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From targeted analysis to non-targeted screening of polar organic micro contaminations in the drinking water production by UPLC-HRMS

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Master thesis, Instrumental Analytics

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INTRODUCTION

Water plays an essential role in our everyday life. Our body consists predominantly of water. It regulates the systemic homeostasis and the main body functions. Since the human body is not able to produce water by itself, it is dependent on a constant uptake, to maintain these functions. Chemical contaminations in the water such as pharmaceuticals, herbicides and personal care products can cause serious diseases. They can hit humans directly as well as indirectly via the uptake of contaminated plants or animals assimilating pollutants. The dependence on water implicates the inevitable necessity of assuring its quality. Industrielle Werke Basel (IWB) supplies Basel and several neighbouring municipalities with potable water. Its responsibility is to ensure the quality of the drinking water and in case of threat to the customer caused by water contamination, stop the supply. For the detection of such an endangerment, IWB purchased a new UPLC-HRMS (**Fig.1**). This system shall not only support the already existing targeted analysis. Furthermore, it shall be used for the screening of suspected and unknown organic micro pollutants in the drinking water, which may arise during the production process. It was shown that emerging metabolites and abiotic transformation products, of these pollutants, can have an enhanced toxicity and larger dispersion in the aquatic system, due to their increased polarity. Therefore, the detection of these is of particular importance. [1][2]

Tab.1: Targeted compounds

Metformin	Clarithromycine
Hydrochlorothiazide	Acesulfame
1H-Benzotriazole	Irbersartan
Amisulpride	Mecoprop
Metoprolol	Diclofenac
5-Methyl-1H-Benzotriazole	Isoproturon
Venlafaxine	Metazachlor
Citalopram	Chloridazone/Chloridazone-Desphenyl
Carbamazepine	Sulfamethoxazole
Candesartan	Acetylsulfamethoxazole

Fig.1: QExactive HF (Thermo), UPLC (Dionex) and PAL HTC sampler (Thermo)

CONCEPT

The aim of this thesis was firstly to successfully implement the new UPLC-HRMS system and secondly to develop and validate a sensitive and robust broad scope trace analysis method. The approach was based on selected target compounds (see. Tab.1), from different industrial sectors, having various physico-chemical properties. These compounds are known to be critical due to their persistence even lasting the sewage water treatment process. The UPLC-HRMS method, including an appropriate sample preparation workflow, shall be used for the quantification of these analytes down to concentrations of several ng/L. It is supposed to regularly monitor the occurrence and the fate of these contaminants in the whole drinking water production process. Furthermore, the method should serve as a basis for the screening of suspected and unknown organic micro contaminations.

RESULTS

After successfully commissioning of the new system. A direct large volume injection UPLC-HRMS method was developed and validated to separate and quantify these targeted compounds (**see Fig.2**). For the quantification a suited mix of isotope labelled internal standards (ISTDs) was developed and utilised.

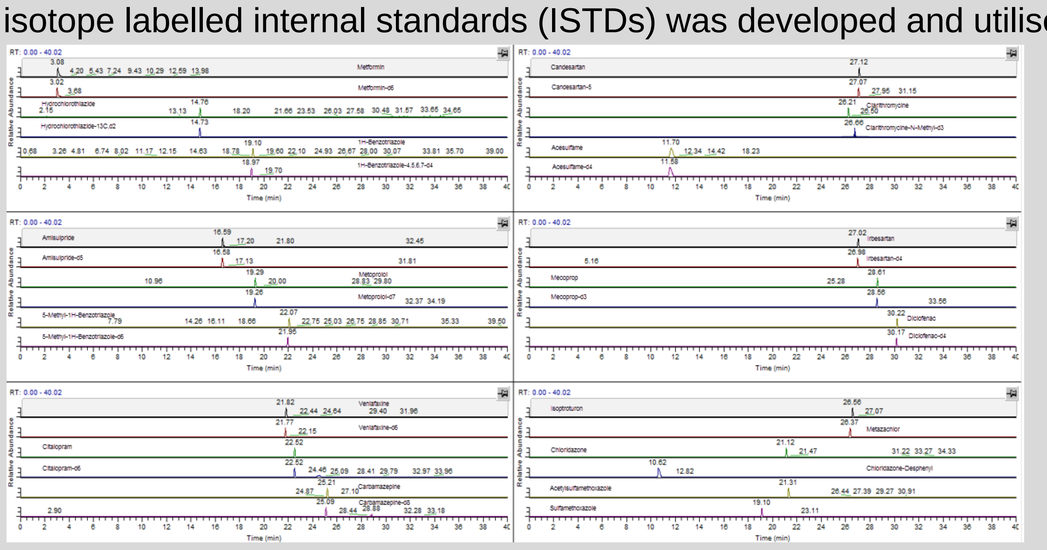

Fig.2: Chromatographic separation of the target compounds and ISTDs

The majority of the targeted compounds have been found in the surface water (see **Fig.3**). Their fate was investigated and an estimation of the degradation on every process step became possible. This revealed that almost all the compounds could have been removed, in one step of the water treatment process (see **Fig.4**).

