

Supporting Information

Hydrophilic polymer monolithic capillary microextraction online coupled to ICP-MS for the determination of carboxyl group-containing gold nanoparticles in environmental waters

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Synthesis of Au NPs. The bare Au NPs with the size of about 3 nm¹, 17 nm and 40 nm² were prepared by reduction of HAuCl₄·4H₂O with NaBH₄ or sodium citrate. The Au NPs modified with MSA or MUA was prepared based on the procedure described in Ref. 3. Briefly, 1 mL of 2.5 mmol L⁻¹ MSA or MUA solution was added to 4 mL of freshly prepared Au NPs solution (about 12.5 mg L⁻¹). The resulting solution was stirred at room temperature for 3 h and used for further experiments.

The stability of Au NPs. The stability of Au NPs with particle size of about 3 nm was investigated for the time span of three weeks. The concentration of Au NPs was quantitatively determined by the standard working solutions of freshly diluted free Au ions and the results are shown in Fig. S1. The black solid curve shows the trend of concentration changes of Au NPs within three weeks, while the dotted curve shows the mean value of all measurements. It can be seen that the determined concentration of Au NPs fluctuated around the average value and this fluctuation was associated with the uniformity and stability of the Au NPs solution. This indicates that the prepared Au NPs with size of 3 nm in solution is stable for at least three weeks with no aggregation.

Effect of sample flow rate and volume. The effect of sample flow rate on CME was evaluated by passing 1 mL of sample solution containing 20 µg L⁻¹ Au NPs (as Au) through the monolithic column with the flow rate varying in the range of 0.05-0.5 mL min⁻¹. The experimental results shown in Fig. S2 demonstrate that Au NPs could be quantitatively adsorbed on the prepared poly(AA-VP-Bis) monolith with flow rate lower than 0.3 mL min⁻¹. The adsorption percentages of Au NPs were decreased with further increase of the flow rate to 0.5 mL min⁻¹ possibly due to decreased adsorption kinetics at higher flow rate. Accordingly, a sample flow rate of 0.25 mL min⁻¹ was employed in subsequent experiments.

To study the effect of sample volume on the recoveries of Au NPs, sample solutions of 1, 2, 4 and 8 mL containing 20 ng Au NPs (as Au) were passed through the poly(AA-VP-Bis) monolithic capillary at a flow rate of 0.25 mL min⁻¹ (accordingly, the adsorption time were 4, 8, 16, and 32 min, respectively), and the adsorbed Au NPs were eluted with 0.1 mL 4% cysteamine. The experimental results in Fig. S3 indicate that no obvious influence of the sample volume on the recoveries of Au NPs was observed and all target Au NPs could be quantitatively recovered in

the tested range. Despite of an enrichment factor of 80-fold achievable, it will take much more time for 8 mL sample solution loading through the monolith, which is unfavorable for the improvement of sample throughput. To trade off the enrichment factor and analytical speed, 1 mL sample solution was employed for real-world sample analysis.

Effect of eluent concentration and volume. With cysteamine as eluent (pH 7), the effect of its concentration and volume on the elution of Au NPs from the poly(AA-VP-Bis) monolithic capillary was investigated with the flow rate of eluent keeping at 0.05 mL min^{-1} . As shown in Fig. S4, the recovery of Au NPs was $\sim 90\%$ when 0.1 mL 3% (m/v) cysteamine was used as eluent. To ensure quantitative elution of Au NPs from the column, 0.1 mL 4% (m/v) cysteamine was chosen as the eluent, accordingly, the desorption time is 2 min. In order to reduce any memory effect and increase the reuse times of the monolith, the monolith was cleaned by 0.1 mL 4% (m/v) cysteamine at a flow rate of 0.05 mL min^{-1} and conditioned by 0.4 mL water at a flow rate of 0.2 mL min^{-1} after each desorption.

