Check for updates

Proficiency test of non-target screening with gas chromatography mass spectrometry to confirm a detected contamination of raw and drinking water

Michael Petri, Jia-Qian Jiang and Matthias Maier

ABSTRACT

Much of the water supply industry has implemented online monitoring and warning systems for chemical or biological contaminations. When a contamination is detected, further investigations are necessary to confirm or to cancel the initial alarm. The proficiency of a non-target screening approach with solid phase extraction and GCMS in full-scan mode was examined. A selection of pesticides and industry chemicals was used for proficiency testing in extracts of raw and drinking water from Lake Constance. All total ion chromatograms (TIC) of extracted water samples showed a significant chemical background that have an adverse effect on compound identification. The TIC was evaluated with a two-dimensional search algorithm considering mass spectra similarity and retention index for identification, which was used an additional identification criteria to increase the confidence in identification. At a spiking level of 0.50 μg/l, up to 70% of the pollutants were unambiguously assignable. The sample pre-treatment was kept as simple as possible to reduce analysing time. A solid-phase extraction with extraction disks at flow rates up to 100 ml/min without any precedent filtration step reduces the sample pre-treatment time for a 1 l-sample below one hour. The recovery rates for most of the examined pollutants were above 60%.

Key words | contamination warning system, gas chromatography mass spectrometry, non-target screening, qualitative analysis, retention index, solid-phase extraction

Michael Petri (corresponding author)
Zweckverband Bodensee-Wasserversorgung,
Betriebs- und Forschungslabor,
Süßenmühle 1,
D-88662 Überlingen,
Germany
E-mail: *michael.petri@zvbwv.de*

Jia-Qian Jiang
School of the Built and Natural Environment,
Glasgow Caledonian University,
Cowcaddens Road,
Glasgow G4 0BA,
UK
E-mail: *JiaQian.Jiang@gcu.ac.uk*

Matthias Maier
Faculty of Engineering and Physical Science (C5),
University of Surrey,
Guildford, Surrey GU2 7XH,
UK
E-mail: *matthias.maier@stadtwerke-karlsruhe.de*

INTRODUCTION

In the last decade many drinking water suppliers have improved steadily the physical protection for intake areas of raw water, treatment plants, distribution pipes and reservoirs and they implemented early warning systems (EWS) or contamination warning systems (CWS) with online-monitoring systems for raw and drinking water. The state-of-art technologies of EWS and CWS for source and drinking water were reviewed in several publications (Gullick *et al.* 2003; Hasan *et al.* 2004; States *et al.* 2004; USEPA 2005). Online monitoring parameters like temperature, pH, conductivity, UV-absorbance and turbidity provide a robust, fast and continuous monitoring, but they could not detect contaminations in low concentrations. Because of their lack of sensitivity they can provide only little information on accidental or intentional contaminations, which can limit their use in a EWS or CWS (States *et al.* 2003; Calles *et al.* 2005). Dynamic biomonitoring systems survey the changes in the behaviour of living organism like fish, water fleas or mussels and detect contaminations by their toxic effect on the organisms. Biomonitoring systems can detect that there is something in the water which affects the organism, but they cannot identify and quantify the toxic contaminant. Therefore, any detection of a possible contamination should be confirmed to prevent false-positive results that could lead to unnecessary measures and increasing costs. It is needless to say that

doi: 10.2166/ws.2010.191

Downloaded from http://iwaponline.com/ws/article-pdf/10/5/806/416302/806.pdf
by guest

false-negative or false-positive results will result in a loss of confidence in drinking water suppliers and their EWS or CWS. That means, if a possible contamination is detected in the water, further investigations with sophisticated analytical methods in a laboratory are necessary to confirm or to cancel the initial alarm (States *et al.* 2003).

GC–MS with solid-phase extraction as sample pre-treatment is a very common and accepted technique used in most laboratories for monitoring of priority pollutants that are of public concern or legally regulated (Brauch 1993; Hübschmann 2009). The usage of GC–MS for non-target screening needs the full-scan mode to detect unexpected contaminants in the sample without any kind of selection (Ferretti *et al.* 2007). The identification of unknown compounds is possible with standardized spectral libraries, such as NIST/EPA/NIH Mass Spectral Library. However, in the full-scan mode all compounds eluting from the column are visible in a total ion chromatogram (TIC), such as interfering compounds from the sample pre-treatment and from the chromatography system, but also matrix components naturally occurring in the sample. All these interfering and co-eluting compounds increase the chemical background in a TIC, so that the identification and confirmation of unexpected compounds is getting much more difficult (Boyd *et al.* 2008). To minimize the possibility of false-negative and false positive results great attention should be focused on the procedure for recognition and identification of suspicious peaks within the matrix peaks.

