Supplementary information

UV photochemical vapor generation of Cd from formic acid based medium: optimization, efficiency and interferences

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S1: UV spectra of potential sensitizers in UV-PVG of Cd

We measured UV spectra of the promising reaction sensitizers to examine their effect on the absorption of the 253.7 nm Hg line produced by the ultraviolet lamp in the reactor. The individual spectra of solutions of 100 µg mL^{-1} Cu(II), Fe(II), Ni(II) and Co(II) in 0.4M HCOOH were recorded. Significant absorption by formic acid occurs at wavelength below 250 nm (see black line in Fig. S1A). The change in the absorption spectrum was identified when Cu(II) ions (increased absorption and shift of the absorption band) and Fe(II) ions (weak band between 250 and 320 nm) were added to formic acid. Fig. S1B shows that increased pH of the photochemical reagent solution has no effect on the absorption spectrum. We also measured the spectrum of photochemical reagent with added Cd(II). The results show no evidence for interaction of Cd(II) and Fe(II). Last experiment studied the effect of UV irradiation on the reaction mixture. No change in the spectra of photochemical reagent solutions was observed after their irradiation in the reactor in the usual way (not shown).

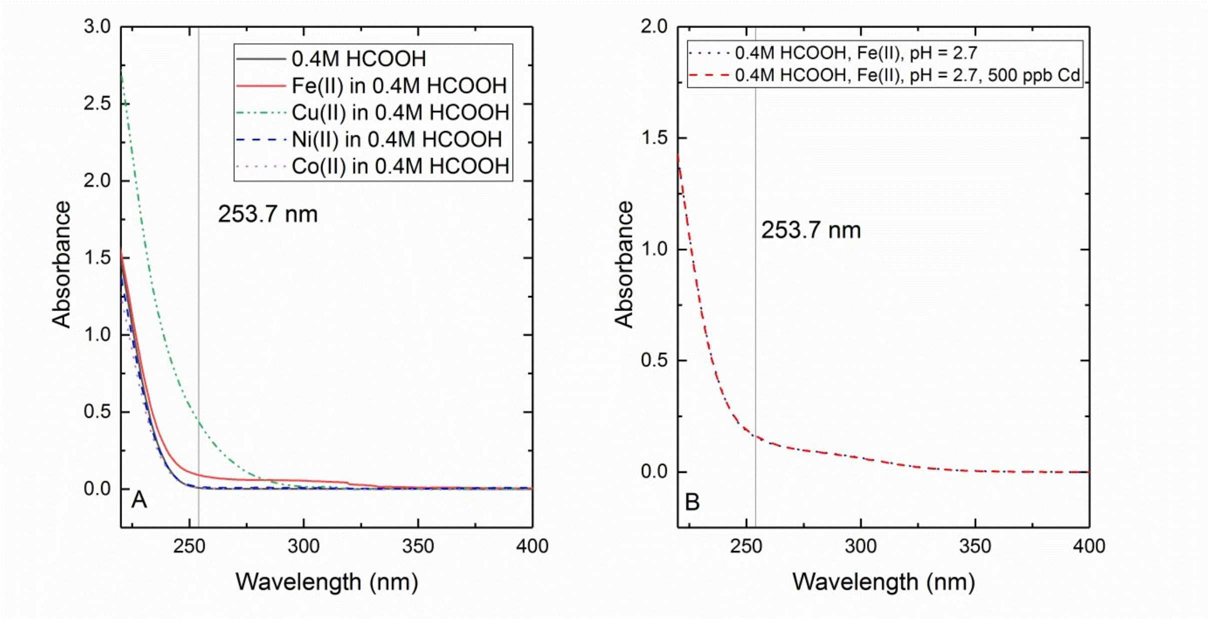

Fig. S1: UV spectra of potential sensitizers, spectra measured against deionized water, vertical line shows the position of 253.7 nm Hg line, A) spectra of potential sensitizers in 0.4M HCOOH, concentration of each metal 100 µg mL^{-1}, B) spectrum of photochemical reagent solution (optimum composition) with and without Cd(II) ions