Effect of common coexisting ions. In environmental waters, the existence of organic acid and free ions may affect the stability and extraction efficiency of Au NPs^{4,5}. Humic acid was the main organic acid in common environmental waters, so the effect of different concentration of humic acid on the recovery of Au NPs was investigated in detail. As seen from the Figure S5, the recovery of Au NPs was higher than 85% when the concentration of humic acid was below 20 mg L^{-1} , while it was reduced to 77% with the further increase of humic acid concentration from 20 to 30 mg L^{-1} . Besides the humic acid, the commonly coexisting ions in environmental water, such as cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+}) and anions (Cl^- , SO_4^{2-}) may change the surface electron density of Au NPs thereby impairing their preconcentration. To investigate the interference of the common coexisting ions on extraction of Au NPs, sample solution containing $20 \text{ } \mu\text{g L}^{-1}$ target Au NPs and a certain amount of coexisting ions (K^+ 1.6 mg L^{-1} , Na^+ 11 mg L^{-1} , Ca^{2+} 95 mg L^{-1} , Mg^{2+} 38 mg L^{-1} , SO_4^{2-} 71.5 mg L^{-1} , Cl^- 25 mg L^{-1}) was prepared and subjected to on-line CME-ICP-MS detection. The spiked amount of the coexisting ions was referred to the concentration level of coexisting ions in the natural fresh water⁶. The experimental results indicate that the average recovery of Au NPs in the simulated water samples was 86%. Due to the

concentration of humic acid in common fresh water is below 20 mg L^{-1} , and the studied foreign ions in the Yantze River and the East Lake water were all below the concentration of simulated water ⁷, the developed method could be applied for Au NPs analysis in natural fresh waters.

Effect of coexisting free Au ions. Since ICP-MS cannot recognize different species of Au NPs and free Au ions, it is important to establish a method for selective extraction of Au NPs in environmental samples. Herein, the effect of the concentration of free Au ions on the recovery of Au NPs was investigated. The experimental results in Figure S6 demonstrate that the interference of free Au ions on the determination of Au NPs was negligible when the concentration of free Au ions was less than $8 \mu\text{g L}^{-1}$. However, the recovery of Au NPs increased with the further increase of the concentration of free Au ions. This positive interference is probably caused by the adsorption of free Au ions on the surface of Au NPs because Au NPs have large specific surface area and plenty of negative charge on their surface. Considering the concentration of free Au ions is usually low in environmental water, so it can be concluded that the coexisting Au ions in environmental water will not interfere with the analysis of Au NPs in natural waters.

References

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Table S1 Operating conditions of ICP-MS.

ICP-MS plasma	
Rf power	1250 W
Plasma gas (Ar) flow rate	14 L min ⁻¹
Auxiliary gas (Ar) flow rate	0.88 L min ⁻¹
Carrier gas (Ar) flow rate	0.97 L min ⁻¹
Sampling depth	7.0 mm
Sampler/skimmer diameter orifice	Nickel 1.0 mm/0.4 mm
Time-resolved data acquisition	
Scanning mode	Peak-hopping
Dwell time	60 ms
Integration mode	Peak area
Points per spectral peak	1
Isotopes	¹⁹⁷ Au, ¹⁰⁹ Ag, ¹⁰⁷ Ag

Table S2 An analytical performance comparison of this method with other methods for the determination of Au NPs.

Particle size (nm)	Time	Sample volume (mL)	LOD	Linear range	Detection	On/off line	Ref.
15 nm	-	40	5 ng L ⁻¹	12-240 ng L ⁻¹	ET-AAS	off	18
10 nm	>45 h	>50	-	-	GF-AAS	off	19
10 nm	>3 h	>10	-	-	GF-AAS	off	20
39 nm	15-20 min	3	1.7 fmol L ⁻¹	1.7-17.2 fmol L ⁻¹	UV-Vis, Raman spectrometer	off	13
17 nm	17 min	25	0.31 ng L ⁻¹ ; 0.16 fmol L ⁻¹	0.001-10 µg L ⁻¹	ICP-MS	off	21
3 nm	10 min	1	3.97 ng L ⁻¹ ; 24.2 fmol L ⁻¹	0.02-20 µg L ⁻¹	ICP-MS	on	This work