The objective of this study was to examine the proficiency of non-target screening with GCMS in full-scan mode, focused on qualitative detection of a contamination in surface water and drinking water from Lake Constance. A set of different organic compounds were selected from an enormous number of diverse possibilities based upon usage, accessibility or potential toxicity to prove the unambiguity of detection and identification within the chemical background of the sample matrix.

METHODS

Chemicals and materials

A customized n-alkane stock solution (C10–C32, in hexane) with each 23 compound at 50 μg/ml each, a phenols stock solution (8,270 acid calibration check mix in methylene chloride) with each 6 compounds at 2,000 μg/ml and a organophosphorus pesticides stock solution (Canada drinking water organophosphorus pesticides in acetonitrile) were obtained from Restek (Bad Homburg, Germany). A triazine stock solution (in acetone) with each 11 compounds at 100 μg/ml were purchased from Ultra Scientific (North Kingstown, USA). A organochlorine pesticides stock solution (EPA TCLP pesticides mix in methanol) with each 5 compounds at 1,000 μg/ml and a base/neutral compound mixture (EPA 8270A base neutrals mix in methanol) with each 10 compounds at 2,000 μg/ml were purchased from Supleco (Bellefonte, USA). Acetone in ultra-residue-analysed-quality was from Mallinckrodt J.T. Baker (Griesheim, Germany) and methanol in picograde-quality was from LGC-Promochem (Wesel, Germany). Ultra-pure water was made with Milipore Elix-3 and Milli-Q Gradient A10 (Molsheim, Germany). The working standard solutions were obtained by dilution to 10 μg/ml with acetone. All solutions were stored at 4–8°C.

Bakerbond Speedisk extraction disks H_2O-philic DVB were purchased from Mallinckrodt J.T. Baker (Griesheim, Germany). Due to their special construction Bakerbond Speedisk extraction disk were useful for the extraction of aqueous samples with a high flow rate without any precedent filtration step. Before sample loading the SPE extraction disks were conditioned with 2 × 5 ml acetone, 2 × 5 ml methanol and 50 ml ultra-pure water. The solid-phase extraction was done with the 6-port extraction station from Mallinckrodt J.T. Baker (Griesheim, Germany).

Sample preparation

Raw water and drinking water samples were collected in 1,000 ml glass bottles and extracted within 2 days. The water samples were stored 4–8°C until extraction. 1,000 ml of an unfiltered sample were sucked through the conditioned extraction disks by vacuum at a flow rate of 100 ml/min and dried for 30 min under vacuum. The elution was performed with three successive portions of 2 ml acetone and a soak time of 5 min between each solvent step. The combined extracts of each sample were concentrated to 1 ml at 40°C with a gentle stream of nitrogen and

Downloaded from http://iwaponline.com/ws/article-pdf/10/5/806/416302/806.pdf
by guest

transferred into GC vials without any further clean-up or internal standardization.

GCMS analysis

The analysis were carried out using a Clarus 500 GCMS system (Perkin-Elmer, Rodgau-Jügesheim, Germany) equipped with a PSS injector and a low resolution quadrupole mass spectrometer. The column was a Rxi-5ms (30 m × 0.25 mm I.D., 0.25 μm film thickness) from Restek (Bad Homburg, Germany). Helium (99.9995%, Linde, Stuttgart, Germany) was used as carrier gas with a flow rate of 1 ml/min in the constant flow mode. 15 μl of the sample were injected in the injector with solvent purge for 0.05 min at 56°C. After solvent purge the injector was heated up to 320°C splitless in 0.75 min. The oven temperature program started with 40°C (held for 5 min), increased with 30°C/min to 120°C (held for 1 min), increased with 3°C/min to 180°C (held for 5 min) and increased with 3.5°C/min to 300°C (held for 5 min). The capillary column was coupled to the mass spectrometer directly into the ion source and was heated to 250°C in the transfer section. The quadrupole mass spectrometer was operated by electron impact ionization with a voltage of 70 eV. The temperature of the ion source was 250°C. After a solvent delay of 8 min, the analyses were performed in full-scan mode from m/z 40 to m/z 450 and a scan time of 0.35 s.

