Synthesis of reference substances and method development for the analysis of chlorinated and brominated methanesulfonic acids

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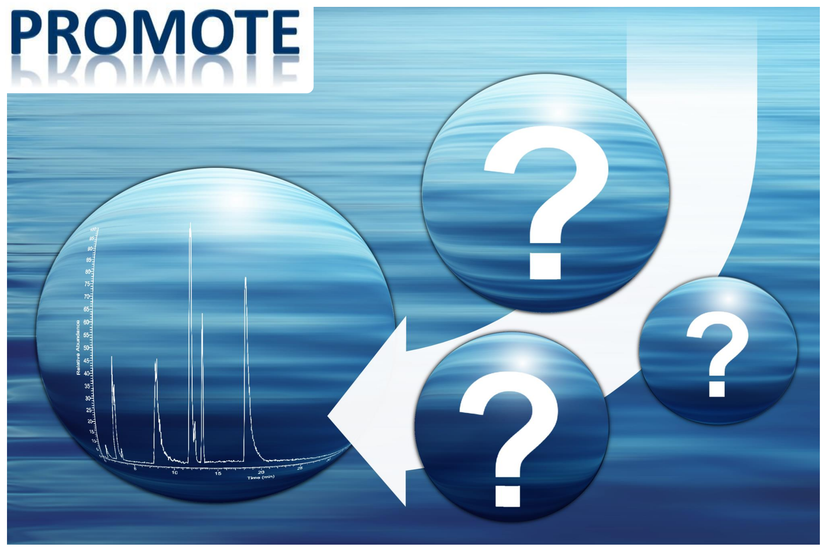
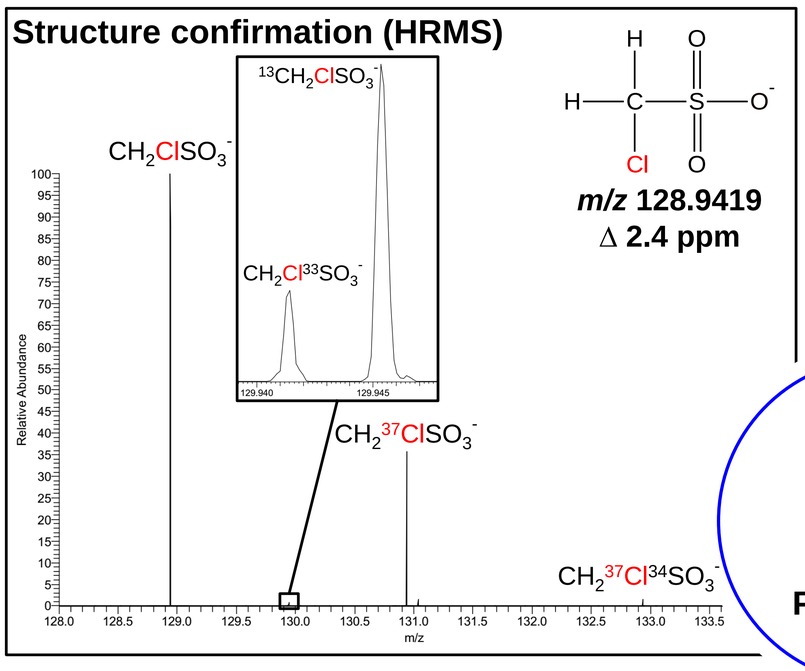
Introduction

Persistent and mobile organic contaminants may pose a risk to our drinking water resources[1]. Chlorinated and brominated methanesulfonic (Cl- and Br-MSAs) acids are recently discovered water contaminants[2] that were predominantly detected in drinking water samples and are probably derived from water disinfection. So far, reliable quantitative analysis of these substances, and thus a comprehensive monitoring, is hindered by the lack of commercially available reference standards. To tackle this issue, we synthesized chlorinated methanesulfonic acids (Cl_xMSAs) by **hydrolysis** of their respective sulfonyl chlorides and performed **halogen exchange** to obtain their brominated congeners (Br_xMSAs). With these standards, it was possible to develop the first quantitative method for these substances.