ET-AAS: electrothermal atomic absorption spectrometry

GF-AAS: graphite furnace atomic absorption spectrometer

UV-Vis spectrometer: Ultraviolet–visible spectrometer

ICP-MS: inductively coupled plasma mass spectrometry

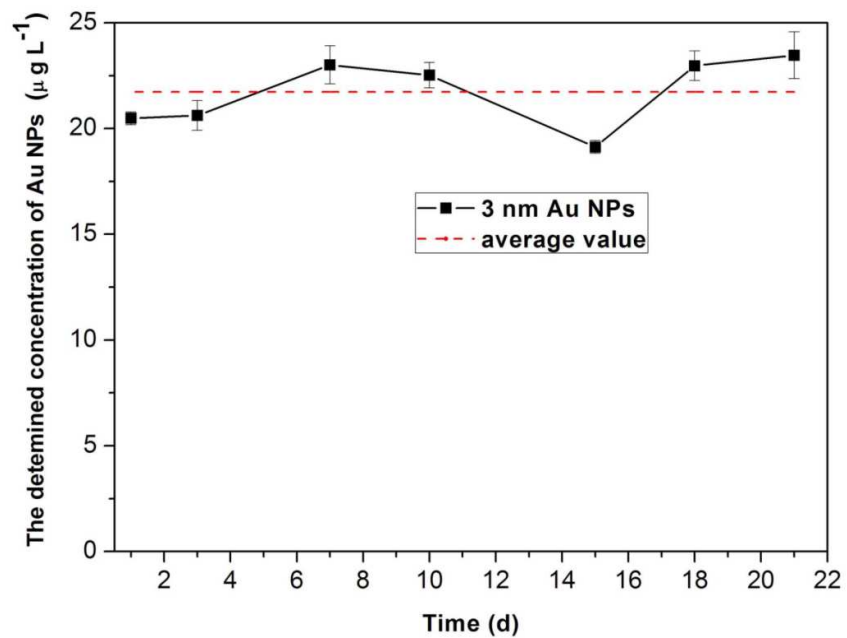


Figure S1 Concentration of 3 nm Au NPs over a period of 3 weeks.

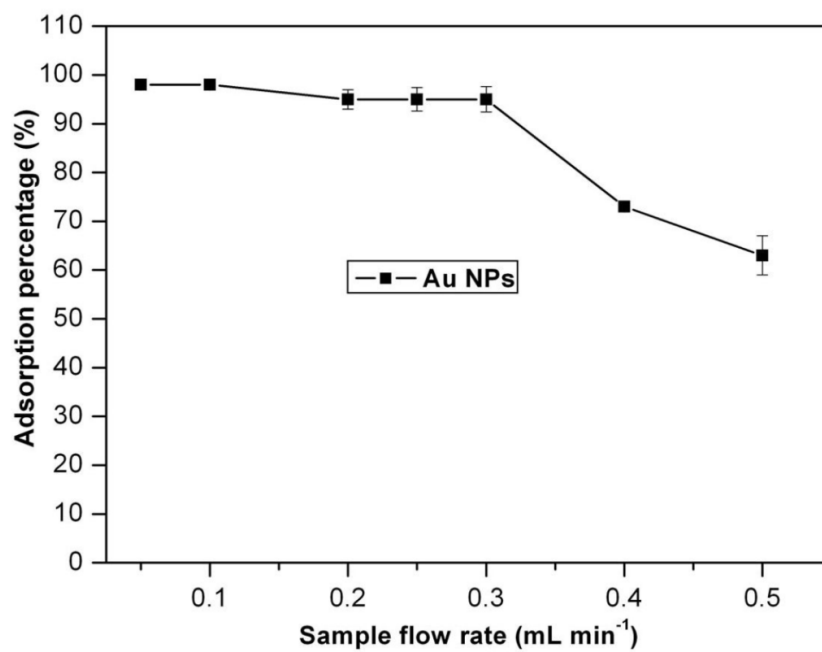


Figure S2 Effect of sample flow rate on the adsorption percentage of Au NPs. Experimental conditions: the concentration of Au NPs $20 \mu\text{g L}^{-1}$ (Au); sample volume: 1 mL; pH = 5.5.