To calculate the retention index an acetone solution of C10 – C32 n-alkanes was analysed as external standard once a fortnight and after a GC maintenance (change of column or column shortage). van den Dool & Kratz (1963) used the retention times (RT) of the n-alkanes to calculate and standardize the retention index (RI) for linear temperature-programming conditions. The software MassFinder 4.2 from Dr. Hochmuth Scientific Consulting (Hamburg, Germany) was used for calculating the retention indices for all GCMS scans and for peak-compound assignment after employing our own specific spectra library with interfering compounds and potentially harmful pollutants like pesticides and industry chemicals. A two-dimensional search algorithm considering mass spectra similarity (library match threshold ≥ 60%) and retention index (max. RI deviation ± 10) was used for identification and assignment. Identification of unknown compounds was attempted by comparison of the experimental mass spectrum with a commercial mass spectra library (NIST/EPA/NIH Mass Spectral Library, version 2.0d).

RESULTS AND DISCUSSION

Characterization of total ion chromatograms

Up to 100 different peaks were detectable in total ion chromatograms (TIC, full-scan mode from m/z 40 to m/z 450) of raw water and drinking water samples from Lake Constance (Figure 1). Several compounds could be assigned to impurities from the sample pre-treatment or GCMS-system (Spiteller & Spiteller 1973; Hübschmann 2009):

- various phthalates from plasticizers widely used in many plastics, like SPE cartridges, solvent bottle tops and tubes,
- various cyclic siloxanes from septa and column bleeding,
- stabilizers in acetone, like 2,6-di-tert-butyl-4-methyl-phenol (18.12 min, RI: 1,502) and 2,4-di-tert-butylphenol (18, 20 min, RI: 1,505).

Other impurities like benzothiazol (11.47 min, RI: 1,234), diphenyl ether (15.27 min, RI: 1,404) or benzophenone (22.04 min, RI: 1,624) have had an unclear origin and were not present in all blanks or samples. Peak area and peak height of all impurities were not constant and varied between each solvent lot and analysis series.

All chromatograms of raw and drinking water samples looked very similar and showed a chemical background in the first 30 min of a TIC with decreasing intensity (Figure 1). Due to the mass spectra and the proposals from library search we suspect different long chained and branched hydrocarbons, long chained aldehydes, ketones, carboxylic acids and esters, that have their origin in the natural organic matter (NOM) of the lake water or from decomposition of high molecular humic substances in the injector or on the column during the chromatographic separation. For the interpretation of mass spectra of unknown compounds in natural samples a major problem is, that it is never for sure that the mass spectrum is from one compound or from a co-elution with two or more compounds. Clean-up procedures with gel permeations chromatography, silica gel or florisil columns can reduce

Downloaded from http://iwaponline.com/ws/article-pdf/10/5/806/416302/806.pdf
by guest