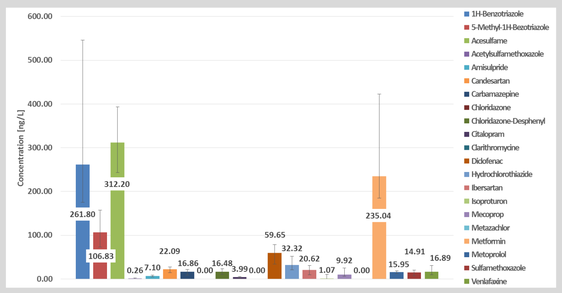

Fig.3: Average target concentrations in the Rhine

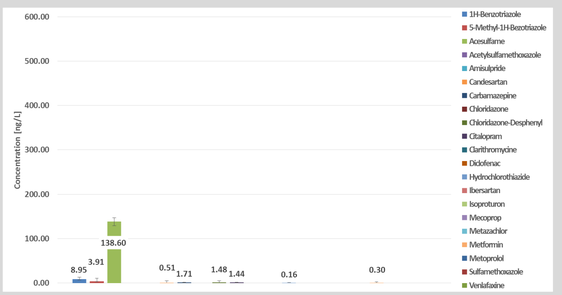

Fig.4: Average target concentrations in the drinking water

The analysed real world samples covered all the relevant matrixes such as surface, ground and drinking water. Moreover, the influences of these matrices were investigated. No significant impact was found for approximately all of the targets (see **Fig.5**). A first estimation of daily freights in the Rhine water was also conducted (see **Fig.6**). Furthermore, the five so far unknown analytes Gabapentine (79ng/L), Lamotrigine (43ng/L), Aliskiren (17ng/L), Valsartan (59ng/L) and the main metabolite of the target Metformin, Guanylurea (890ng/L) were detected and their concentrations were estimated. Moreover, their elimination in the drinking water process was confirmed. In addition to the validation data given in Tab.2, the selectivity and the robustness of the developed trace analysis method were shown.

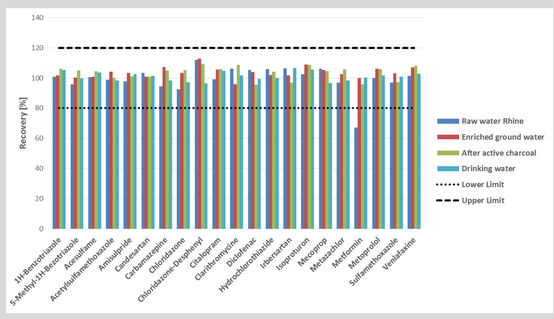

Fig.5: Influence of different matrices

Tab.2: Validation data

Parameter	Resulting values
Limit of quantification (LOQ)	5-40 ng/L
Linearity	$R^2 \geq 0.995$
Precision	Lower concentration range 4-19%
	Higher concentration range 2-7%
Accuracy	78-115% (Ø= 99%)
Estimated uncertainty of measurement	8-47%

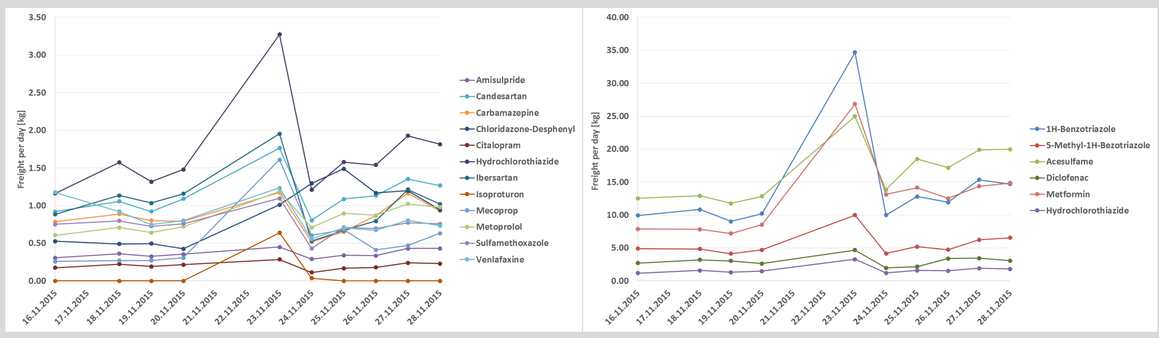

Fig.6: Estimation of the daily freights in the Rhine

Conclusion

A validated chromatographic separation within 40min, working with a polarity switch, was developed. This led to a halving of the times and costs of the water analyses. Besides, no laborious and expensive sample preparation was necessary, because of the direct large volume injection. Therefore, reproducible quantifications of the broad scope analytes, down to ng/L concentrations, were achieved. In addition it was shown that at least a polarity range of -2.38 to +12.19 (Log P) can be covered with this trace analysis method. Moreover, the necessity of isotope labelled internal standards and the difficulty of estimating a concentration without reference material were proved. Furthermore, five so far unknown compounds were identified in the screening and an estimation of their concentrations and their fate, was conducted.

REFERENCES

[1] C. J. Sinclair und A. B. A. Boxall, „Assessing the Ecotoxicity of Pesticide Transformation Products", Environ. Sci. Technol., Bd. 37, Nr. 20, S. 4617–4625, Okt. 2003.

[2] R. Pinhancos, S. Maass, und D. M. Ramanathan, „High-resolution mass spectrometry method for the detection, characterization and quantitation of pharmaceuticals in water", J. Mass. Spectrom., Bd. 46, Nr. 11, S. 1175–1181, Nov. 2011.