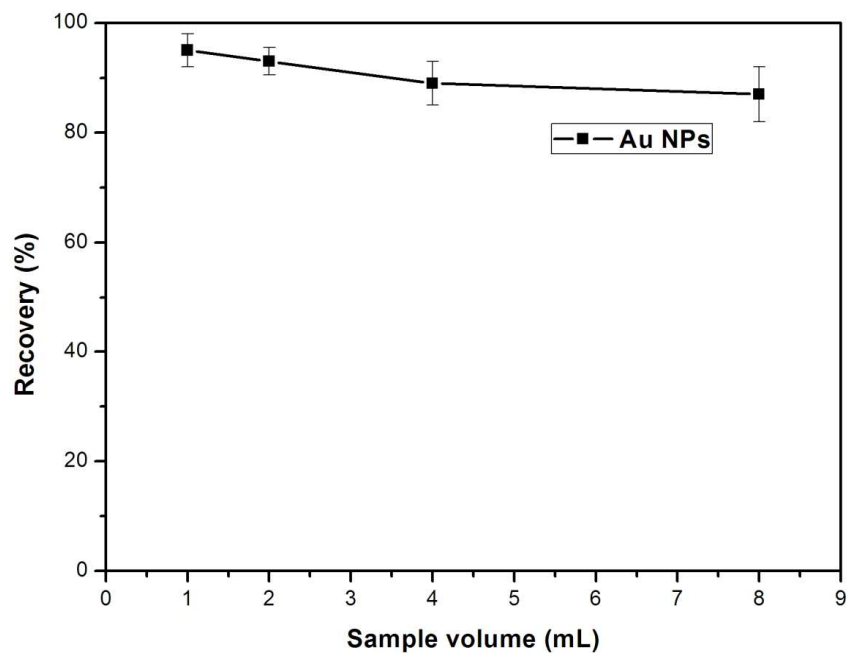


Figure S3 Effect of sample volume on the recovery of Au NPs. Experimental conditions: $m = 20$ ng (Au); pH = 5.5; sample flow rate: 0.25 mL min^{-1} ; eluent: 0.1 mL 4% cysteamine.

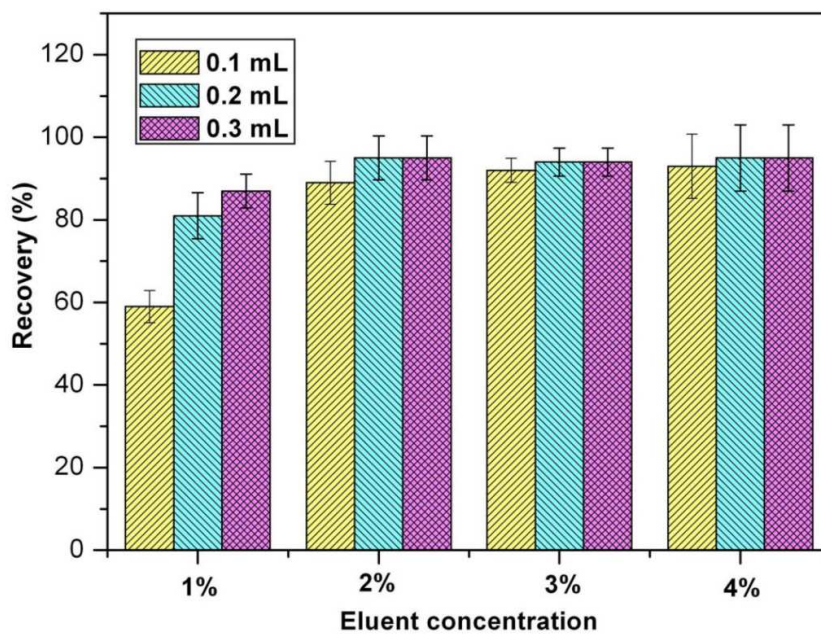


Figure S4 Effect of eluent concentration and volume on the recovery of Au NPs. Experimental conditions: the concentration of Au NPs $20 \mu\text{g L}^{-1}$ (Au); sample volume: 1 mL; pH = 5.5; sample flow rate: 0.25 mL min^{-1} .

