Electronic Supplementary Information (ESI) for Analytical Methods

MSIS-MP-AES determination of As and Sb in complex matrices by magnetic nanoparticles - assisted hydride generation

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Standard and sample preparation

Experimental evidences have been described in the literature, confirming that L-cysteine can be used only at limited acid media (References 13, 16, 44). It was experimentally proved that the optimum pH, when L-cysteine is used as pre-reducing agent is 1.5-1.8 (Reference 25). Therefore, in all standards, blanks and samples, the pH was maintained in the optimal interval pointed above.

Standard
For total As estimation, a pre-reduction of As(V) to As(III) was performed by adding L-cysteine powder to each standard using final concentration of 0.5% m/m L-cysteine. The same preparation was applied for blank solution. All solutions (standards and blank) were left to stand overnight at room temperature. The pH was adjusted to 1.5-1.6 with HCl 1 mol L^{-1}.

Industrial electrolyte sample
The dilution was followed by pH adjustment to 1.5-1.6 by addition of HCl 1 mol L^{-1} to the sample (with initial pH = 4.5). L-cysteine powder was added to each solution to final concentration of 0.5% m/m L-cysteine. All solutions (standards, samples and blank) were left to stand overnight at room temperature. The sample solutions are stable more than a week.

Human urine
preparation I: fresh urine sample was diluted with HCl 0.1 mol L^{-1} (DF tested – DF5 v/v, DF10 v/v) and was analyzed by *"dilute-and-shoot method"*. The sample pH was adjusted to 1.5-1.6 with HCl 1 mol L^{-1}. For total As and Sb determination pre-reduction step was performed with L-cysteine powder, added directly to solutions to final concentration of 0.5% m/m L-cysteine.
preparation II, (Aqua Regia acid digestion): 20 mL of urine aliquot was placed in loosely caped 50 mL plastic tube to which 20 mL of Aqua Regia (HNO_3:HCl, 1:3) was added. The digestion was performed by heating on a hotplate water bath at T=90°C, applying ultrasound agitation for 1h. Digested solutions were diluted with BDW (DF5 v/v, DF10 v/v) and the pH was adjusted to 1.5-1.6 with NaOH 2 mol L^{-1}. L-cysteine powder was added to final concentration 0.5% m/m L-cysteine and solutions were heated again to T=80°C for 30 min. The stability study for urine samples were not performed. Only freshly prepared solutions were tested.

Sparkling water with high level of minerals (Na 413 mg L^{-1}, Ca 190 mg L^{-1} , Mg 40 mg L^{-1}, K 30 mg L^{-1}, HCO_3^- 1465 mg L^{-1} , SO_4^{2-} 264 mg L^{-1}, total mineral content 2370 mg L^{-1})
Sample was sonicated 60 min. pH was adjusted to 1.5-1.6 with HCl 1 mol L^{-1}. For total As determination L-cysteine powder was added directly to undiluted solutions to final concentration of 0.5% m/m L-cysteine. The prepared solutions were left to stand overnight at room temperature.

CRM surface water
The CRM solution was diluted with BDW (DF2.4), pH was adjusted to 1.5-1.6 with HCl 1 mol L^{-1}. L-cysteine powder was added directly to solutions to final concentration of 0.5% m/m L-cysteine. The solutions were left to stand overnight at room temperature.

CRM urine – Seronom^{tm}
After reconstitution of the CRM according to provider described procedure, 5 mL of sample was placed in loosely caped 50 mL plastic tube. The aliquot was prepared and proceeded in the same way as real samples (Sample preparation I and II were compared). The final dilution factor was DF49 m/m.

