Investigation of aromatic amines in municipal wastewaters using Stir Bar Sorptive Extraction with derivatization

Adam Březina[1], Marek Stiborek[1], Branislav Vrana[1]

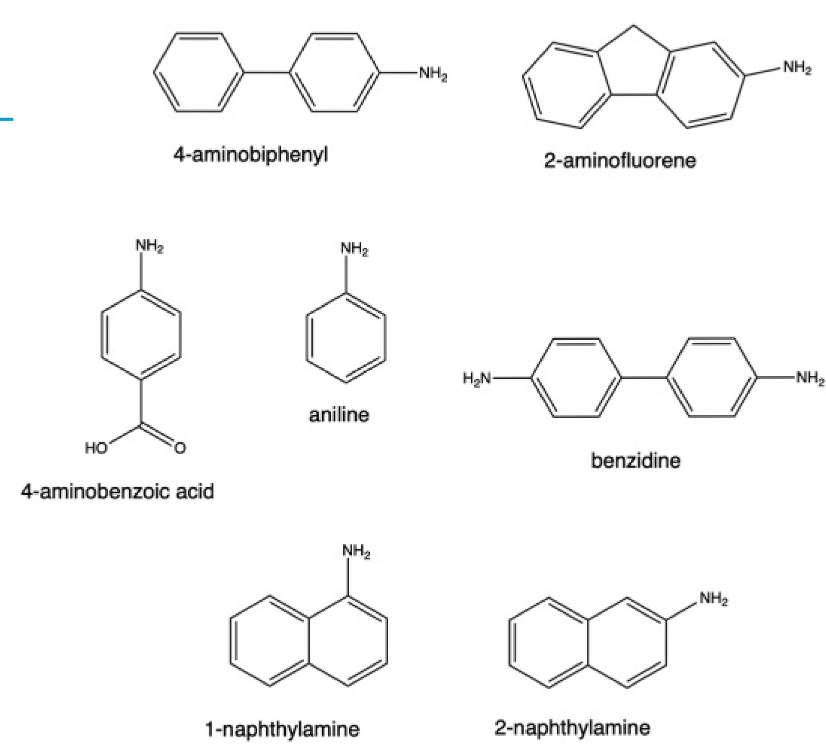
[1]Masaryk University, Faculty of Science, Centre RECETOX, Czech Republic

email: adam.brezina@recetox.muni.cz

Introduction

Aromatic amines (AAs) are organic compounds characterized by the presence of an amine group (-NH_2) attached to an aromatic ring, such as benzene. Their sources can be various industrial applications, including the synthesis of dyes, pharmaceuticals, cigarette smoke, grilling meat, detergents and many more. They are known to be associated with mutagenicity.

Due to their nature, some of them are not completely removed by wastewater (WW) treatment. In addition, hydrophobic AA are expected to sorb onto activated sludge in the WW. Presence of AA in effluent WW and land application of AA-containing sludge as a soil fertilizer may cause a potential risk for the environment and the human health.



