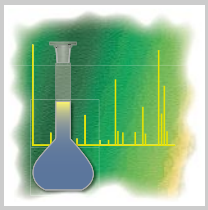
doi:10.2533/chimia.2013.86



# Highlights of Analytical Sciences in Switzerland

## Division of Analytical Sciences

A Division of the Swiss Chemical Society

## Structure Elucidation in Water Analysis – A Need?

Jean-Daniel Berset*[a], Markus Godejohann*[b], and Daniel Muff[a]

*Correspondence: Dr. J.-D. Berset[a], Tel.: +41 31 634 23 83, E-mail: jean-daniel.berset@bve.be.ch; Dr. M. Godejohann[b], Tel.: +49 721 5161 0, E-mail: Markus.Godejohann@bruker-biospin.de; [a]Water and Soil Protection Laboratory, Office of Water and Waste Management (AWA), Schermenweg 11, CH-3014 Bern; [b]Bruker Biospin GmbH, Silberstreifen 4, D-76287 Rheinstetten

**Keywords:** HPLC-time slice-SPE-NMR/TOF-MS · Non-target analysis · Structure elucidation · Wastewater effluents

Wastewater treatment plants (WWTP) are important point sources for environmental, organic micropollutants (OMPs) such as pesticides, drugs, artificial sweeteners and personal care products due to incomplete or no degradation at all. Once released, they can be found in river water, ground water and even in low ng/L levels in drinking water samples. Among the myriad of OMPs, transformation products (TPs) have attracted a broad scientific interest as evidence is increasing that OMPs are only slightly modified, frequently to more polar, hydrophilic compounds which seem to be persistent in the aquatic environment. In recent years, efforts have been made to establish the ecotoxicological risks of such complex mixtures of compounds in water samples taking into account also their environmental concentration. As it is not possible to perform an analysis of all possible compounds in a targeted approach by predefining each component and analyzing them by traditional HPLC-tandem mass spectrometry (MS/MS) using the multiple reaction monitoring technique, complementary analytical tools are essential to track such new substances.

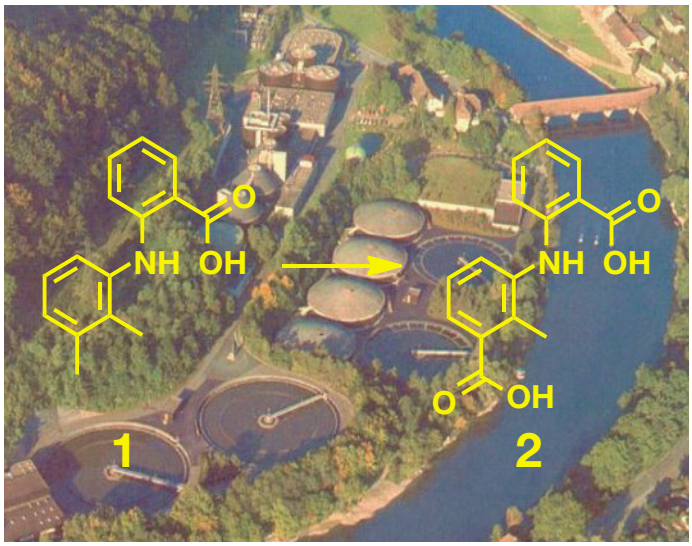
Proton detected nuclear magnetic resonance ($^1$H-NMR) represents the most powerful spectroscopic technique for structure elucidation and has been used in the past in a non-targeted approach for the investigation of environmental water samples. Its combination with HPLC is meanwhile well known and applied in natural product and pharmaceutical analysis. Due to technical improvements such as cryogenically cooled NMR probe heads and post-column solid-phase extraction (SPE) trapping, detection limits have dramatically improved to the mid- to upper ng-range of analyte injected on the column.

HPLC-time slice-SPE-NMR/TOF-MS was applied to 2-weeks WWTP effluent composite samples by injecting 4 × 12.5 µL of a concentrated extract onto a 250 × 4 mm C18 column using a shallow gradient and performing 1-minute post column SPE fractions. Many pesticides such as linuron, metazachlor, ethofumesate, metamitron and propazine could be confirmed by NMR. Among the non-targets, a TP of mefenamic acid, a drug used to treat pain, namely 3-carboxymefenamic acid, could unambiguously be identified using TOF-MS and NMR. **To summarize, the combined HPLC-SPE-NMR/TOF-MS shows great potential for the structure elucidation of unknowns, particularly of transformation products of organic micropollutants.**

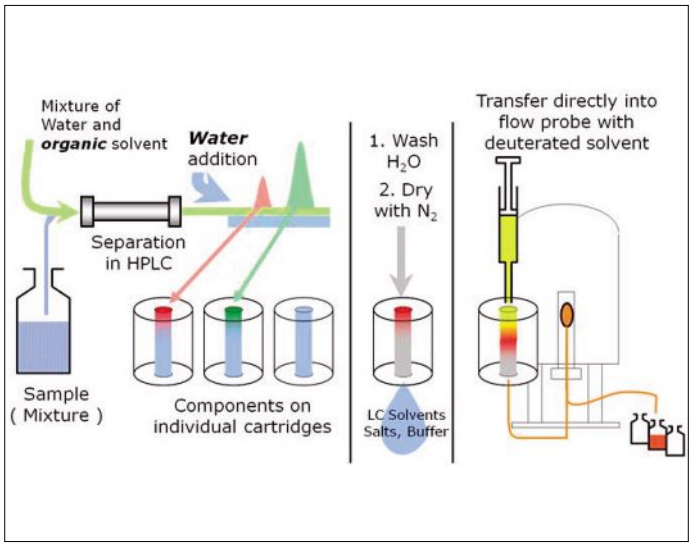
Received: November 23, 2012

**Reference**

M. Godejohann, J. D. Berset, D. Muff, *J. Chromatogr. A* **2011**, *1218*, 9202.




Identification of 3-carboxymefenamic acid (**2**), a transformation product of mefenamic acid (**1**); in the background WWTP Bern.




Basic steps of time-slice SPE-NMR (kindly provided by the Bruker company).

**Can you show us your analytical highlight?**
Please contact: Dr. Veronika R. Meyer, EMPA St.Gallen, Lerchenfeldstrasse 5, 9014 St.Gallen
Phone: +41 58 765 77 87, Fax: +41 58 765 77 62, Mail to: veronika.meyer@empa.ch