S2: Effect of Triton X-100 detergent

We have previously observed positive effect of Triton X-100 on the sensitivity of electrochemical generation of cadmium volatile species.[1] As described in this publication, Triton X-100 beneficently influences the separation/release of volatile species from the liquid matrix if it is added upstream of the gas-liquid separator. The same effect was confirmed in this study. Introduction of $1 \cdot 10^{-3}$ mol L^{-1} of Triton X-100 at flow rate 0.4 mL min^{-1} resulted in 1.5-fold increase in fluorescence intensity compared to addition of water at the same flow rate.

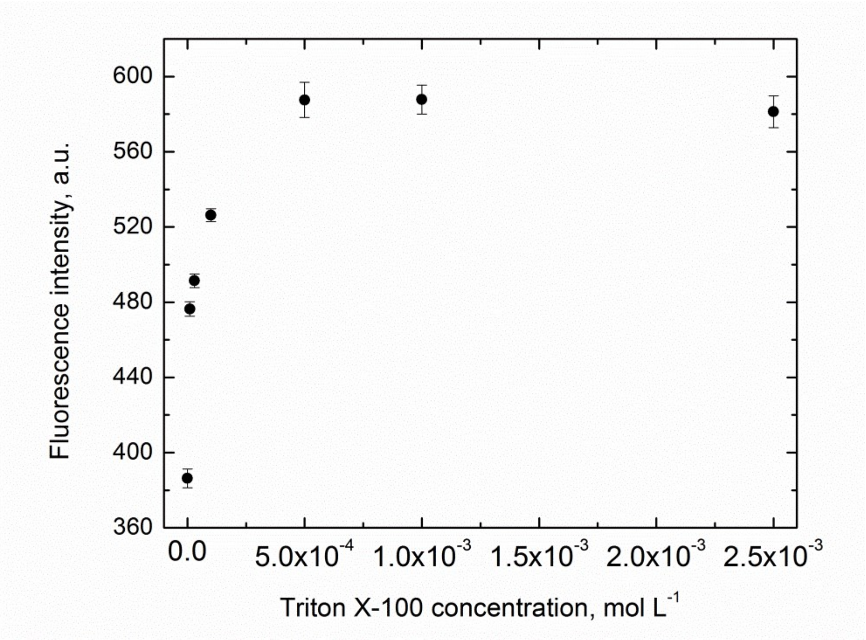

Fig. S2: Effect of Triton X-100 on measured fluorescence intensity, 100 µg mL^{-1} Fe(II), pH = 2.7, sample flow rate 1.0 mL min^{-1} and Triton X-100 flow rate 0.4 mL min^{-1}

S3: Overall generation efficiency – comparison of UV-PVG with nebulization ICP-MS

The overall generation efficiency was determined in the same way as described previously[2,3] and calculated as the product of an enhancement factor (ratio of sensitivities obtained with UV-PVG and nebulization) and nebulization efficiency.

The outlet from the UV-PVG system (see Fig. S3) was coupled to the dilution gas inlet (marked as HMI) of the ICP-MS using 310 mm long PTFE tube. The only change to the UV-PVG apparatus was the use of an injection valve with a 1.33 mL loop to introduce the defined amount of the sample to the system. Unless otherwise stated, the drying membrane was included to mimic the transport route used in AFS. The instrument parameters were set for optimum operation with UV-PVG during all experiments (See Table S1). UV-PVG calibration curve was measured with 0, 5, 10, 20 and 50 ng mL^{-1} Cd prepared in 0.4M HCOOH with the addition of 100 µg mL^{-1} Fe(II), $1 \cdot 10^{-3}$M Triton X–100 and pH adjusted to 2.7 while nebulizing only 1% HNO_3 and internal standards (10 ng mL^{-1} Rh and 500 ng mL^{-1} Te) prepared in 1% HNO_3. Nebulization calibration curve was measured with 0, 5, 20 and 50 ng mL^{-1} Cd in 1% HNO_3. Slopes of linear calibration curves were recalculated to equal injected volume of the samples, related and an enhancement factor was calculated.