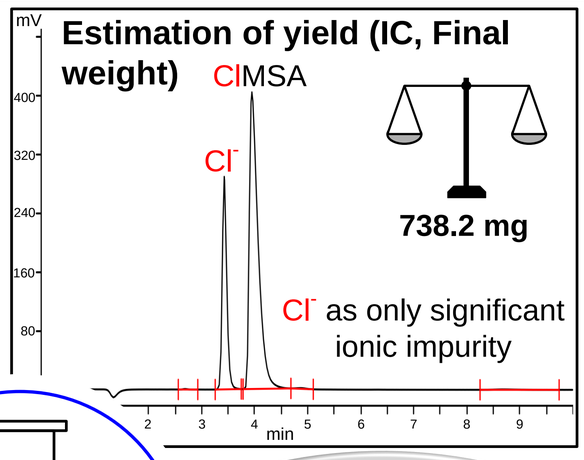


Structure confirmation (HRMS)



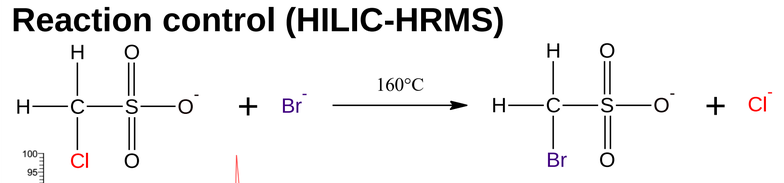
***m/z* 128.9419**
Δ 2.4 ppm

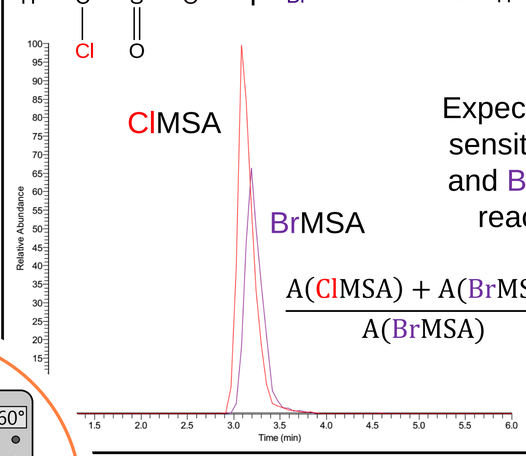
Estimation of yield (IC, Final weight)



738.2 mg

Reaction control (HILIC-HRMS)

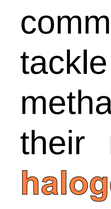




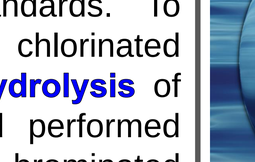
Expected similar ESI sensitivity of ClMSA and BrMSA enables reaction control

$$\frac{A(ClMSA) + A(BrMSA)}{A(BrMSA)} * 100\% = Yield\%$$

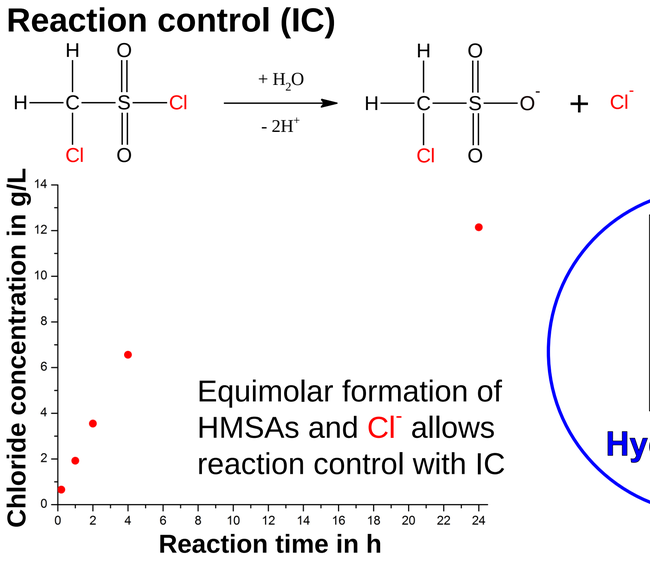
Purification with SPE



Halogen exchange with excess Br^-

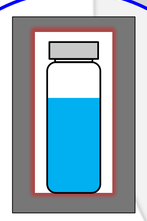


Reaction control (IC)