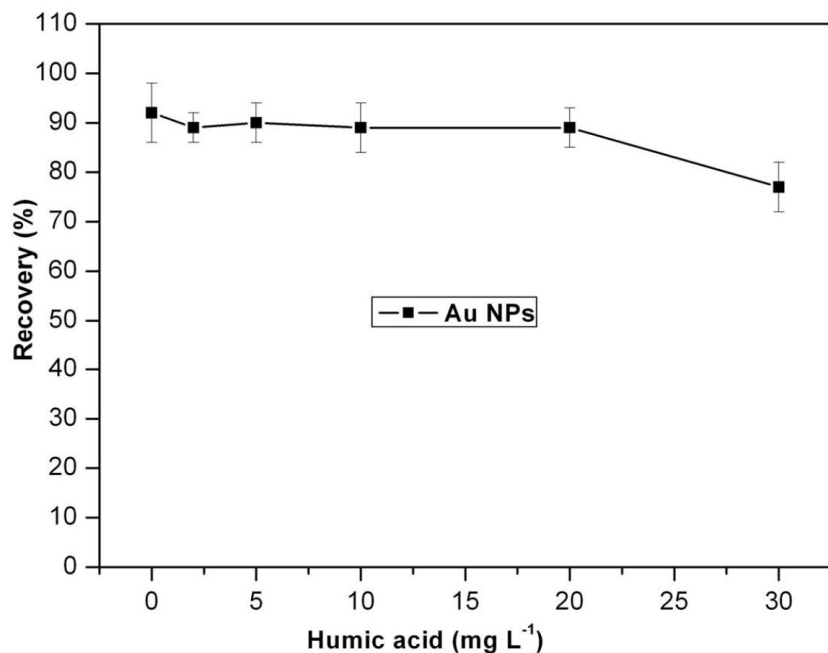


Figure S5 Effects of humic acid on the recovery of Au NPs. Experimental conditions: the concentration of Au NPs 20 $\mu\text{g L}^{-1}$ (Au); sample volume: 1 mL; pH = 5.5; sample flow rate: 0.25 mL min^{-1} ; eluent: 0.1 mL 4% cysteamine.

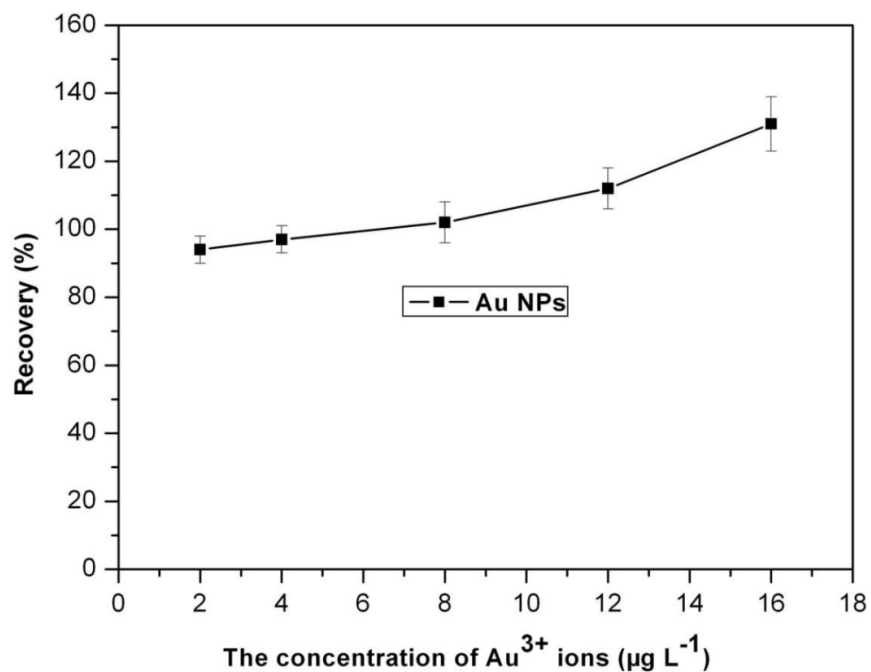


Figure S6 Effects of the concentration of Au³⁺ ions on the recovery of Au NPs. Experimental conditions: the concentration of Au NPs 20 $\mu\text{g L}^{-1}$ (Au); sample volume: 1 mL; pH = 5.5; sample flow rate: 0.25 mL min^{-1} ; eluent: 0.1 mL 4% cysteamine.

