

Supplementary Information

Technical Note

An automatic cryotrapping and cryofocussing system for parallel ICP-MS and EI-MS detection of volatile arsenic compounds in gaseous samples

Gunter Ilgen^a and Jen-How Huang^{*b}

^a*Chemische Analytik, BayCEER, University of Bayreuth, Dr. Hans-Frisch Straße 1-3, D-95448, Bayreuth, Germany.*

^b*Institute of Environmental Geosciences, University of Basel, CH-4056 Basel, Switzerland*

**Corresponding author. Email: jen-how.huang@unibas.ch; Phone: +41 61 2670483 ; Fax: +41 61 2670479.*

(8 pages, 9 figures)

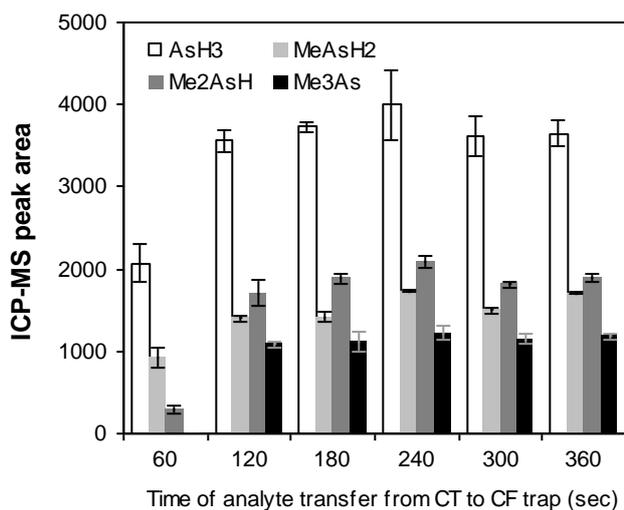


Fig. S2. ICP-MS based peak areas of of different arsine (AsH_3), monomethylarsine (MeAsH_2), dimethylarsine (Me_2AsH) and trimethylarsine (Me_3As) at different time length for transfer from the cryotrapping (CT) trap to the cryofocussing (CF) trap. The experimental results show more than 120 seconds is sufficient for a complete transfer of As compounds from the CT trap to the CF trap. The CT unit was consist of silcosteel tubing (65 cm length, 5.33 mm ID, 6.35 mm OD, Restek, USA) using liquid N_2 as the coolant. Heating rate was $11 \text{ watt} \times 360 \text{ sec}$. Sample trapping rate was 200 mL min^{-1} . Each arsine compounds containing 100 μg As was prepared in 1000 mL N_2 . Mean values and standard deviations of triplicates are shown.

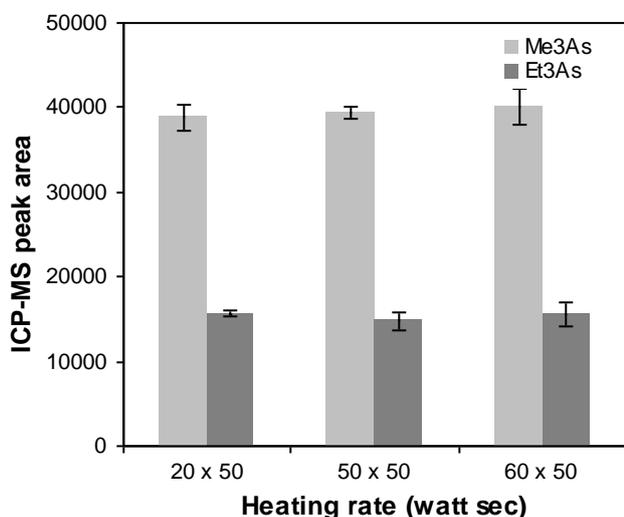


Fig. S3. ICP-MS based peak areas of trimethylarsine (Me_3As) and triethylarsine (Et_3As) at different heating rates of cryofocussing trap (CF). The results indicate that CF heating rate did not influence the recovery of As compounds significantly. The cryotrapping (CT) unit was consist of silcosteel tubing (65 cm length, 5.33 mm ID, 6.35 mm OD, Restek, USA) using liquid N_2 as the coolant. CT heating rate was $11.3 \text{ watt} \times 360 \text{ seconds}$. Sample trapping rate was 200 mL min^{-1} . 1 ng As of each arsine compounds was prepared in 1000 mL N_2 . Mean values and standard deviations of triplicates are shown.