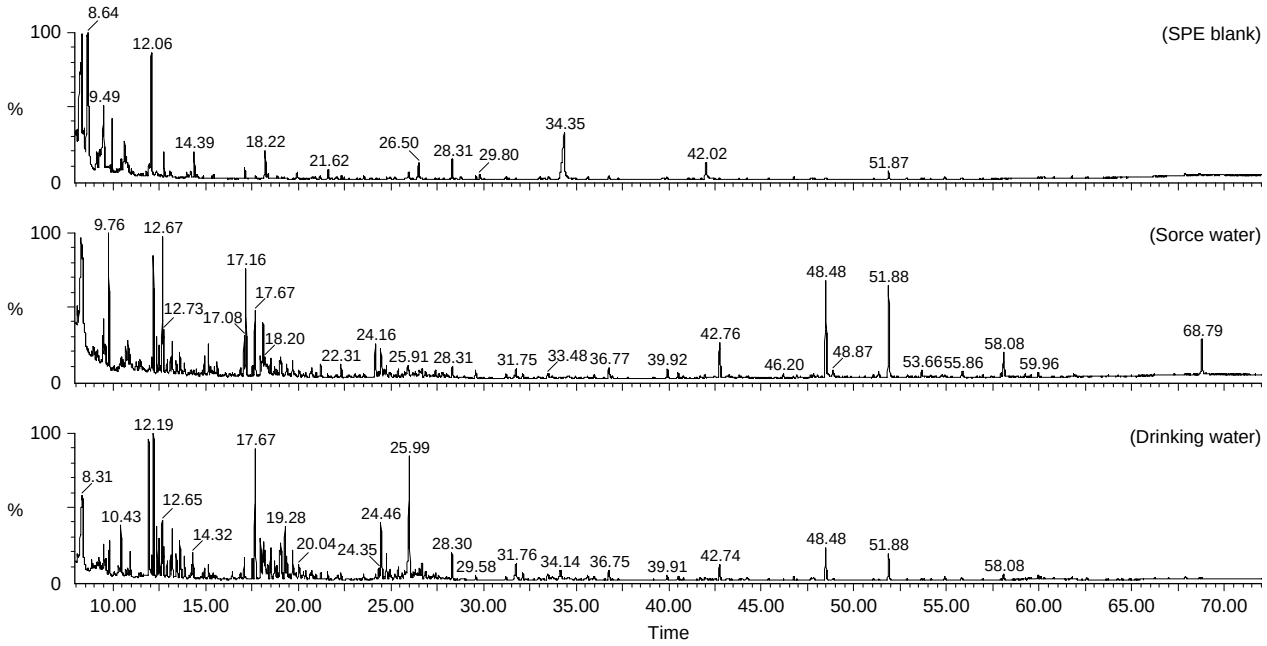

Figure 1 | Total ion chromatograms of a solid-phase extraction blank (SPE blank), an extract of raw water from Lake Constance (source water) and an extract of drinking water from Lake Constance (drinking water).

the chemical background by removing co-extracted NOM from the crude extract (Boyd *et al.* 2008; Leeuwen van & Boer de 2008; Hübschmann, 2009). But any additional clean-up is time consuming and can probably discriminate contaminants that should be detected with the non-target screening.

Qualitative detection with non-target screening

In spite of the complex chemical background of raw water and drinking water samples, it should be investigated if pesticides or industry chemicals are detectable with GCMS in the full-scan mode even in low concentrations. We choose a set of 41 different pesticides and industry chemicals that cover a wide pH-range from acidic to base and that could behave very different during sample pre-treatment and GCMS-analysis: 11 triazine pesticides, 9 organophosphorus pesticides, 5 chlorinated pesticides, 6 phenols, 7 aromatic amines, benzyl alcohol, 2-methyl-naphthalene and dibenzofuran (Table 1). Mixtures of this potentially harmful compounds were added to Lake Constance raw and drinking water extracts in concentration of 0.05, 0.10, 0.25 and 0.50 μg/l. The GCMS system showed a very poor performance for azinphos-methyl, dimethoate, malathion, metoxychlor, 4-nitroaniline and temephos because no peaks of this compounds were detectable in spiked raw water and drinking water extracts.

All TICs were evaluated for retention index and mass spectra similarity with MassFinder-software without any precedent background correction or subtraction. The assignment of a peak to a pollutant was done by a two-dimensional search algorithm considering the retention index and the mass spectra similarity. All pollutants of this investigation were analysed as external standards in acetone with the GCMS-method described above. The retention index and mass spectra were included into the MassFinder specific spectra library.

At a spiking level of 0.05 μg/l only 2 pollutants (simetryn and dibenzofuran) were unambiguously assigned in extracts of raw water and 21 pollutants were not assigned by the software due to the chemical background (Table 1). 18 pollutants were not detectable at all in spiked raw water extracts at this concentration level. In drinking water extracts 4 spiked pollutants (secbumeton, simetryn, ametryn and 2-methylnaphthalene) were assignable. 18 pollutants co-eluted with matrix compounds could not be assigned by mass spectra similarity whereas 19 spiked pollutants were not detectable at all. With an increasing spiking level the

Downloaded from http://iwaponline.com/ws/article-pdf/10/5/806/416302/806.pdf
by guest

Table 1 | Detectability and peak-compound assignment of pesticides and industry chemicals in with GCMS in full scan mode without any background correction or subtraction. Compounds were spiked to extracts of raw water and drinking water samples from Lake Constance