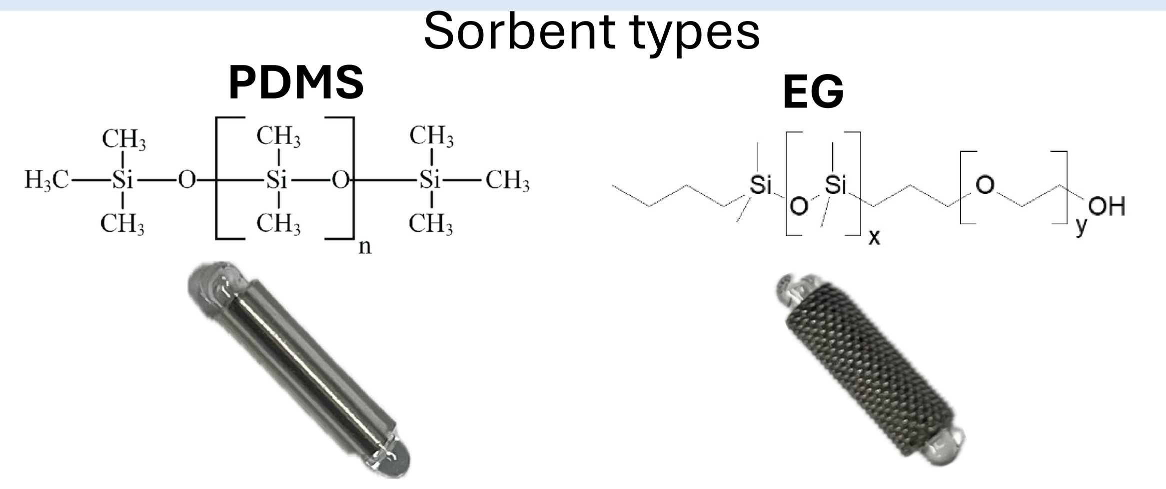
Stir Bar Sorptive Extraction

Stir bar sorptive extraction (SBSE), is a sample preparation technique in analytical chemistry utilized to extract and concentrate analytes from liquid samples for example wastewater or solids suspected in water. Stir bar is coated with a sorbent material, typically Poly-dimethylSiloxane (PDMS) or silicon modified with EthyleneGlycol (EG). Stir bar is typically agitated in sample and then desorbed either thermally or by solvent to release the analytes for analysis. SBSE offers notable benefits, including high sensitivity and selectivity, compatibility with various analytical instruments equipped with thermal desorption units (TDUs), such as gas chromatography-mass spectrometry (GC-MS), and the ability to concentrate analytes from complex matrices, making it invaluable for environmental monitoring.

Objectives

The primary aim of this study is to devise an effective analysis method for detecting AAs within complex matrices, notably WW treatment plant's activated sludge and wastewater. Due to the presence of numerous interferents in such matrices, conventional extraction techniques like Soxhlet extraction are not suitable. Therefore, there is a need for a selective isolation of AAs from the sludge matrix and to reduce the detection limits in the following analysis. We tested the **hypothesis** that isolation of AAs from the sludge matrix can be achieved by a combination of selective derivatization followed by enrichment of the derivatives by SBSE.

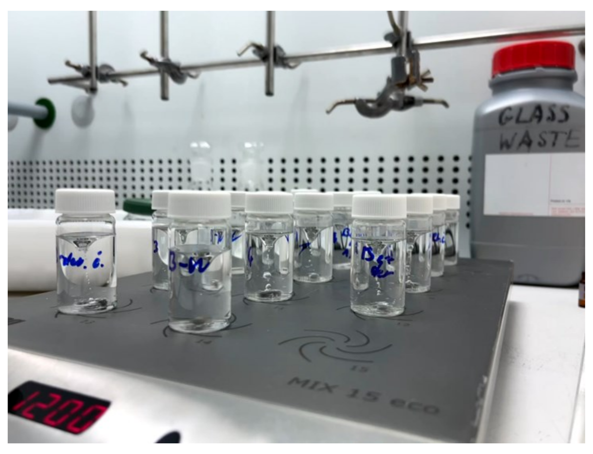
Sorbent types

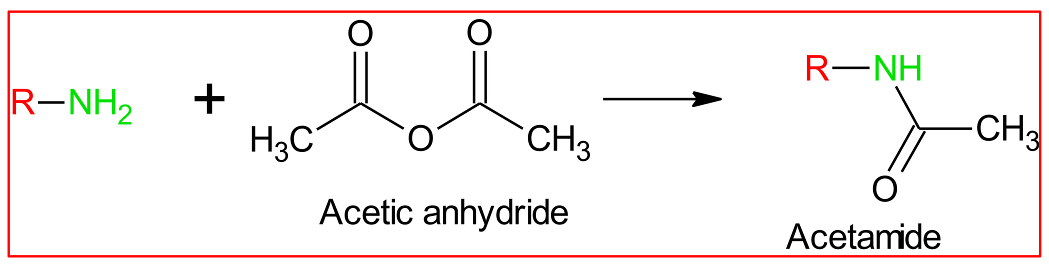


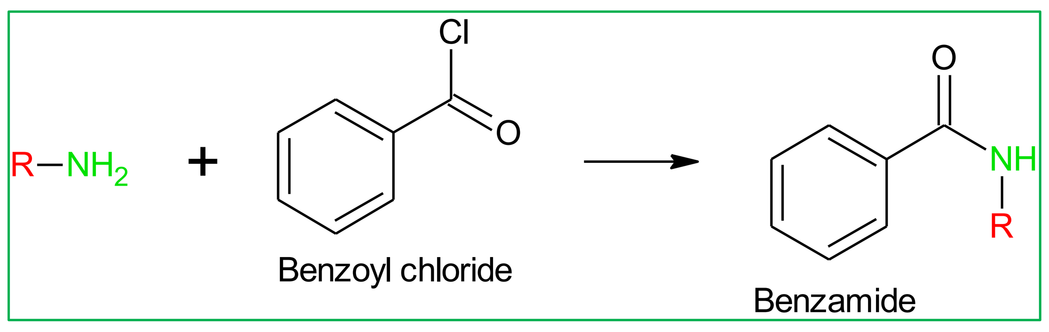
Derivatization

In this study, derivatization was used to enhance the hydrophobicity of aromatic amines for effective extraction via SBSE. By modifying the molecular structure of compounds the log*P* value were increased, improving their successful extraction efficiency and enabling analysis.

