Supplementary information

Selenium preconcentration in a gold "amalgamator" after hydride generation for atomic spectrometry

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1 Experimental

1.1 Compact trap unit for ICP-MS

To allow coupling of the trap packed with amalgamator filling to the ICP-MS detector (see section 1.2) a compact trap unit for ICP-MS, was constructed by modification of the conventional high matrix introduction (HMI) interface mating the spray chamber and the ICP torch which serves to introduce dilution gas. A new piece of the HMI interface was made by a glassblower. The only difference was that the inlet for the optional gas being realized by a 15 mm long quartz tube (2 mm i.d., 4 mm i.d.) in the conventional design was made longer reaching thus 65 mm (see Fig S1) analogously as described previously[1, 2]. As a consequence, the prolonged tube served as the trap. Its downstream part was packed with the amalgamator filling (section 2.3.2) and heated resistively to any desired temperature between ambient and 1075 °C (see section 2.3.3 for description of the fast heating device). To avoid removal of the amalgamator filling by a stream of the carrier gas, the quartz tube had a dent in its downstream part, ca 6 mm from its junction with the quartz tube connector analogously as the commercial amalgamator tubes described in section 2.3.2.

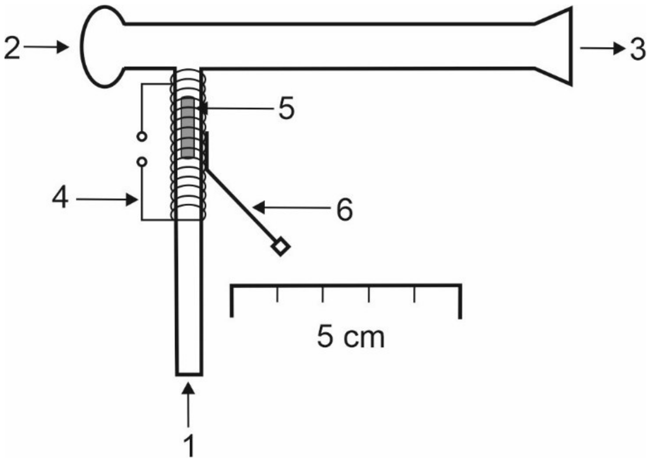

Fig. S1 Schema of the compact trap unit for ICP-MS. 1 – hydride generator, 2 – spray chamber, 3 – torch, 4 – heating coil coupled to the fast heating device, 5 – amalgamator filling, 6 – thermocouple with PID controller

1.2 Inductively coupled plasma mass spectrometry

Feasibility of coupling of the trap packed with gold amalgamator filling to ICP-MS detector was tested owing to the constructed compact trap unit for ICP-MS (see section 1.1 in ESI†). A 8900 ICP-MS/MS spectrometer (Agilent) was used. The configuration of the instrument consisted of a double-pass spray chamber, MicroMist nebulizer and 1.5 mm injector torch. The operating parameters were 1550 W RF power, 0.60 l min^{-1} Ar nebulizer gas, 0.36 l min^{-1} Ar make-up gas, 8.0 mm sampling depth and 40% O_2 reaction cell gas. 100 ng ml^{-1} Te(VI) solution (BDH, United Kingdom) in 0.2% (m v^{-1}) HNO_3 was co-nebulized as an internal standard to provide robust wet plasma conditions. Measurements were carried out with O_2 in the reaction cell in a mass-shift mode and selenium as well as tellurium as internal standard were measured as $^{78}Se^{16}O^+$ and $^{125}Te^{16}O^+$ at m/z 94 and 141, respectively.

2 Results and discussion

2.1 Comparison of slow heating device and fast heating device with temperature feedback control

The heating rate of both devices is compared in Fig. S2.