Equimolar formation of HMSAs and Cl^- allows reaction control with IC

Hydrolysis at 60° C



Conclusion

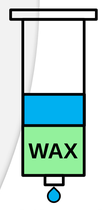
Cl-MSA, Br-MSA, Cl_2-MSA and ClBr-MSA could be synthesized

Identity and purity of standards was tested with IC and HRMS

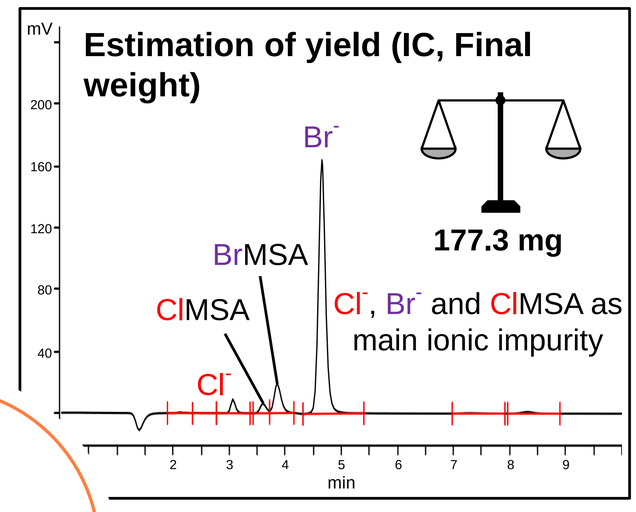
Additional reaction time will be required to obtain Br_2-MSA in relevant amounts

The final method will allow accurate quantification of chlorinated and brominated HMSAs for the first time

Purification with SPE

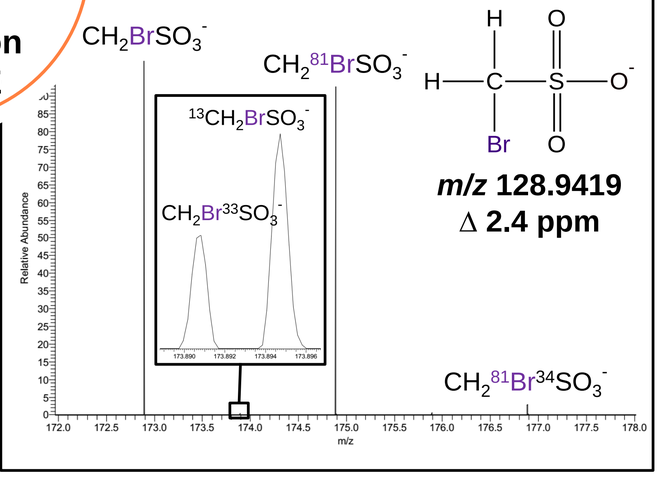


Estimation of yield (IC, Final weight)



177.3 mg

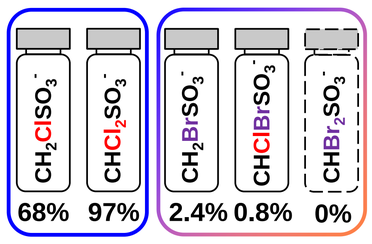
Structure confirmation (HRMS)