We tested two derivatization approaches with different derivatization agents. The derivatization was performed in basic environment (by addition of Na_2CO_3) using **acetic anhydride** and **benzoyl chloride** as derivatization agents, resulting in derivative **acetamides** and **benzamides**, respectively.

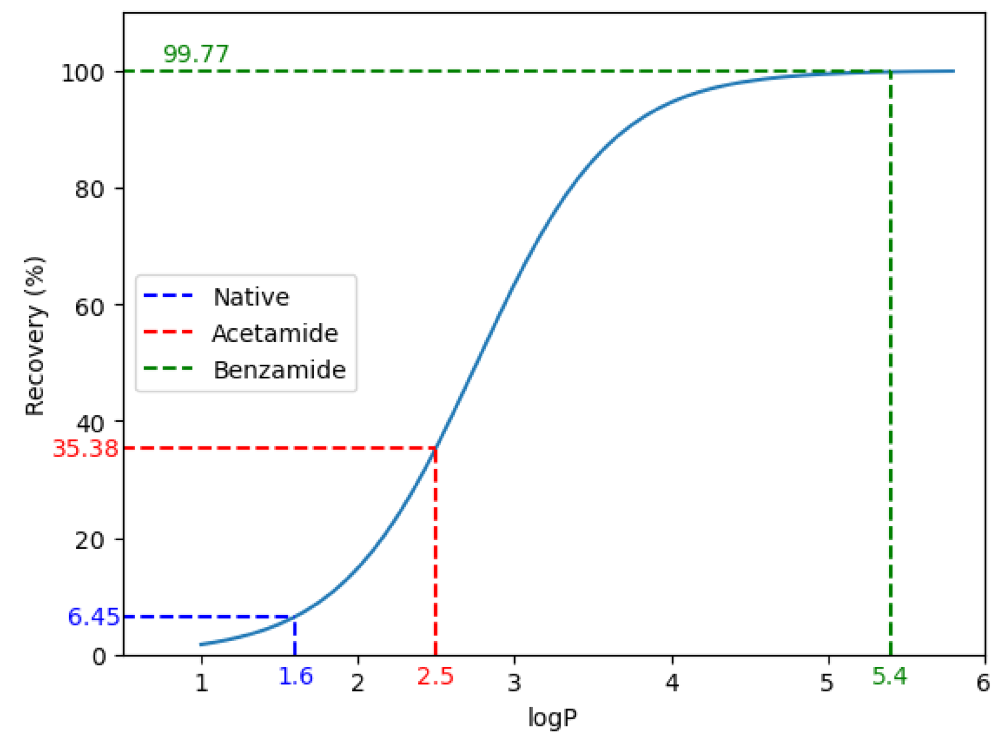




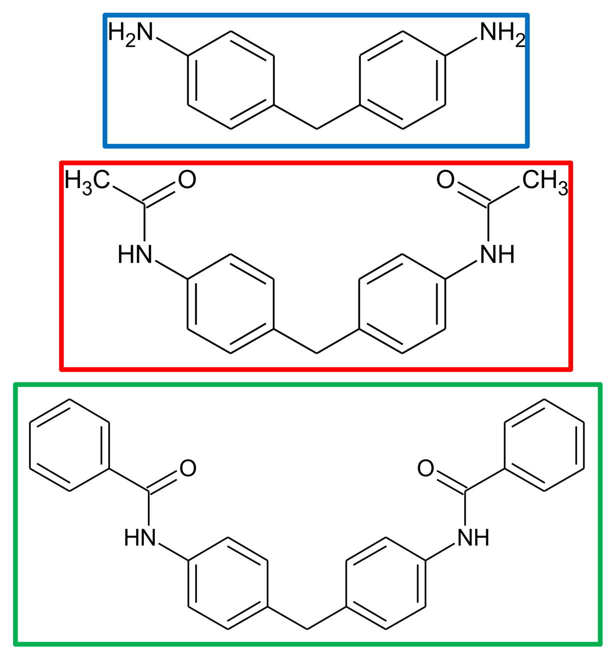


Effect of logP on theoretical recovery

With derivatization it is possible to increase hydrophobicity and with that increase theoretical efficiency