			Raw water				Drinking water			
Compound	**RT (min)**	**RI**	**0.05 (μg/l)**	**0.10 (μg/l)**	**0.25 (μg/l)**	**0.50 (μg/l)**	**0.05 (μg/l)**	**0.10 (μg/l)**	**0.25 (μg/l)**	**0.50 (μg/l)**
Triazines										
Atraton	25.34	1,724	u	u	u	+	u	u	+	+
Simazine	25.67	1,734	u	u	u	+	u	u	u	+
Prometon	25.77	1,737	u	u	u	+	u	u	+	+
Atrazine	25.99	1,744	u	u	+	+	u	u	u	+
Propazine	26.23	1,751	u	u	+	+	u	u	+	+
Terbutylazine	26.82	1,769	u	+	+	+	u	u	u	+
Secbumeton	28.15	1,809	u	u	u	+	+	+	+	+
Simetryn	30.99	1,888	+	+	+	+	+	+	+	+
Ametryn	31.41	1,899	u	+	+	+	+	+	+	+
Prometryn	31.75	1,907	u	u	u	+	u	u	u	+
Terbutryn	32.73	1,928	u	u	+	+	u	+	+	+
Cl-pesticides										
Lindan	26.05	1,746	u	u	+	+	u	u	u	u
Heptachlor	30.72	1,880	−	−	u	+	−	−	+	+
Heptachlorepoxide	37.05	2,026	u	u	+	+	u	+	+	+
Endrin	42.98	2,191	−	−	u	+	−	u	+	+
Methoxychlor*	−	−	−	−	−	−	−	−	−	−
P-pesticides										
Phorate	23.96	1,683	u	+	+	+	u	+	+	+
Terbufos	26.64	1,764	u	u	+	+	u	u	u	+
Diazinon	27.38	1,786	u	+	+	+	u	+	+	+
Chlorpyrofos	34.15	1,959	−	u	+	+	−	u	u	+
Parathion	34.82	1,974	−	−	u	+	−	−	+	+
Dimethoat*	−	−	−	−	−	−	−	−	−	−
Malathion*	−	−	−	−	−	−	−	−	−	−
Azinphos-methyl*	−	−	−	−	−	−	−	−	−	−
Temephos*	−	−	−	−	−	−	−	−	−	−
Phenols										
Phenol	8.12	980	u	u	u	u	u	+	+	+
2-nitrophenol	9.67	1,143	−	−	−	u	−	−	−	u
2,4-dichlorophenol	10.16	1,176	u	u	+	+	u	u	u	u
4-chloro-3-methylphenol	12.06	1,288	−	u	+	+	−	+	+	+
2,4,6-trichlorophenol	13.46	1,351	u	u	+	+	u	u	+	+
Pentachlorophenol	25.05	1,738	−	u	u	+	−	u	u	u
Aromatic amines										
Aniline	8.16	981	−	−	u	u	−	−	u	u
o-toluidine	9.08	1,066	u	u	u	u	u	u	u	u
4-chloroaniline	10.91	1,205	−	u	+	+	−	+	+	+

Downloaded from http://iwaponline.com/ws/article-pdf/10/5/806/416302/806.pdf
by guest

Table 1 | (*continued*)

			Raw water				Drinking water			
Compound	**RT (min)**	**RI**	**0.05 (μg/l)**	**0.10 (μg/l)**	**0.25 (μg/l)**	**0.50 (μg/l)**	**0.05 (μg/l)**	**0.10 (μg/l)**	**0.25 (μg/l)**	**0.50 (μg/l)**
2-nitroaniline	15.34	1,407	−	−	u	+	−	−	+	+
3-nitroaniline	17.56	1,483	u	u	u	u	−	−	u	u
2-naphtylamine	19.55	1,547	−	−	+	+	−	−	u	+
4-nitroaniline*	−	−	−	−	−	−	−	−	−	−
Others										
Benzyl alcohol	8.83	1,042	−	u	u	u	−	u	u	u
2-methylnaphthalene	12.71	1,299	u	u	+	+	+	+	+	+
Dibenzofuran	18.48	1,514	+	+	+	+	u	u	+	+

*Compounds were not detectable in GCMS even at a concentration level of 0.50 μg/l.

+, peak detected and compound identified by retention index and mass spectra similarity; u, interference due to chemical background or co-elution prevented unambiguous identification and compound assignment by mass spectra similarity; −, no peak detected.

