions: sample volume: 25 mL; concentration: 2 ng mL<sup>-1</sup>; elution volume: 0.5 mL; eluent for Au ions: 10 mmol L<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>; eluent for Au NPs: 0.15 mmol L<sup>-1</sup> NH<sub>3</sub>·H<sub>2</sub>O.



**Fig. S6** Effect of the ratio of Au ions and AuNPs. Conditions: sample volume: 25 mL; elution volume: 0.5 mL; eluent for Au ions: 10 mmol L<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>; eluent for Au NPs: 0.15 mmol L<sup>-1</sup> NH<sub>3</sub>·H<sub>2</sub>O.



**Fig. S7** Effect of the concentration of humic acid on the recovery of the AuNPs and Au ions without (a) and with (b) addition of  $10 \text{ mg L}^{-1} \text{ Al}^{3+}$ . Conditions: sample volume: 25 mL; concentration:  $2 \text{ ng mL}^{-1}$ ; elution volume: 0.5 mL; eluent for Au ions:  $10 \text{ mmol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3$ ; eluent for Au NPs:  $0.15 \text{ mmol L}^{-1} \text{ NH}_3 \cdot \text{H}_2\text{O}$ .



**Table S1** Tolerance Limit of Interfering Ions

Coexisting ions	Tolerance limit of ions (mg L <sup>-1</sup> )
K <sup>+</sup>	5000
Na <sup>+</sup>	5000 <sup>a</sup> /10000 <sup>b</sup>
Ca <sup>2+</sup>	2000
Mg <sup>2+</sup>	2000
Zn <sup>2+</sup>	10
Fe <sup>3+</sup> , Cu <sup>2+</sup> , Cd <sup>2+</sup> , Pb <sup>2+</sup>	1
Hg <sup>2+</sup>	0.1
Cl <sup>-</sup>	7500 <sup>a</sup> /15000 <sup>b</sup>
NO <sub>3</sub> <sup>-</sup>	8000
SO <sub>4</sub> <sup>2-</sup>	1000

<sup>a</sup> Au ions, <sup>b</sup>AuNPs.