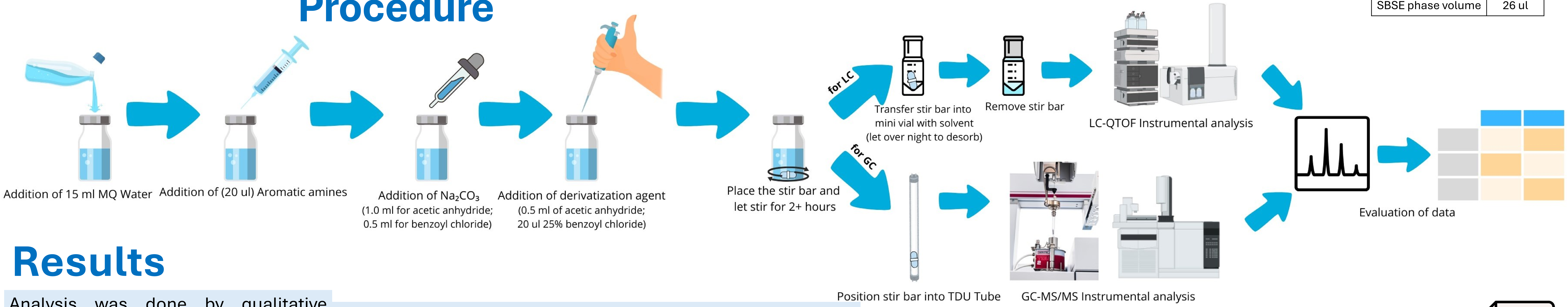


Dianilinomethane (DADPM)



Sample Volume	15 ml
SBSE phase volume	26 ul

Procedure



Results

Analysis was done by qualitative identification in all cases possible

A) for each derivatization method
a) without derivatization Native
b) with acetic anhydride Acetamide
c) with benzoyl chloride Benzamide

B) for each coating of SBSE
a) PDMS
b) EG

C) for each instrumental analysis
a) GC MS/MS
b) LC QTOF

		GC-MS/MS						LC-QTOF					
		PDMS			EG			PDMS			EG		
Compound	logP	Native (without der. ag.)	Acetamide (acetic anhydride)	Benzamide (benzoyl chloride)	Native (without der. ag.)	Acetamide (acetic anhydride)	Benzamide (benzoyl chloride)	Native (without der. ag.)	Acetamide (acetic anhydride)	Benzamide (benzoyl chloride)	Native (without der. ag.)	Acetamide (acetic anhydride)	Benzamide (benzoyl chloride)
2,4-Diaminotoluene	0.1												
4-Methoxyaniline	0.9												
Benzidine	1.3												
o-Toluidine	1.3												
4,4'-Oxydianiline	1.4												
4,4'-Methylenedianiline	1.6												
p-Cresidine	1.7												
5-Nitro-o-toluidine	1.9												
4-Chloroaniline	1.9												
4-Chloro-o-toluidine	1.9												
3,3'-Dimethoxybiphenyl-4,4'-diamine	2.2												
4,4'-Thiodianiline	2.2												
2,4,5-Trimethylaniline	2.3												
Naphthalen-2-amine	2.3												
3,3'-Dimethylbiphenyl-4,4'-diamine	2.3												
4,4'-Methylenebis(2-methylaniline)	2.6												
Biphenylamine	2.9												
4-Aminobiphenyl	2.9												
3-Chloro-2-methylaniline	3.0												
Aniline Yellow	3.4												
3,3'-Dichlorobenzidine	3.5												
o-Aminoazotoluene	3.7												
4,4'-Methylenebis(2-chloroaniline)	3.8												
SUM (23)	-	4	8	9	2	0	3	15	11	22	14	0	6

Legend	
Detected	
Not detected	

Conclusion

In conclusion, this study highlights several key findings:

- selective AA derivatization in combination with SBSE and liquid chromatography with high resolution mass spectrometry (LC-QTOF) presents an efficient tool to identify AA in complex matrices
- PDMS coating is more efficient in extraction of derivatives than EG silicone
- derivatization with acetamide enabled isolation of 11 of 23 primary AAs
- benzoyl chloride was effective in isolation of 22 of 23 investigated primary AAs

Future plans

- Develop quantitative method for analysis AA with SBSE and derivatization
- Do screening of real samples from WWTP Modřice (Brno)

Acknowledgement

Authors thanks for financial support by the Czech Science Foundation (GF22-06020K), the Deutsche Forschungsgemeinschaft (DFG, MU 4728/2-1), and the European Union's Horizon 2020 research and innovation program (grant agreement no. 857560). We also acknowledge the support of Research Infrastructure RECETOX RI (No. LM2018121) and Operational Programme Research, Development and Education (No. CZ.02.1.01/0.0/0.0/17_043/0009632).