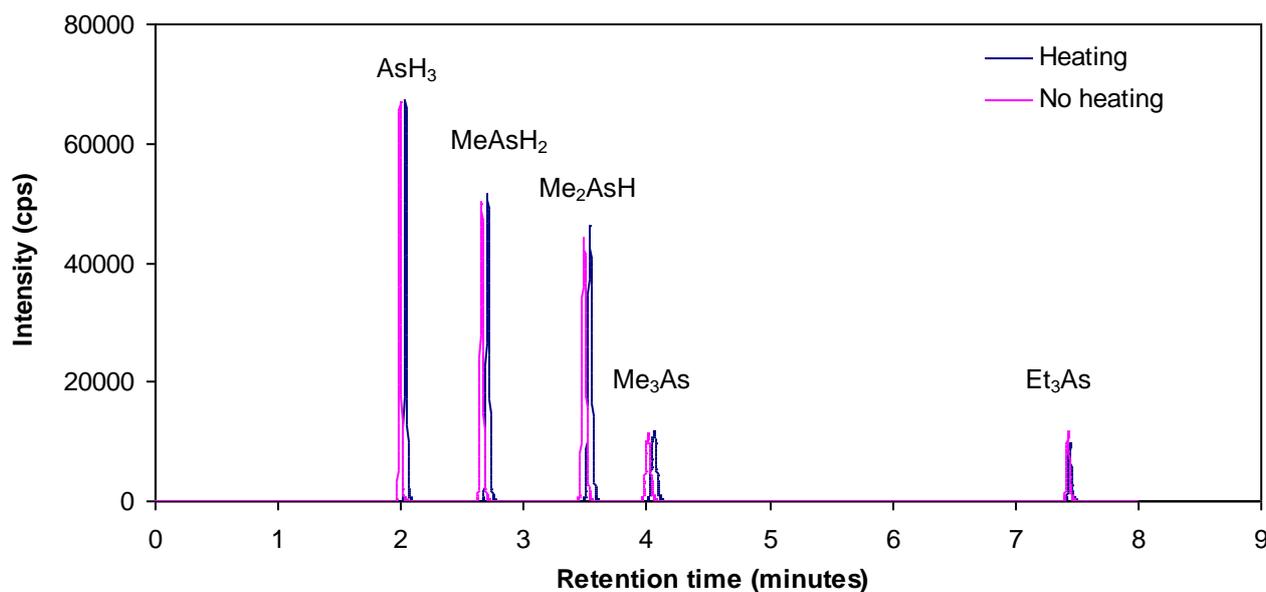


Fig. S4. ICP-MS chromatograms of arsine (AsH₃), monomethylarsine (MeAsH₂), dimethylarsine (Me₂AsH), trimethylarsine (Me₃As) and triethylarsine (Et₃As) with (at 100°C) and without heating transfer line show no significant effect of heating on peak width. 1 ng As of each arsine compounds was prepared in 1000 mL N₂.