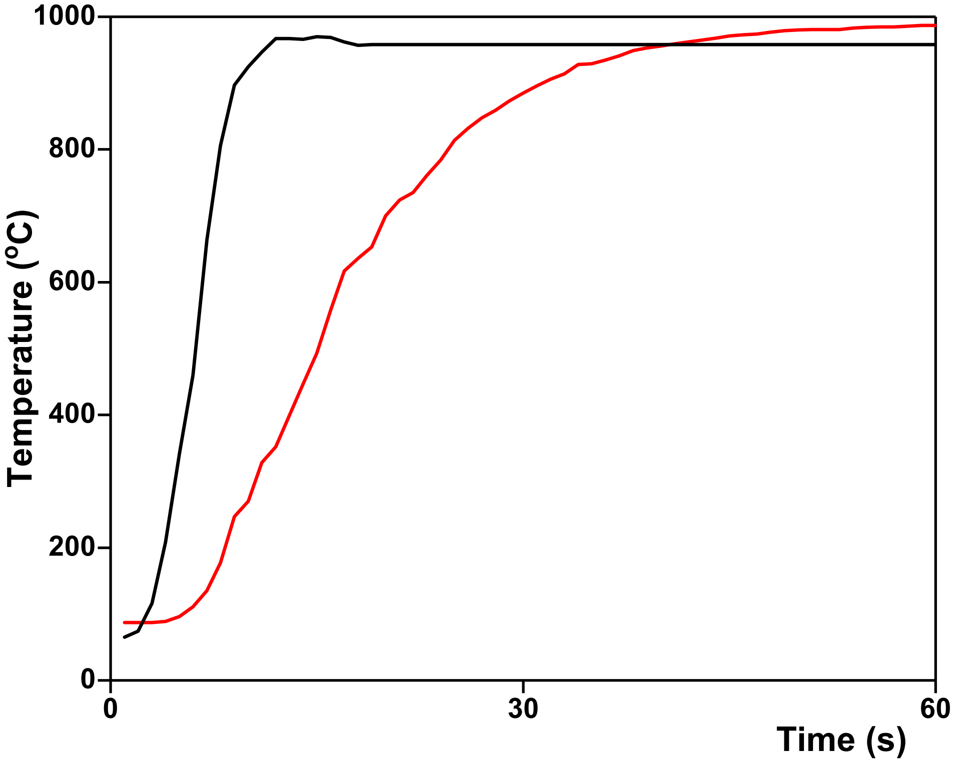

Fig. S2 Comparison of heating rates of the heating device with no temperature feedback control (red line) and a fast heating device with thermocouple feedback temperature control (black line). Temperature to be reached was 960 °C with heating from ambient temperature in both cases.

2.2 Interferences

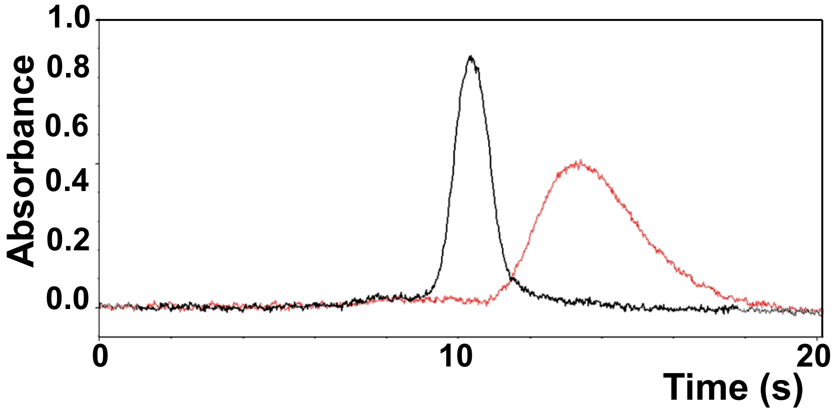

Fig. S3 Comparison of the signals of 3 ng ml^{-1} Se in presence of 3 000 ng ml^{-1} As (black line) and absence of As (red line). Trapping temperature 450 °C, volatilization temperature 970 °C, carrier gas flow rate 75 ml min^{-1} H_2, 40 ml min^{-1} O_2 as outer gas.

2.3 Quartz compact trap unit with ICP-MS detection

Effort was made to couple the gold amalgamator packed trap (see section 1.1 of ESI† for details) also with ICP-MS detection. Pilot experiments were performed without preconcentration, i.e. with on-line selane transfer from hydride generator into ICP-MS. The trap was thus not packed with amalgamator filling in these experiments. A calibration curve was measured in this mode using Se standards in the range from 0.1 to 1 ng ml^{-1}. The ratio of the slopes for the calibration curves for both on-mass and mass-shift modes were in agreement with natural abundance of the monitored isotopes. LOD calculated according to IUPAC[3] was 0.1 pg ml^{-1}. This is still favourable compared to instrumental LOD of 9 pg ml^{-1} reported for nebulization[4].