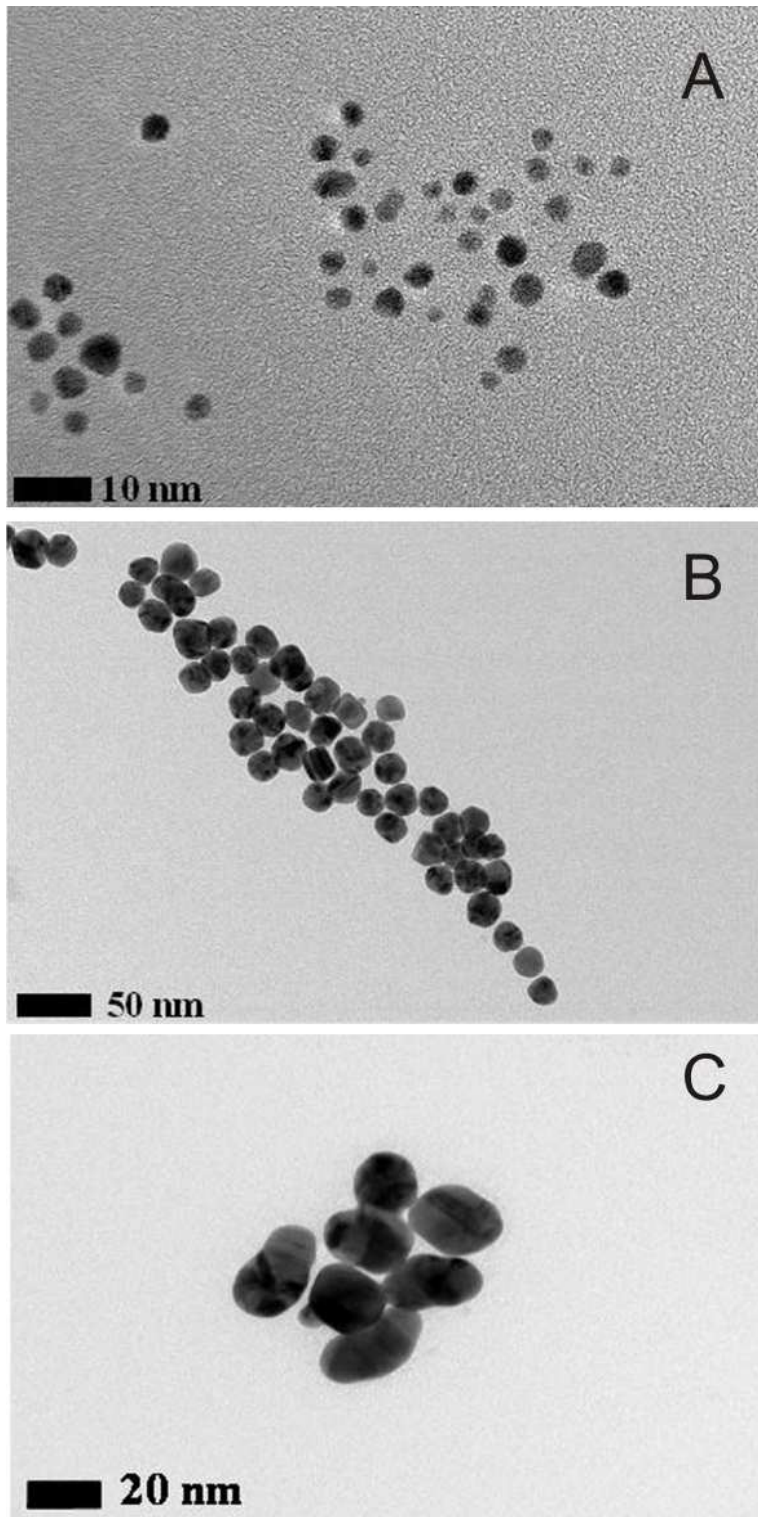


Figure S7 TEM of different size of Au NPs. A: 3 nm Au NPs; B: 17 nm Au NPs; C: 40 nm Au NPs.