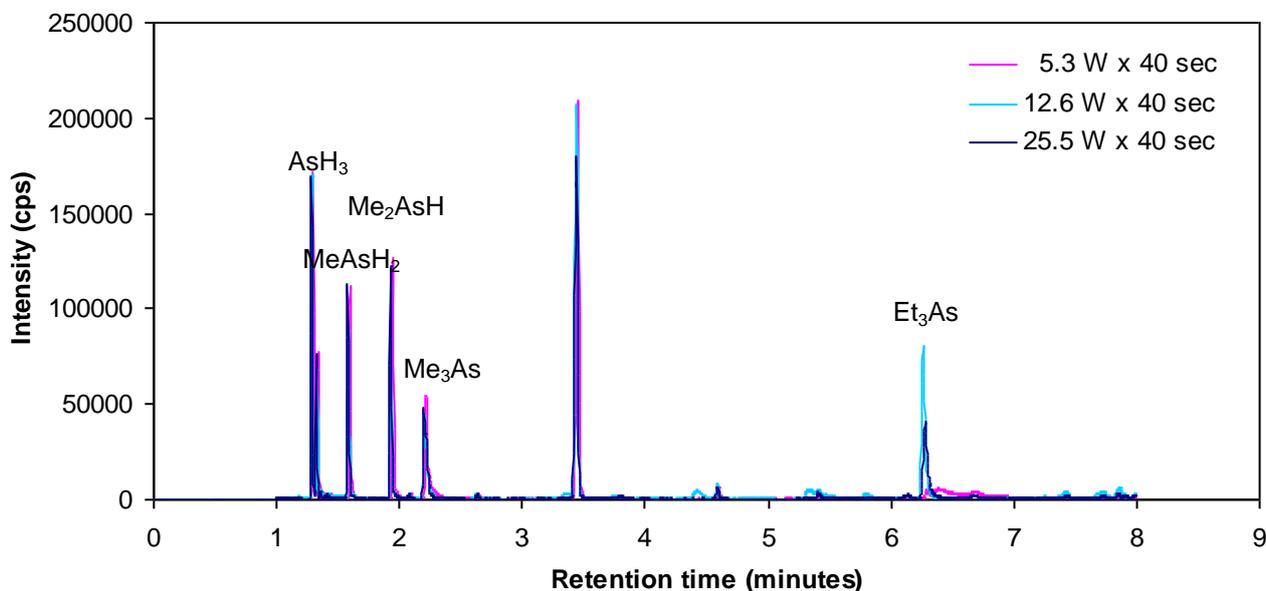


Fig. S5. EI-MS chromatograms of arsine (AsH₃), monomethylarsine (MeAsH₂), dimethylarsine (Me₂AsH), trimethylarsine (Me₃As) and triethylarsine (Et₃As) show the influence of CT heating rates on Et₃As analysis. The chromatographic peak of Et₃As became smaller at the higher heating rates (25.5 W × 40 seconds) and deformed at the lower CT heating rate (5.3 W × 40 seconds). 10 ng As of AsH₃, MeAsH₂, Me₂AsH and Me₃As and 11.3 ng of Et₃As was prepared in 1000 mL N₂.