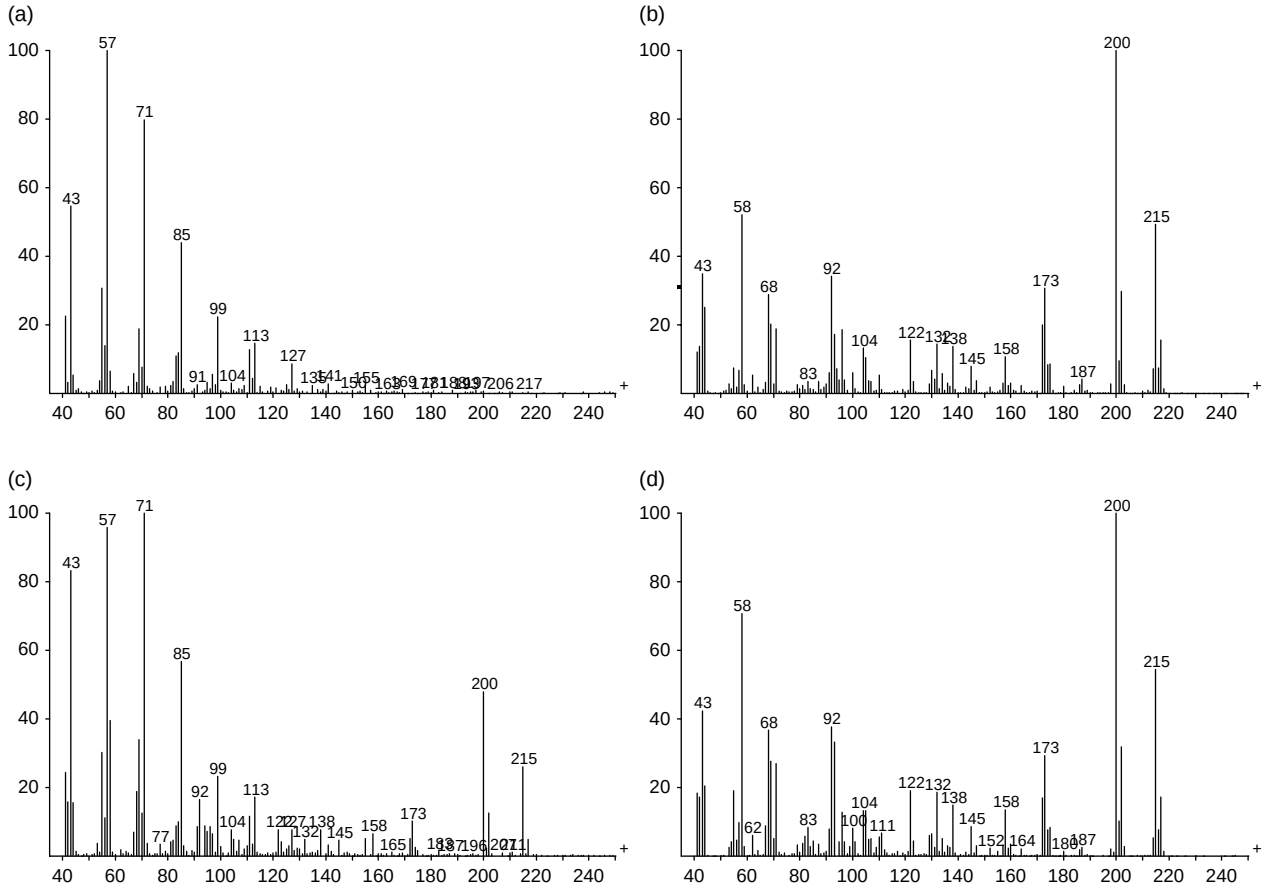

Figure 2 | Mass spectra of raw water extracts at a retention index of 1,744 (RT: 25.99 min) (unspiked and spiked with atrazine). (a) mass spectrum of chemical underground in unspiked raw water extract (b) mass spectrum of atrazine as external standard in acetone (c) mass spectrum of raw water extract spiked with 0.1 μg/l atrazine (d) mass spectrum of raw water extract spiked with 0.5 μg/l atrazine.

Downloaded from http://iwaponline.com/ws/article-pdf/10/5/806/416302/806.pdf
by guest

Table 2 | Recoveries and RSD ($n = 3$) for solid phase extraction with Bakerbond Speedisk extraction disks of 1,000 ml samples spiked with pesticides and industry chemicals. Compounds were spiked to raw water of Lake Constance at a level of 0.50 μg/l