***m/z* 128.9419**
Δ 2.4 ppm

Educts

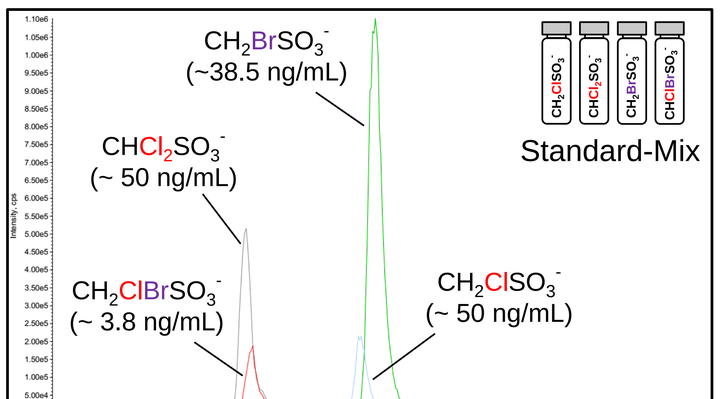
Products

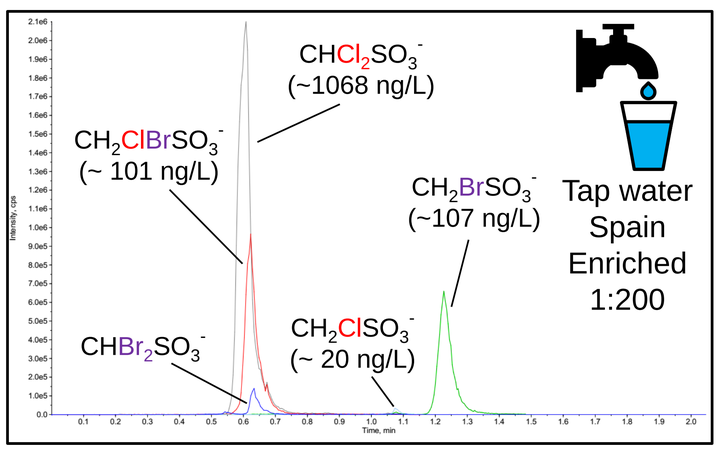


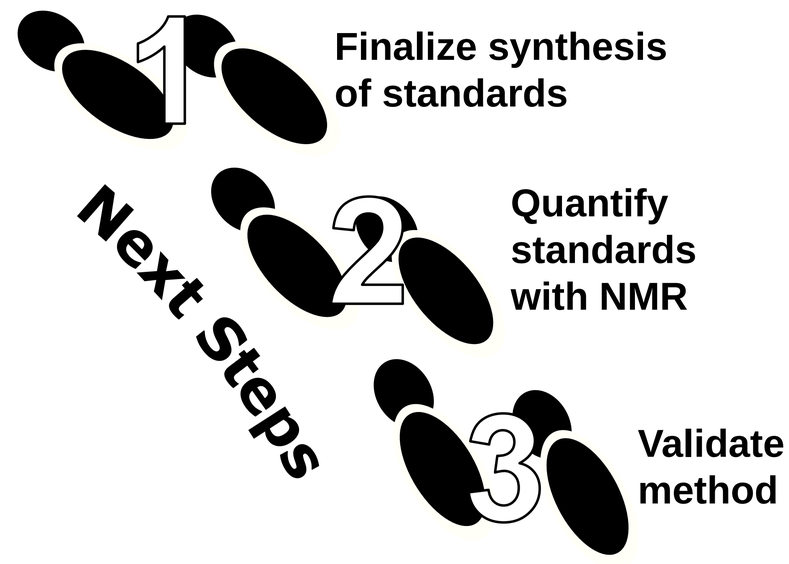
Chloro- and dichloromethane sulfonylchlorides were **hydrolyzed** at 60° C to form the respective chlorinated methanesulfonic acids. After purification with SPE **halogen exchange** was performed with an aliquot of the reaction product and an at least 10 times molar excess of Br^- (added as NaBr) at 160° C. IC and HRMS were used to analyze impurities and confirm the identity of the reaction products.

UHPLC-HILIC-sMRM analysis

- The synthesized standards were used to integrate HMSAs in an UHPLC-HILIC-sMRM method[3]
- Transitions for Br_2-MSA were derived from Br-MSA
- The sensitivity for brominated congeners seems to be their higher than for their chlorinated counterparts, but the selective is lower since Br^- isotopes are the only fragments of significant intensity
- Sample enrichment was based on an mmSPE method[4]
- So far only approximate standard concentrations are known
- Estimated concentrations in a tap water sample range from low ng/L to the low µg/L
- Observed retention time shift (BrMSA) and the lack of isotopically labeled internal standards indicates that analysis of fortified samples will be required for accurate quantification







References:

[1] Reemtsma, T., *et al. Environmental Science & Technology* **2016**, *50*, 10308-10315.

[2] Zahn, D., *et al. Water Research* **2016**, *101*, 292-299.

[3] Zahn, D. *et al*. in preparation

[4] Köke, N., *et al*. in preparation

Acknowledgement:

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