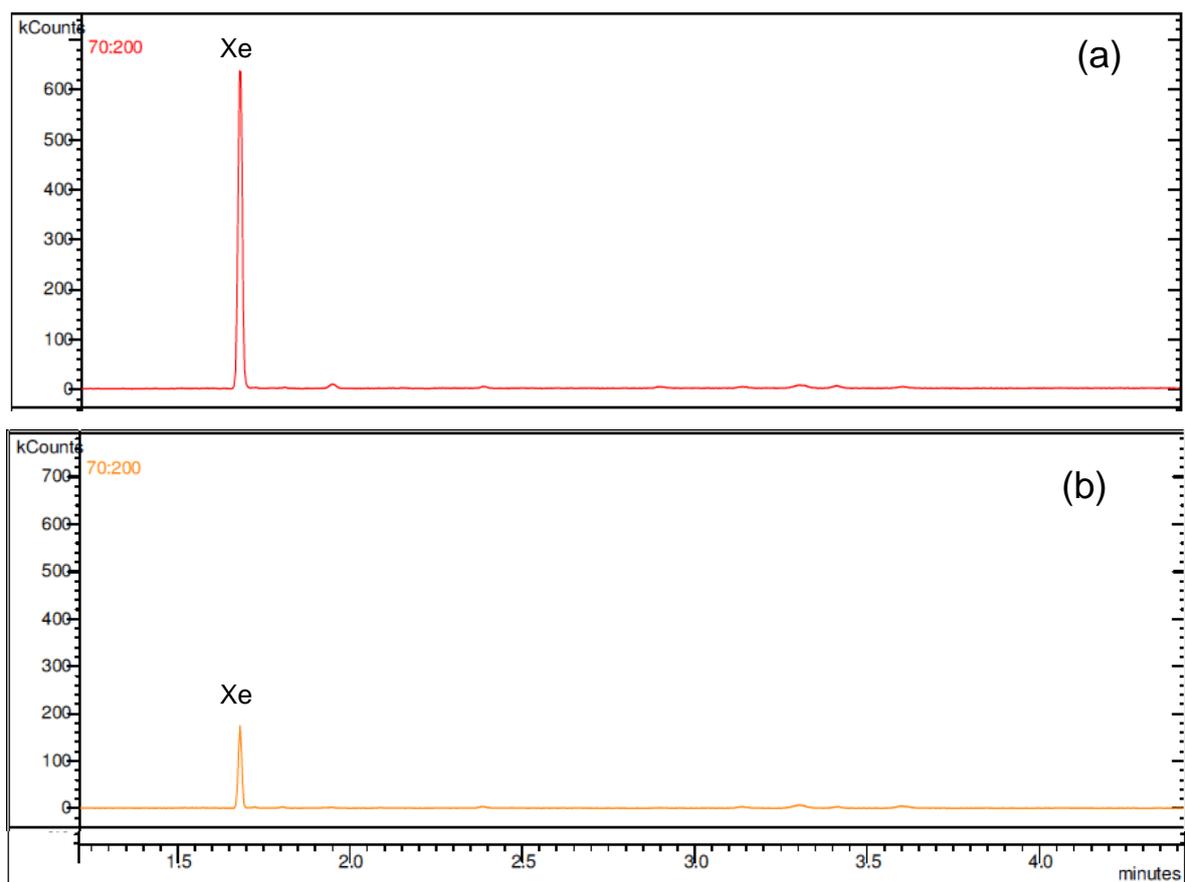


Fig. S6. EI-MS chromatograms show the presence of Xe in (a) N_2 used throughout this study and (b) in the air.