The nebulization efficiency, using the MicroMist nebulizer, was determined by a waste collection method. Approximately 15 mL of solution containing 25 ng mL^{-1} Cd, 2 ng mL^{-1}

Rh and 100 ng mL^{-1} Te in 1% HNO_3 was placed in a vial on an analytical balance. We immersed tubing for aspiration of a carrier liquid, internal standard and waste from the cooled spray chamber into this solution. The tubing did not contact the walls of the vial. After stabilization (30 min) the weight of the solution was recorded every 5 min over a 120 min period. Recorded weights were plotted against time. The nebulization efficiency was calculated by dividing the slope of this weight loss plot by the total solution flow rate (carrier plus internal standard) entering the nebulizer.

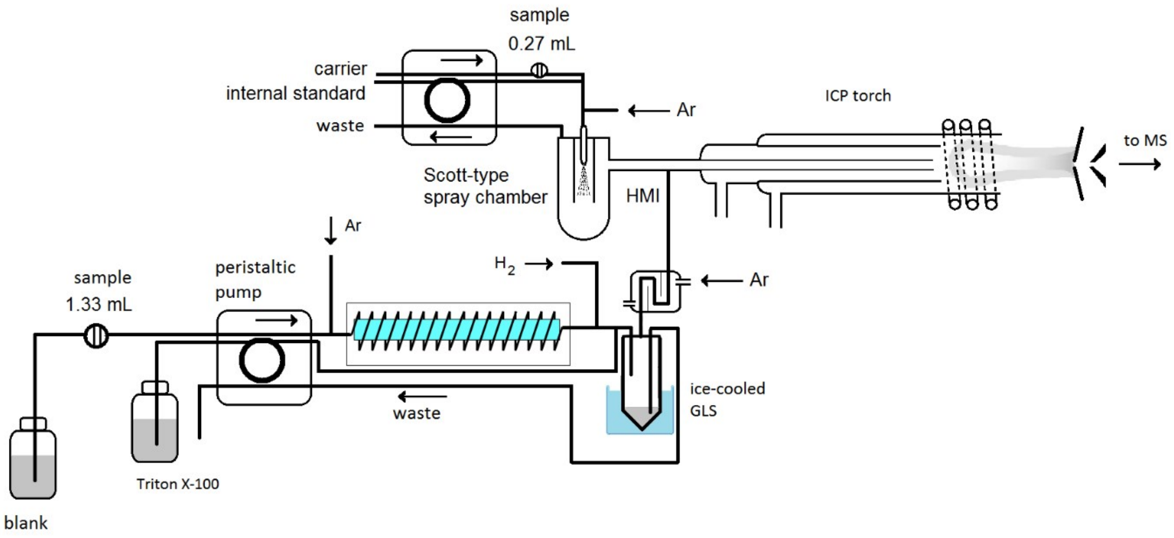

Fig. S3: The setup employed for determination of the overall generation efficiency by comparison with nebulization ICP-MS

Table S1: ICP-MS conditions for coupling with UV-PVG

Parameter	Value
RF power, W	1600
Nebulizer Ar, L min^{-1}	1.05
Ar for UV-PVG, mL min^{-1}	200
H_2 for UV-PVG, mL min^{-1}	40
Carrier liquid flow, mL min^{-1}	0.343
Internal standard flow, mL min^{-1}	0.070
Reaction/collision cell mode	no gas
ICP-MS spray chamber temperature	2 °C
Measurement mode	time resolved analysis
Measured isotopes	^{103}Rh(IS), ^{111}Cd, ^{125}Te(IS)

References:

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2 J. Šoukal, R. E. Sturgeon and S. Musil, *Anal. Chem.*, 2018, **90**, 11688–11695.
3 J. Vyhnanovský, R. E. Sturgeon and S. Musil, *Anal. Chem.*, 2019, **91**, 13306–13312.