Compound	Qualifier ion	Mean recovery (%)	RSD (%)	Compound	Qualifier ion	Mean recovery (%)	RSD (%)
Triazines				*Phenols*			
Atraton	196	81.0	6.4	Phenol	94	87.1	9.2
Simazine	201	86.6	8.3	2-nitrophenol	139	–	–
Prometon	210	80.8	7.8	2,4-dichlorophenol	162	87.5	7.1
Atrazine	200	79.8	6.0	4-chloro-3-methylphenol	107	79.8	7.3
Propazine	214	81.2	7.9	2,4,6-trichlorophenol	196	65.7	6.3
Terbutylazine	214	81.2	7.9	pentachlorophenol	266	57.6	14.9
Secbumeton	196	82.7	4.5	*Aromatic amines*			
Simetryn	213	106.4	6.5	Aniline	93	61.2	4.1
Ametryn	227	94.8	7.3	o-toluidine	106	72.0	3.3
Prometryn	184	82.7	5.7	4-chloroaniline	127	79.5	3.2
Terbutryn	185	86.1	5.7	2-nitroaniline	138	83.8	3.4
Cl-pesticides				3-nitroaniline	138	67.0	2.6
Lindan	181	71.4	16.7	2-naphtylamine	143	28.1	6.7
Heptachlor	100	65.4	5.6	*Others*			
Heptachlorepoxide	81	84.2	3.8	benzyl alcohol	79	82.1	2.3
Endrin	67	85.0	4.9	2-methylnaphtalin	142	81.8	14.1
P-pesticides				dibenzofuran	168	101.8	2.7
Phorate	75	66.1	9.3				
Terbufos	57	102	11.8				
Diazinon	137	78.3	4.6				
Chlorpyrofos	97	95.8	6.5				
Parathion	109	89.4	4.3				

number of unambiguously assignable pollutants increased from below 10% to over 60%. At a spiking level of 0.50 μg/l 29 pollutants were unambiguously assigned by retention index and mass spectra in fortified raw water extracts and 27 pollutants in fortified drinking water extracts. Due to the chemical background 6 pollutants remained unassigned in spiked raw water extracts and 8 pollutants in spiked drink water extracts (Table 1).

For o-toluidine and benzyl alcohol a co-elution with matrix compounds prevented an assignment by mass spectra similarity for all spiking levels in extracts of raw water and drinking water from Lake Constance. The same was for lindan and 2,4-dichlorophenol in all spiked drinking water extracts and for phenol in all spiked raw water extracts.

Figure 2 demonstrate the influence of the chemical background on the assignment of a possible pollutant in a full-scan chromatogram. Figure 2 shows a co-elution of a natural hydrocarbon with atrazine, so that an unambiguously assignment of atrazine based only on mass spectra similarity is very difficult at a concentration level of 0.10 μg/l or below. The ion intensities of the co-eluted hydrocarbon (m/z 43, 57, 71, 85) are much higher than the ion intensities of atrazine (m/z 173, 200, 215) and makes an identification by mass spectrum similarity impossible. A simple visual comparison between the mass spectrum of the fortified raw water extract at retention index 1,744 (Figure 2c) and the library mass spectrum of atrazine (Figure 2b) indicate a possible contamination with atrazine (RI: 1,744, indication ions: m/z 173, 200, 215). This means a possible

Downloaded from http://iwaponline.com/ws/article-pdf/10/5/806/416302/806.pdf
by guest

contaminant with a known RI can easily be positioned or assigned in a TIC by its RI. In a second step characteristic ions of the contaminant in its mass spectrum can support the confirmation even in a very complex chemical background. All pollutants marked with "u" in Table 2 could be confirmed in the second step by comparing of characteristic ions. Therefore, the usage of the retention index RI as an additional identification criteria increase the confidence of positive identification or exclusion of a contaminant (Babushok *et al.* 2007).

Recovery of high flow solid-phase extraction

A recovery experiment were done by spiking three 1,000 ml samples of raw water from Lake Constance with the mixtures of organic pollutants listed in Table 2 at a level of 0.5 μg/l prior to solid-phase extraction with a flow rate of 100 ml/min. The extracts were analysed with GCMS in full-scan mode. The calculation of the recovery rates was based on extraction of the qualifier ion for each pollutant (Table 2) from the TIC to minimize interferences by co-eluting matrix.

A summary of the recovery values and the relative standard deviation (RSD; $n = 3$) for spiked pollutants are shown in Table 2 and demonstrate the general suitability of the solid-phase extraction with extraction disks at a high flow rate of 100 ml/min. The recovery rates for 32 pollutants were above 60% except for pentachlorophenol (57.6%), for 2-naphylamine (28.1%) and for 2-nitrophenol which was not detectable in the recovery extracts. The relative standard deviation varied between 2.3 and 16.7%.

CONCLUSION

Any detection of a natural, accidental and intentional contamination in raw water sources or drinking water with EWS or CWS needs an analytical confirmation procedure, that is able to determine a wide range of contaminants in a rapid response with sufficient sensitivity and reliability. A rapid confirmation of a contamination is rather important for the decision making in an emergency action plan of water supply industries. Therefore, the analytical confirmation should not only be focused on toxicological relevant contaminants but also on the analysis of unexpected compounds. GCMS with a high flow solid-phase extraction is a reliable tool for the rapid non-target screening as a confirmation procedure. In a time range of about 4 hours a sample can be extracted, analysed and evaluated.

The chemical background from the sample matrix by natural organic compounds could make a peak-compound assignment very difficult and challenging. A two-dimensional search algorithm with retention index RI and mass spectra similarity could enhance the reliability of peak-compound assignment and support the compound identification, especially when the peak intensity of a co-eluting matrix compound is higher than that of a pollutant. However, if a peak could not be assigned or identified by mass spectra libraries, the identification is still a challenge, especially when there is co-elution with sample matrix.

REFERENCES

Babushok, V. I., Linstrom, P. J., Reed, J. J., Zenkevich, I. G., Brown, R. L., Mallard, W. G. & Stein, S. E. 2007 Development of a database of gas chromatographic retention properties of organic compounds. *J. Chromatogr. A* **1157**, 414–421.

Brauch, H. J. 1993 Gas chromatography for determination of pesticides in aquatic systems – analytical basis. *Acta hydrochim. Hydrobiol.* **21**, 84–88.

Boyd, R. K., Basic, C. & Bethem, R. A. 2008 *Trace Quantitative Analysis by Mass Spectrometry*. Wiley, Chichester, England.

Calles, J., Gottler, R., Evans, M. & Syage, J. 2005 Early warning surveillance of drinking water by photoionization/mass spectrometry. *J. Am. Water Works Assoc.* **97**, 62–73.

Ferretti, E., Lucentini, L., Veschetti, E., Bonadonna, L., Stammati, A., Turco, L. & Ottaviani, M. 2007 Screening and identification of unknown contaminants in water destined to human consumption: a case study. *Microchem. J.* **85**, 57–64.

Gullick, R. W., Grayman, W. M., Deininger, R. A. & Males, R. M. 2003 Design of early warning systems for source waters. *J. Am. Water Works Assoc.* **95**, 58–72.

Hasan, J., States, S. & Deininger, R. 2004 Safeguarding the security of public water supplies using early warning systems: a brief review. *J. Contemp. Water Res. Educ.* **129**, 27–33.

Hübschmann, H.-J. 2009 *Handbook of GC/MS: Fundamentals and Application*, 2nd edition. Wiley-VCH Verlag, Weinheim, Germany.

Downloaded from http://iwaponline.com/ws/article-pdf/10/5/806/416302/806.pdf
by guest

Leeuwen van, S. P. J. & Boer de, J. 2008 Advances in the gas chromatographic determination of persistent organic pollutants in the aquatic environment. *J. Chromatogr. A.* **1186**, 161–182.

Spiteller, M. & Spiteller, G. 1973 *Massenspektrensammlung von Lösungsmitteln, Verunreinigungen, Säulenbelegmaterialien und einfachen aliphatischen Verbindungen*. Springer Verlag, Wien Austria.

States, S., Scheurig, M., Kuchta, J., Newberry, J. & Casson, L. 2003 Utility-based analytical methods to ensure public water supply security. *J. Am. Water Works Assoc.* **95**, 103–115.

States, S., Newberry, J., Wichtermann, J., Kuchta, J., Scheuring, M. & Casson, L. 2004 Rapid analytical techniques for drinking water security investigations. *J. Am. Water Works Assoc.* **96**, 52–64.

USEPA 2005 *Technologies and techniques for early warning systems to monitor and evaluate drinking water quality: a state-of-art review*. US Environmental Protection Agency EPA-600/R-05/156.

van den Dool, H. & Kratz, P. D. 1963 A generalization of the retention index system including linear programmed gas liquid partition chromatography. *J. Chromatogr.* **11**, 463–471.

Downloaded from http://iwaponline.com/ws/article-pdf/10/5/806/416302/806.pdf
by guest