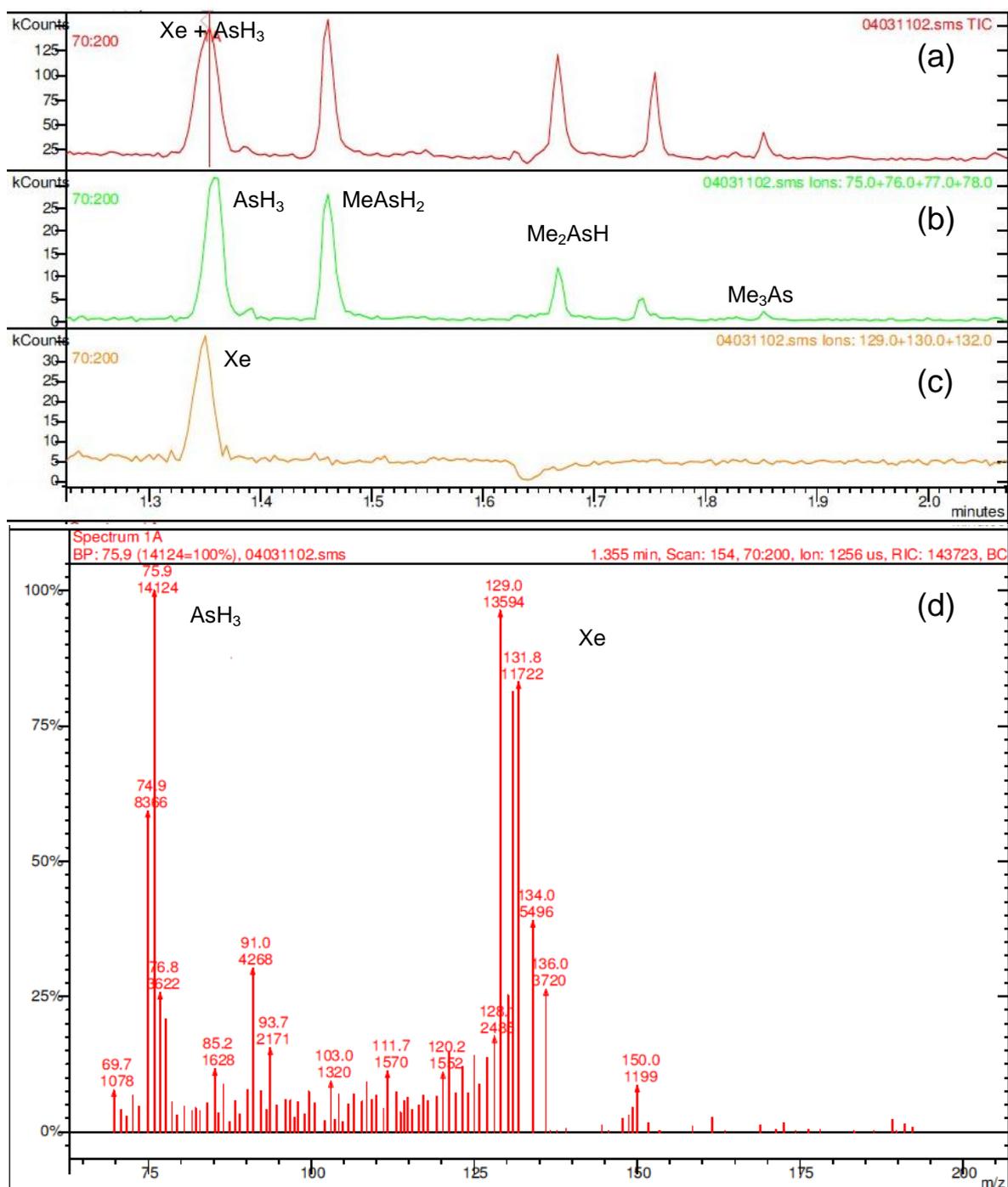


Fig. S7. EI-MS chromatogram of Xe, arsine (AsH₃), monomethylarsine (MeAsH₂), dimethylarsine (Me₂AsH) and trimethylarsine (Me₃As) with (a) total ion current, (b) arsenic, (c) Xe (d) mass spectrum using an analytical column with 0.25 μm film thick. The mass spectrum shows that the peak eluting at 1.35 minutes contains both AsH₃ and Xe.