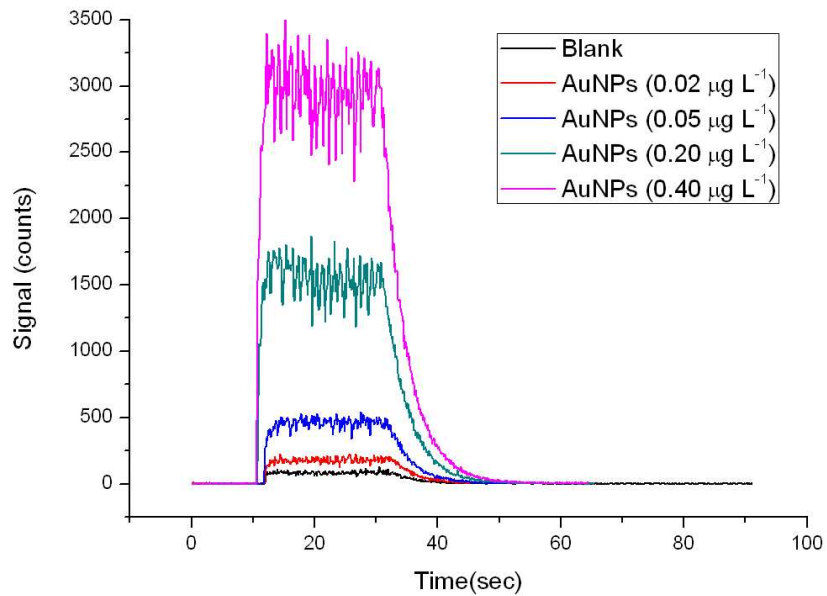


Figure S8 On-line CME-ICP-MS spectra of blank and AuNPs solutions (concentration: 0.02, 0.05, 0.2, 0.4 μg L⁻¹)

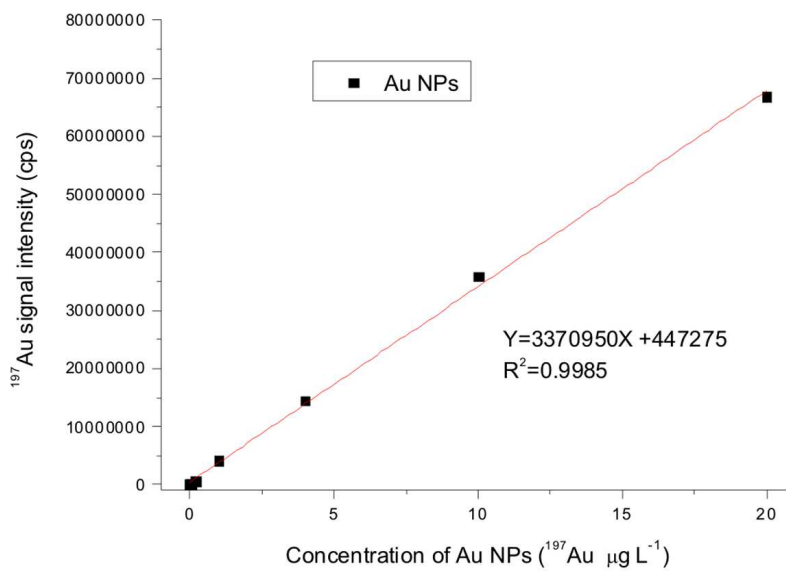


Figure S9 Dynamic range of CME-ICP-MS for the determination of Au NPs.