



Water analysis

Stirred, not shaken

A highly sensitive method for quantitative determination of around 100 contaminants in surface waters with and without sediment has been developed. The key element of this GC-MS/MS-based method is Stir Bar Sorptive Extraction (SBSE) using the GERSTEL Twister. The SBSE technique is the method of choice for analyte concentration, providing simple, yet powerful, water analysis based on the EU Water Framework Directive (EU-WFD) (2013/39/EU).

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In 2000, the EU Parliament and the Council released Directive (2000/60/EC) [1] that focuses on the protection and improvement of the quality of surface waters and ground water. The directive in its own words “lays down a strategy against the pollution of water. That strategy involves the identification of priority substances that pose a significant risk to, or via, the aquatic environment at (European, Ed.) Union level”. The directive was extended and amended in 2008 (2008/105/EC) [2] and in 2013 (2013/39/EU) [3]. In essence, the Water Framework Directive (WFD) of the European Union (EU) makes it mandatory for all member states to take measures to continually monitor and improve the condition and qual-

ity of water bodies in their territory: Various parameters must be monitored, including a range of identified key chemical pollutants. In the EU WFD, priority substances are listed.

EU Environmental quality standards (EQS) specify maximum allowable concentration (MAC) levels for pollutants in surface waters that must be adhered to, at least within a foreseeable future. As the directive is worded: “with the aim of achieving good surface water chemical status in relation to those substances by 22 December 2021 by means of programs of measures included in the 2015 river basin management plans...”. In the Environmental Quality Standards that apply to surface waters, there is

differentiation between annual average concentration (AA-EQS) and Maximum Allowable Concentration (MAC-EQS) levels specified for “inland surface waters”, such as rivers and lakes, or on the other hand for “other surface waters”, listed as transitional, coastal and territorial waters.

A closer look at the requirements

Commission Directive 2009/90/EC provides technical details for the chemical analysis and monitoring specified in the EU WFD. Minimum performance criteria for analytical methods are specified, such as limits of quantification (LOQs). Compound LOQs lower than 30 % of the respective Annual Average EQS (AA-EQS) values are required, for some compounds in the low- to sub-nanogram range per liter. For example, the required LOQ for benzo[a]pyrene is 0.051 ng/L. Reaching such levels requires a highly efficient analyte concentration technique, such as Stir Bar Sorptive Extraction (SBSE), combined with a highly sensitive analysis technique. In addition, the standard deviation (SD) must be lower than 50 % (k=2) of the specified EQS concentration value.

If these criteria cannot be met, due to a lack of suitable analysis methods, the EU-WFD offers some freedom: Monitoring should then be performed using the best available method that doesn't lead to excessive cost.

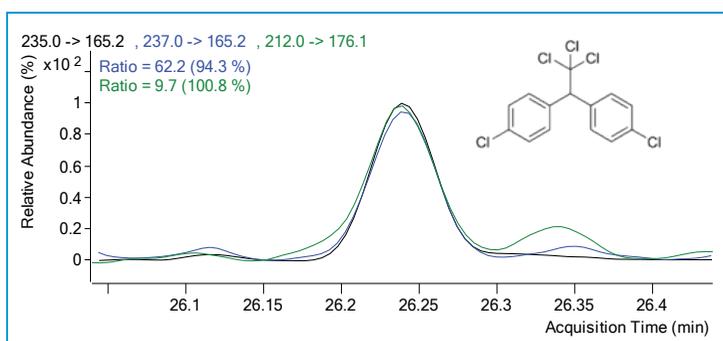
Proven water analysis technique

Stir Bar Sorptive Extraction (SBSE) with the patented GERSTEL Twister® has long been used for environmental water analysis and has performed well in round robin tests. In 2009, the Environmental protection agency of the State of Bavaria, Germany demonstrated SBSE performance in full compliance with the requirements of the German Federal drinking water regulation (TrinkwV 2001). Furthermore, SBSE was previously successfully used for the determination of priority pollutants in surface waters following the EU WFD 2000/60/EU.

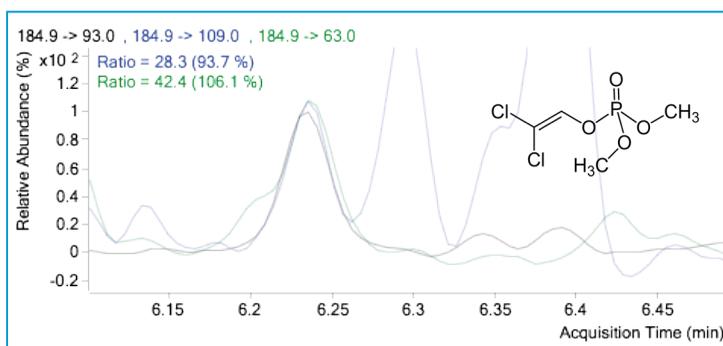
As a result of a significant investment of time and resources, the SBSE method has recently been optimized for highly sensitive determination of the GC compatible priority pollutants listed in EU Directive 2013/39/EU – including particle adsorbed pollutants - using one comprehensive method.