Pilot experiments dealing with Se preconcentration in the compact trap unit for ICP-MS were performed under optimum conditions found in AAS experiments, i.e. with trapping temperature of 450 °C, volatilization at 1 000 °C and carrier gas 75 ml min^{-1} H_2. These experiments revealed that the volatilization peak was unacceptably broad (Fig. S4), even broader than the signal in the on line mode, and with a pronounced tailing. As a consequence, the effect of volatilization temperature on peak profile was studied in the range from 850 to 1075 °C (Fig. S4). Obviously, the peaks become narrower with increased volatilization temperature. However, even at highest volatilization temperature studied, 1075 °C, the volatilization peak was tailing, being unacceptably broad for routine measurements. Higher volatilization temperature than 1075 °C could not be studied because of the risk of gold evaporation from the amalgamator and/or melting the quartz compact trap unit. No breakthrough signal was observed during trapping. However, the signal for preconcentration mode corresponded to ~3% preconcentration efficiency only, assessed by comparison to peak area of on-line signal for 1 ng ml^{-1} Se (with correction to internal standard). This indicates that volatilized Se was trapped on quartz surface downstream to the heated part of the trap. Dark ring deposit was observed at the end of the heated part after these experiments.

Low preconcentration efficiency as well as the pronounced tailing of the volatilization peak can be therefore explained by severe transport losses and analyte delays caused by interaction and condensation of volatilized Se species on colder quartz surfaces downstream the trap, especially in the non-heated quartz tube connector between the trap and torch. Deposits observed directly in L-junction of the inlet arm (trap) and the quartz tube connector give good evidence further supporting this hypothesis. The fact the deposited amount increased with the increase of standard solution concentration confirms the deposits are analyte-related. Losses of volatilized analyte on colder quartz surface were also confirmed by radioactive experiments (see Fig. 4C) and related discussion in section 3.3. The transport losses are negligible in AAS since there is no negative temperature gradient between the trap heated to volatilization temperature and optical arm heated to atomization temperature. On the contrary, the temperature drops to ambient temperature in the zone through which volatilized analyte is transported from the trap to the torch in ICP-MS. Heating of this zone is technically not possible. Although coupling of the gold amalgamator based trap to ICP-MS is feasible, pronounced transport losses in this experimental arrangement resulting in peak tailing and low signals prevent it from routine use.

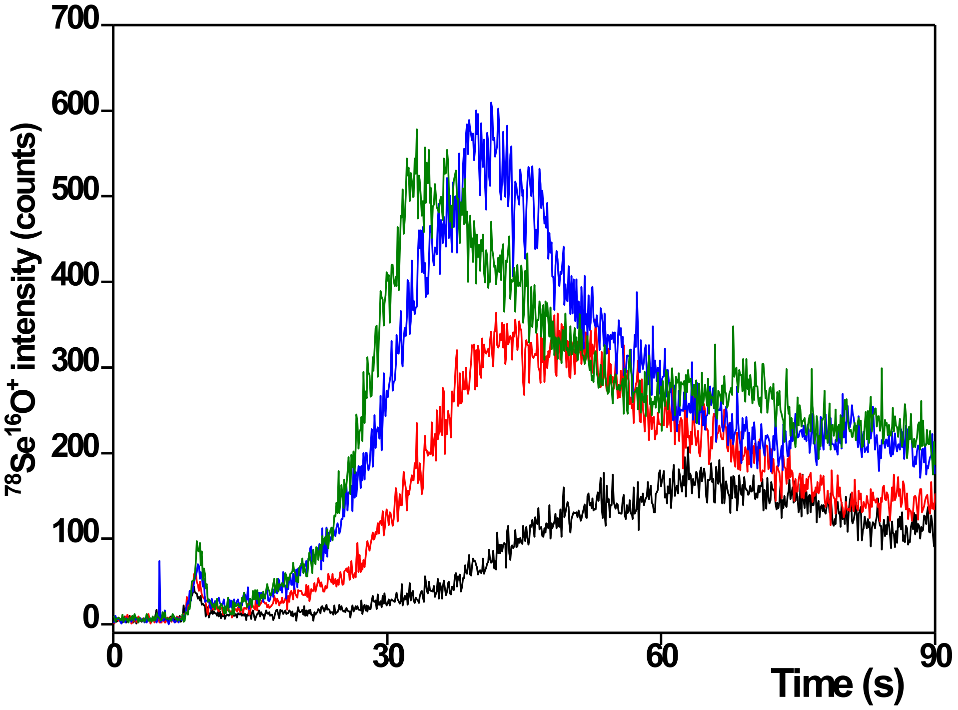

Fig. S4 Effect of volatilization temperature on signal profile measured with ICP-MS. Volatilization temperature of 850 °C (black line), 900 °C (red line), 1000 °C(blue line) and 1075 °C (green line). Sample introduction time 30 s, 1 ng ml^{-1} Se standard solution, 75 ml min^{-1} H_2 carrier gas, trapping temperature 450 °C.

References

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3 IUPAC (International Union of Pure and Applied Chemistry) (1997). Compendium of chemical terminology. (2nd ed.). http://www.chemsoc.org/chembytes/goldbook/ Accessed 27.11.2019.

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