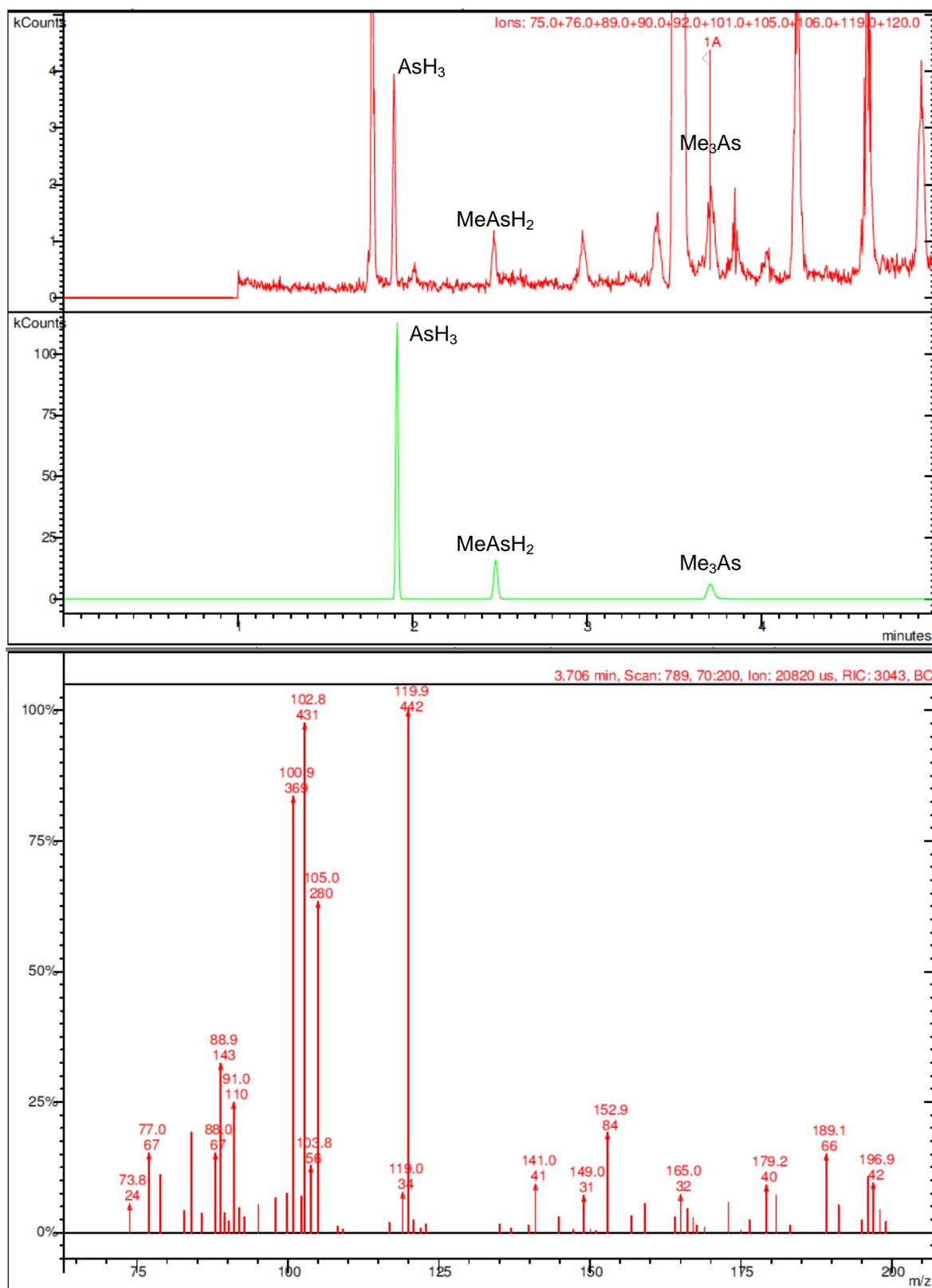


Fig. S8. (a) EI-MS and (b) ICP-MS chromatograms of arsine (AsH₃), monomethylarsine (MeAsH₂), dimethylarsine (Me₂AsH) and trimethylarsine (Me₃As) in headspace of wetland soil incubation at 15°C for 9 days without additional spiking of As(III) (250 µg As) (see Table 3). The incubation was achieved with 60 g of Histosol (sampled in Fichtelgebirge, NE-Bavaria, Germany) with water content of 93% w/w overflowed with 100 mL artificial rainwater. (c) The corresponding mass spectrum of Me₃As.