GERSTEL MPS-SBSE-TDU-GC-MS/MS system used for the determination of around 100 contaminants including priority pollutants as specified in the EU Water Framework Directive (EU WFD).



Chromatogram of p,p'-DDT at a concentration of 0.068 ng/L spiked in river water.



Chromatogram of dichlorvos at a concentration of 0.12 ng/L, spiked in river water.

A detailed look at SBSE

The extraction medium used in SBSE is the patented GERSTEL Twister®. It is a glass coated magnetic stir bar mounted with a substantial sorbent layer. The sorbents used are either polydimethylsiloxane (PDMS) or an ethyleneglycol-silicone polymer (EG-Silicone Twister).

The extraction principle of SBSE, like that of liquid-liquid extraction (LLE), relies on partitioning, reaching

Table 1: Limits of quantitation, determined according to DIN 32645, reflecting the results for precision and accuracy. In case the water samples were free from - or had only very little - contamination with individual analytes, the limits of quantitation were determined in the matrix surface water.

Analyte	Limit of Quantitation [ng/L]	Analyte	Limit of Quantitation [ng/L]	Analyte	Limit of Quantitation [ng/L]
Acenaphthene	1.00	alpha-Endosulfan	0.070	PCB 81	0.039
Acenaphthylene	0.10	beta-Endosulfan	0.059	PCB 105	0.043
Aclonifen	0.56	Endosulfan sulfate	0.052	PCB 114	0.036
Alachlor	0.42	Endrin	0.043	PCB 118	0.012
Aldrin	0.066	Endrin ketone	0.052	PCB 123	0.037
Ametryn	0.069	Ethofumesat	0.073	PCB 126	0.050
Anthracene	0.061	Fenitrothion	0.024	PCB 156	0.046
Atrazine	0.18	Fenpropimorph	0.13	PCB 157	0.047
Benz[a]anthracene	0.076	Fluoranthene	1.00	PCB 167	0.044
Benzo[a]pyrene	0.033	Fluorene	0.45	PCB 169	0.054
Benzo[b]fluoranthene	0.078	Heptachlor	0.052	PCB 189	0.054
Benzo[g,h,i]perylene	0.049	Heptachlorepoide	0.052	Pendimethalin	0.094
Benzo[k]fluoranthene	0.081	Hexachlorobenzene	0.10	Pentachlorobenzene	0.075
Bifenox	0.47	Hexachlorobutadiene	0.043	Pentachlorophenol	3.00
Biphenyl	9.00	alpha-Hexachlorocyclohexane	0.052	Phenanthrene	2.50
Bis(2-ethylhexyl)phthalate (DEHP)	134	beta-Hexachlorocyclohexane	0.13	Picolinafen	0.26
Chlordane, cis	0.052	gamma-Hexachlorocyclohexane	0.052	Prometon	0.18
Chlordane, trans	0.026	delta-Hexachlorocyclohexane	0.052	Prometryn	0.13
Chlorfenvinphos	0.084	Indeno[1,2,3-cd]pyrene	0.044	Propazine	0.057
Chlorpyrifos-Ethyl	0.024	Isodrin	0.16	Propiconazol	0.14
Chrysene	0.027	Methoxychlor	0.083	Propyzamide	0.35
Cybutryn (Irgarol 1051)	0.030	Metolachlor	0.064	Pyrene	0.45
Cypermethrin (Isomerenmix)	0.12	Naphthalene	5.00	Quinoxifen	0.087
p,p'-DDD	0.020	Nonylphenol	8.80	Simazine	1.90
p,p'-DDE	0.017	Octylphenol	0.46	Terbutryn	0.10
o,p'-DDT	0.052	Oxadiazon	0.082	Triallate	0.084
p,p'-DDT	0.067	PBDE 28	0.018	Tributyl phosphate	9.70
Dibenz[a,h]anthracene	0.073	PBDE 47	0.015	1,2,3-Trichlorobenzene	0.95
Dichlobenil	2.10	PBDE 99	0.050	1,2,4-Trichlorobenzene	1.20
Dichlorvos	0.073	PBDE 100	0.011	1,3,5-Trichlorobenzene	0.18
Dicofol	0.15	PBDE 153	0.032	Triclosan	1.40
Dieldrin	0.034	PBDE 154	0.020	Trifluralin	0.19
Diffufenican	0.16	PBDE 183	0.13	Tris(2-chloroisopropyl)-phosphate (TCPP)	29.00
2,6-Di-tert-butyl-4-methylphenol	5.90	PCB 77	0.041		

equilibrium between the aqueous sample and the sorbent phase. In the work described here, PDMS Twisters were used. Analyte extraction and concentration takes place while the Twister stirs the sample. Subsequently, the Twister is removed from the sample, quickly dried, placed in a glass liner for thermal desorption, and the liner placed in a sealed sample tray position on the MultiPurpose Sampler (MPS). The MPS performs fully automated processing of large sample batches in combination with a thermal desorber. Following thermal desorption, analytes are focused in a GC inlet (GERSTEL CIS 4) and subsequently transferred to the GC column in split or splitless mode using programmable heating. This approach ensures that extracted analytes can be transferred up to 100 % to the column for extreme sensitivity. The PDMS Twister is well suited for non-polar to medium polarity compounds while the EG-Silicone Twister is mainly used for polar compounds that form hydrogen bonds as proton donor, for example phenols, alcohols and organic acids.