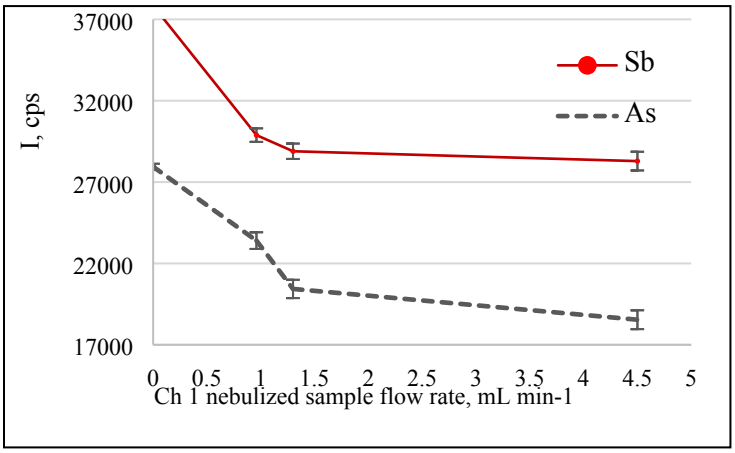

Fig. S1. Effect of different flow rates of nebulized sample at MSIS dual mode on signal intensities of $As_{193.695\ nm}$ and $Sb_{217.581\ nm}$; test solution (0.2 mg L^{-1} As and Sb in 0.5 mol L^{-1} HCl); sample channel (Ch 2) 12 mL min^{-1}; sample channel (Ch 1) variable (from 0 to 4.5 mL min^{-1}); the $NaBH_4$ delivery (Ch 5) 7mL min^{-1}. The error bars represent the signal uncertainty (Type A) estimated as ± 2SD from 5 replicates.

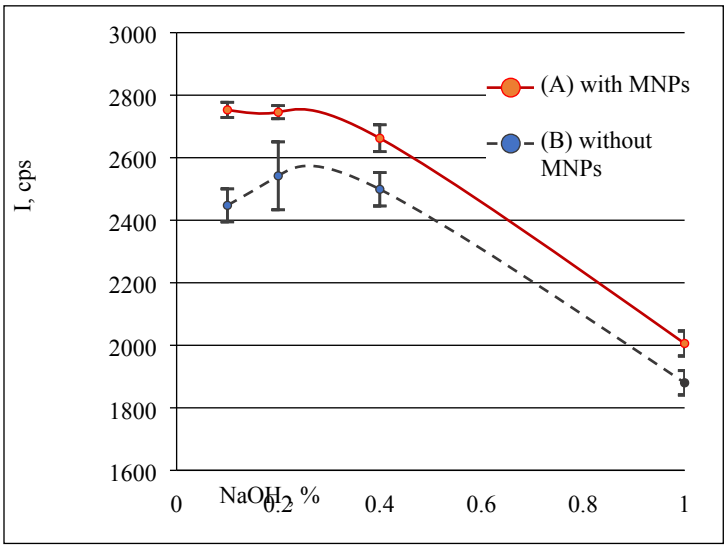

Fig. S2. Effect of NaOH concentration in $NaBH_4$ solution on As(III) 10 µg L^{-1} signal (error bars ±2SD, N=5):
(A) 1.5% $NaBH_4$ + 3% C_2H_5OH + 2 mg mL^{-1} MNPs;
(B) 1.5% $NaBH_4$ only.

VIDEO FILES
Irregular and uncontrolled interruptions in the hydrogen generation reaction recorded as a supplementary file "Video without MNPs" on the address: https://youtu.be/ZKTR6I3gFts.
Suppression of the hydrogen bubbles and to eliminations of the flow's segmentation by MNPs-HG/MISI-MP-AES recorded as a supplementary file "Video with MNPs" on the address: https://youtu.be/2ih2PyC8_EI

MNPs recycling procedure

The magnetic nanoparticles were separated from waste solution by means of an external magnet and washed with double distilled water several times. The water phase was discarded, magnetic nanoparticles were covered with ethanol and sonicated for 30 min. MNPs were separated from ethanol fraction and stored as suspensions in 50 mL double distilled water.

Fig. S3. MSIS with foam originated from human urine without MNPs.

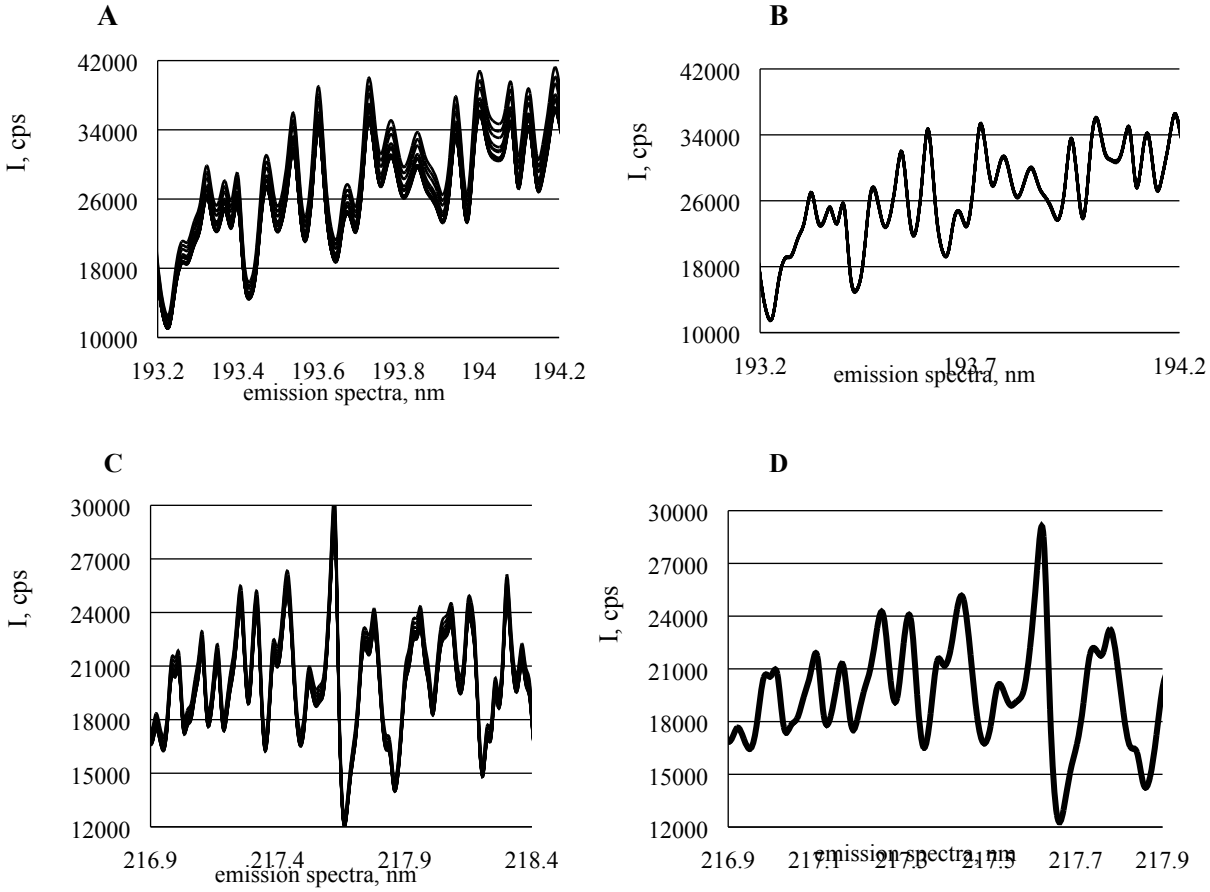

Fig. S4. Spectra of urine sample (DF10) (20 consecutive injections overlayed) (A) and (B) As spectral window; (C) and (D) Sb spectral window. (A) and (C) without MNPs; (B) and (D) with 2 mg mL^{-1} MNPs in the $NaBH_4$.

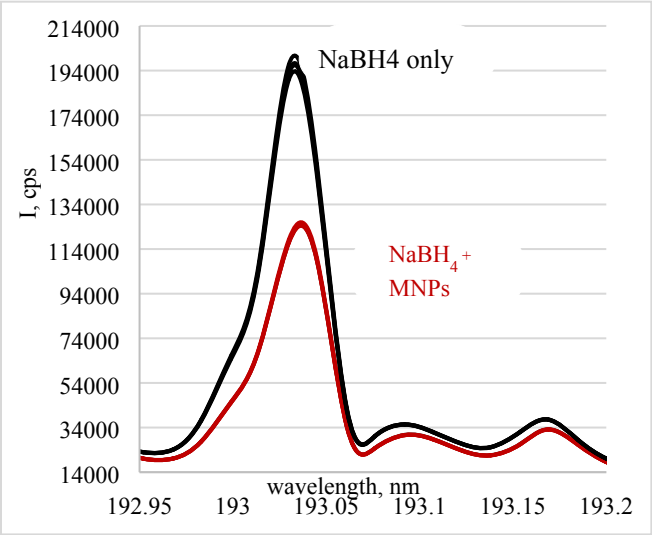

Fig. S5. Carbon 193.045 nm overlapped signals from 5 measurements of Sparkling water.

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