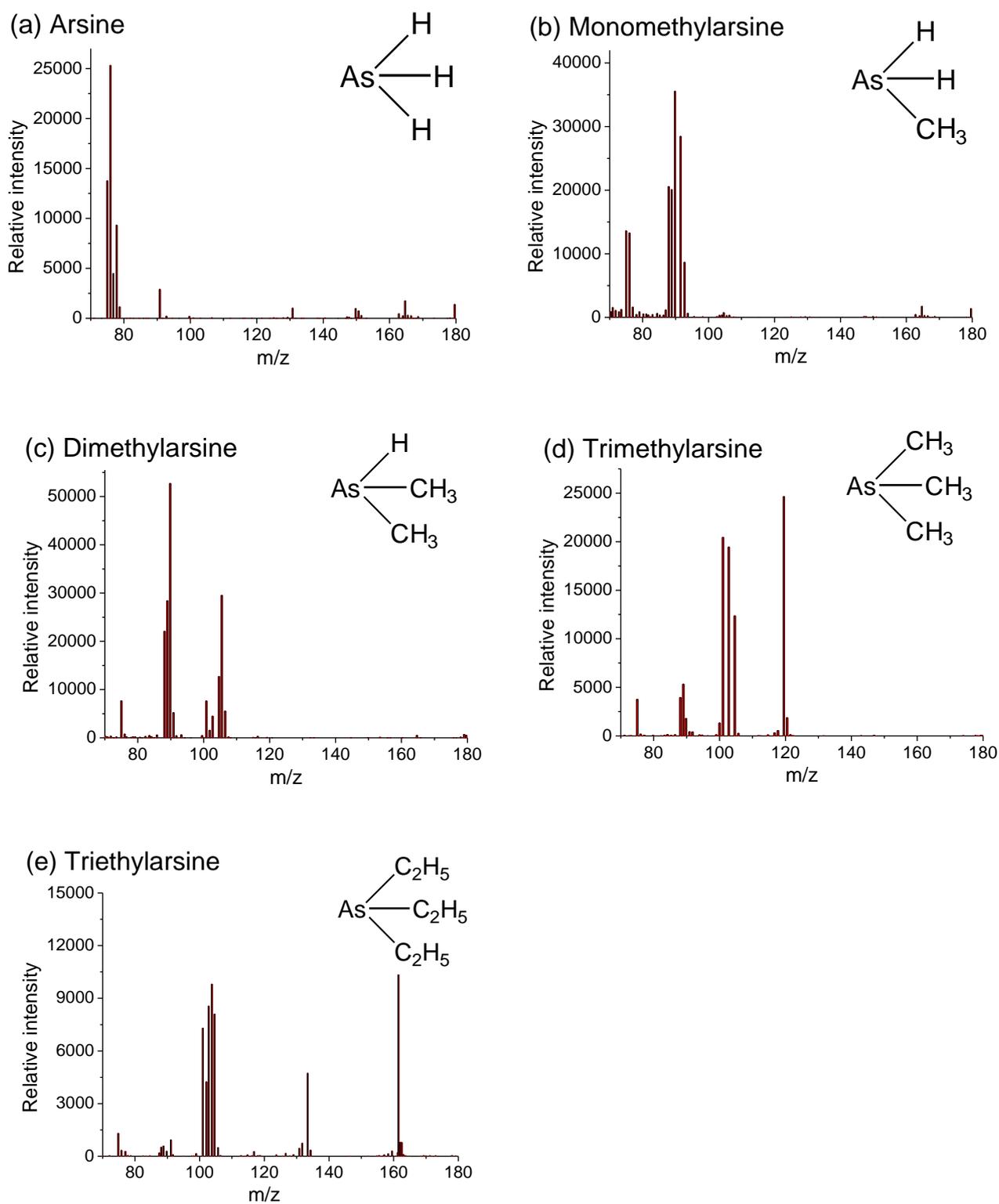


Fig. S9. EI-MS spectra of (a) arsine, (b), monomethylarsine, (c) dimethylarsine (d), trimethylarsine (from Fig. 4) and (e) triethylarsine (from EI-MS chromatogram of the measurement in ESI, Fig. S5[†]).