Simple and efficient water analysis

In this work, SBSE, using the GERSTEL Twister, was our method of choice for the GC compatible compounds

listed in the EU Water Framework Directive (WFD). In addition to reaching the prescribed LOQs, we also wanted to perform quantitative determination of compounds adsorbed on particulate matter, as demanded by the EU WFD, including polyaromatic hydrocarbons (PAHs). The overall analysis requires a special approach: At first, we performed classical SBSE on individual 100 mL samples, which is a large enough volume to generate meaningful results. After adding an internal standard, we let a Twister stir the sample for five hours to extract free organic compounds. The Twister was then removed, an organic modifier was added to the sample along with a second Twister, and the sample extracted at elevated temperature overnight. Using this approach, compounds adsorbed on particulate matter were successfully released and extracted. The two Twisters were transferred to a TDU glass liner and simultaneously desorbed in the Thermal Desorption Unit (TDU) using a temperature program (90 – 300 °C). The analytes were focused in the Cooled Injection System (CIS 4) at – 40 °C. The CIS is a PTV type Universal GC inlet, which can be heated very rapidly in order to release analytes to the GC column, in our case a HP 5ms Ultra Inert (30 m x 0.25 mm x 0.25 µm) from Agilent Technologies. Following separation, the analytes were deter-



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Analytes are extracted and concentrated in the sorbent phase while the Twister stirs the sample. The stir bar is then removed, dabbed dry, and placed in a TDU liner, which is placed in an individually sealed tray position in the GERSTEL MPS. Thermal Desorption of the concentrated analytes is performed in the Thermal Desorption Unit (TDU), the process is fully automated using the MPS. After being focused in the GERSTEL Cooled Injection System (CIS), analytes are transferred to the GC column where they are separated and finally determined using a mass spectrometer.

mined using a Triple Quadrupol MS (Agilent Technologies 7010) in Multi-Reaction Monitoring (MRM) Mode.

Successful determination of water contaminants

The newly developed SBSE-GC-MS/MS method presented here is both efficient and highly sensitive. We were able to determine the GC compatible compounds listed in the EU WFD at the levels specified – or even well below – with three exceptions: Cypermethrin, heptachlor, and heptachlorepoxyde. Those three are also notoriously hard to determine at the required levels down to sub-pg/L using conventional techniques.

In the following, we list a few examples of required limits of quantitation for surface water following the EU guidelines. For dichlorvos: 0.18 ng/L; using SBSE, we reached 0.073 ng/L. For benzo(a)pyrene: 0.051 ng/L;

using SBSE, we reached 0.033 ng/L. For pentachlorobenzene: LOQ of 2.1 ng/L; with SBSE, we lowered it to 0.075 ng/L (see table 1). Comparable results were achieved for around 100 other contaminants relevant for surface water analysis.

Relative standard deviations (RSDs) near the respective limits of quantitation were between two and ten percent for the vast majority of compounds with a median of 6.9 percent. Trueness was between 90 and 110 percent in most cases. The extractability and quantifiability of particle adsorbed analytes was tested and confirmed using a certified reference sediment (WEPAL SETOC 745). Certified analysis results were available for PAHs and a few chlorinated compounds.

Assessing SBSE

SBSE using the GERSTEL Twister is simple to perform and highly efficient, resulting in high sensitivity, not only in the case described here, in which we successfully determined priority pollutants listed in the EU WFD. The high sensitivity is mainly due to the large volume of Twister sorbent phase, in our case 63 μ L, which guarantees a high concentration factor when doing trace analysis. When the Twister is thermally desorbed, the analytes extracted from the sample are transferred quantitatively to the GC, whereas when performing liquid extraction and injection, only a small aliquot is injected. SBSE performed on a 100 mL water sample coupled with thermal desorption and a highly sensitive triple quadrupole mass spectrometer provides extremely low limits of detection, reaching the sub-ng/L range. A further bonus when using Twister technology: The entire method requires only a very small amount of solvent. And since many solvents are toxic, hazardous and harmful to the environment, a reduction in the amount used would seem particularly meaningful and fitting in order to reach environmentally sustainable solutions for chemical analysis.

References

- [1] DIRECTIVE 2000/60/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 October 2000 establishing a framework for Community action in the field of water policy
- [2] Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council
- [3] DIRECTIVE 2013/39/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy.