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## Drinking Water Analysis

# Efficient monitoring of disinfection byproducts in chlorinated drinking water

Water is chlorinated to eliminate potentially harmful bacteria. In the process, unwanted disinfection byproducts (DBPs) are formed such as halogenated acetic acids (HAAs), which could themselves be harmful, albeit probably to a lesser degree. The US Environmental Protection Agency (EPA) mandates monitoring of HAAs in water using US EPA method 552.3. The procedure in the method is very labor intensive, limiting the number of samples analyzed per day to about 8 or 9 for a seasoned laboratory technician. In this article a system is described, which enables much more efficient monitoring of HAAs. In addition, a method is described for monitoring how polymer materials react with disinfection chemicals.

*By Guido Deussing*

A GC/MS system with Multi-Purpose Sampler (MPS) and Thermal Desorption Unit (TDU), both from GERSTEL. Similar systems are used by the Analytical Team at the Veolia Research Center in Paris to test polymer based pipes for potential leaching of chemical compounds.



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The use of chlorinated disinfectants in the production of safe drinking water is aimed at killing or disabling pathogens such as harmful bacteria in the water. The disinfectants of course also react with other dissolved or suspended matter, forming unwanted disinfection byproducts (DBPs) in the process. Concentration levels of some of the approximately 600 DBPs identified to date should be monitored closely since they are suspected of being harmful to human health.

## A blessing and a minor curse: Disinfectants

The list of the most unwanted DBPs includes the usual suspects such as trihalomethanes (THMs), with chloroform serving as probably the most prominent representative of this class of compounds.

Another set of DBPs, long in the sights of the US Environmental Protection Agency (EPA), are halogenated acetic acids aka haloacetic acids (HAAs): monochloroacetic acid; dichloroacetic acid; trichloroacetic acid; bromoacetic acid; and dibromoacetic acid. The EPA classifies these compounds and compound classes as „probable carcinogens“ [1] and drinking water has to be monitored for residues. The maximum concentration level (MCL) for total THM (TTHM) in drinking water in the US is 0.08 mg/L [2], the same as in the European Union (EU). In Germany, the MCL is set to

0.05 mg/L [3]. The EPA specifies a total of 0.06 mg/L of the previously mentioned five haloacetic acids (HAA 5) as the maximum concentration limit.

According to Dalel Benali, Senior Scientist for chromatography and water analysis expert working for the lead-

ing French water supplier Veolia in Paris, the European Union (EU) has been given a recommendation to limit the acceptable total concentration of HAAs in drinking water to 0.08 mg/L. The health risk posed by DBPs may be extremely limited compared with the risk posed by waterborne microbial contaminants [4], says Mr. Benanou, but due to their suspected carcinogenic properties, the routine monitoring of THMs and HAAs in drinking water seems a reasonable and prudent precaution. Equally, swimming pool water should be monitored, since urine of adults and children alike has shown markedly increased HAA levels after swimming in chlorinated water, Mrs. Benali adds [5].

## More efficiency and productivity through miniaturization and automation

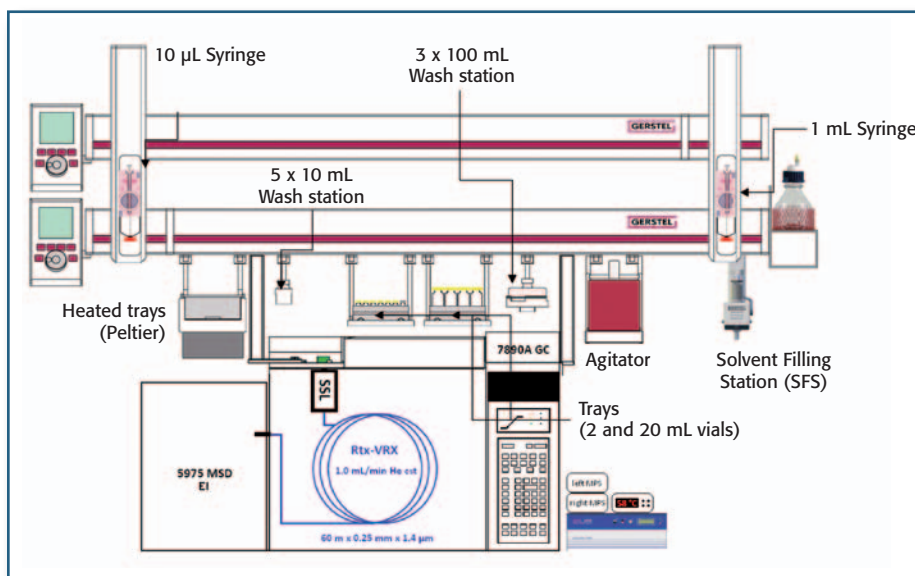
In the point of view of David Benanou and Dalel Benali, who have both been involved in routine monitoring of drinking water for many years, the determination of HAAs in water needs to be automated. The US EPA method 552.3 specifies the determination of HAAs in water by liquid-liquid extraction using MTBE, followed by derivatization (methylation) and GC-ECD [6]. According to Mr. Benanou, this process is too complex and requires too much organic solvent. Even a seasoned technician can only perform 8-9 analyses per day based on manual sample preparation. By miniaturizing and automating the method using a dual rail version of the GERSTEL MultiPurpose Sampler (MPS) for the extraction and derivatization steps, and by using GC/MS instead of GC-ECD, Mr. Benanou and his scientist colleagues succeeded in dramatically improving both efficiency and throughput for the determination of THM and HAA [7].

Key factors in improving the performance are the analyte concentration and derivatization steps. HAAs are present at very low levels, are by nature polar, and are not easily separated by GC making a derivatization step necessary. The standard 552.3 method specifies the following steps: Adjust the sample pH to 0.5. Extract it with MTBE and derivatize with acidified methanol for two hours at ele-

### GERSTEL Twister

The Twister® is used for Stir Bar Sorptive Extraction (SBSE). The Twister is available in different versions, sorbent volumes, and two different sorbent phases: The polydimethylsiloxane (PDMS) Twister is well suited for extraction and concentration of non-polar to medium polarity compounds from aqueous phase; the ethylene glycol (EG) Silicone Twister is mainly useful for more polar species, especially those capable of forming hydrogen bonds as electron pair donors such as phenols, alcohols, and acids. In order to increase the overall analysis sensitivity, several quite simple approaches can be taken: Several Twisters can be desorbed, either sequentially (sequential desorption) or simultaneously and the combined analytes subsequently focused and introduced to the GC column for a single GC/MS analysis run. Using the GERSTEL Twister® accessory, multiple Twisters can be used simultaneously to extract a single sample. For example, one Twister can be placed in the headspace of the vial while the other is immersed in and stirs the liquid phase. These Twisters can be the same or different sorbent types. For more information: [www.gerstel.com](http://www.gerstel.com)

Graphic rendering of the GC/MS system and MultiPurpose Sampler (MPS) used by Veolia in Paris for automated determination of halogenated acetic acids in water. Key, labor intensive sample preparation steps specified in the EPA method were successfully transferred to the autosampler and sample preparation robot, including liquid-liquid extraction and the required analyte derivatization. The Dual Rail or Dual Head versions of the MPS enable the use of syringes with different volumes without time-consuming syringe changes.



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ated temperature. Separate the phases by adding an aqueous sodium sulfate solution and then neutralize by adding sodium bicarbonate ( $\text{NaHCO}_3$ ) in solution. A portion of the MTBE phase is finally injected into the GC.

## Chlorination furthers the extraction of additives from polymer pipes

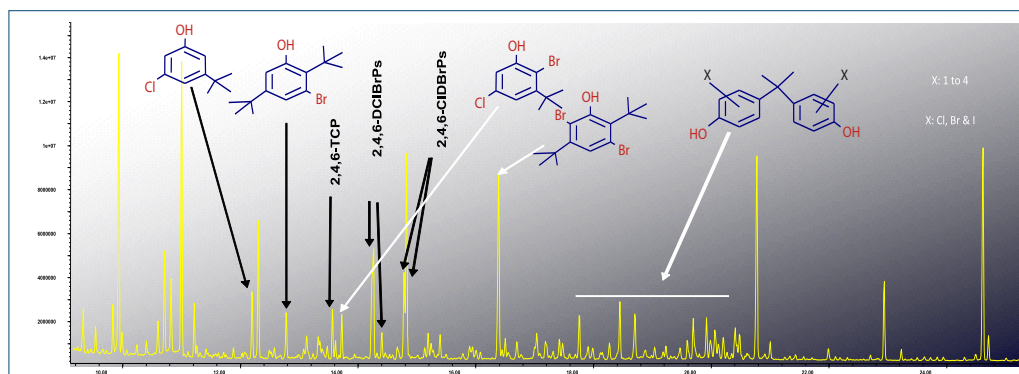
When using an autosampler, in this case a GERSTEL MultiPurposeSampler (MPS), only a fraction of the time is needed for sample processing compared with the manual method. In the case of the MPS, the PrepAhead function even provides overlapping, i.e. parallel sample processing and GC analysis, helping to further accelerate matters and improve throughput. In practice, the system can analyze 32 samples per day following the EPA 552.3 method, requiring only 1 hour of technician time for sample loading, preparation and further processing. Another benefit is that much less solvent is consumed saving cost and improving the overall work environment in the lab. Method performance is equally convincing, the limit of determination is 1 ppb; the method was validated for all determined HAAs showing good linearity up to 50 ppb and a median repeatability (RSD) of 3.2% ( $n=3$  at 1 and 40 ppb) [7].

In practical use, says Mrs Emilie Cocardon, senior sci-

entist at the Veolia Research Center and member of the Analytical Team, the chlorinated disinfectants react with more than just the organic and inorganic matter present in the water: The exposed surfaces of the entire supply system are made up of numerous different polymer materials used in pipes, connectors, gaskets, sieves, filters, or membranes, from which additives can leach into the chlorinated water and/or react with the disinfectant. The experts from Veolia especially focus their attention on additives such as plasticizers and stabilizers, which are used to optimize polymers for their intended use: "It is normally very difficult to predict how a polymer and the additives contained in it react to a chlorinated disinfectant", Mr. Benanou admits, "You really need empirical data". In order to determine DBPs formed as a reaction between disinfectants and polymer materials, scientists developed a special method for Veolia based on the Stir Bar Sorptive Extraction (SBSE) technique using the GERSTEL Twister combined with thermal desorption-GC/MS analysis.

## Twister: The ideal Tool for water analysis

SBSE is a powerful extraction and concentration technique, well suited for ultra-trace analysis and determination of organic compounds in aqueous samples. The SBSE technique is very similar to the solid phase micro-extraction



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SBSE of chlorinated water was used to determine the presence of compounds leached from an experimental polymer pipe material in contact with chlorinated water. Three main compound classes were found: Halogenated phenols such as 2,4,6-trichlorophenol, 2,4,6-dichlorobromophenol, and 2,4,6-Dibromochlorophenol; halogenated alkyl-phenols; as well as various isomers of halogenated bisphenol A. This pipe was rejected.

(SPME) technique. Both techniques enable the extraction of analytes into a polymer sorption phase directly in contact with the sample. The SPME sorption phase is a thin layer applied to a fiber. SBSE uses a glass coated magnetic stir bar known as the GERSTEL Twister, coated with a significantly larger volume of sorbent phase, generally resulting in much higher analyte recovery. Handling the Twister is simple; it is designed for routine use, as Emilie Cocardon and David Benanou explain: “The analyte extraction takes place while the Twister actively stirs the sample, a large number of samples can be extracted

## Twister Tap or ARISTOT

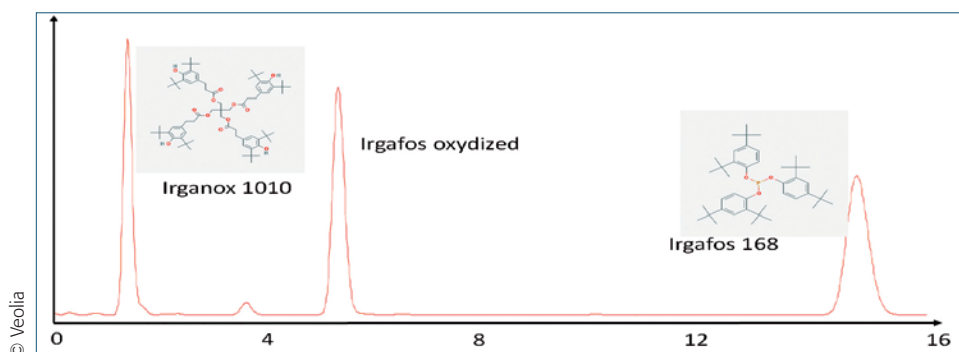
Sometimes drinking water intermittently smells strange, unsettling residents in their home or workplace. When someone finally turns up to take a sample for analysis there may not be a noticeable smell, making trouble shooting and analysis hard to perform. A technology patented by Veolia is available in the form of an adapter for direct mounting onto water faucets that enables time weighted average (TWA) sampling. The Twister Tap adapter holds six GERSTEL Twisters which, extract odor causing compounds and other contaminants over a period of up to several days for subsequent thermal desorption and GC/MS analysis.



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interest in the chromatogram.

Using this method, additives, including stabilizers have been determined in polymer tubing using mineral water as a test solution. Among the DBPs determined in various tested materials are 2,4,6-trichlorophenol, which readily undergoes microbial transformation to the intensely moldy smelling 2,4,6-trichloroanisol (TCA) [8]. Veolia scientists



Chromatogram of a mineral water showing leached chemical compounds from tested polymer pipe material. The water was kept for a specified period of time inside the pipe and then injected directly into the LC/MS for determination. The eluting compounds were identified as the polymer additives Irganox, Irgafos and their byproducts.

in parallel using multi-position stir plates. The Twisters are removed from the samples, dabbed dry on lint-free cloth, transferred to sealed glass tubes and placed in the sample tray for automated thermal desorption using the GERSTEL Thermal Desorption Unit (TDU) or alternatively the Thermal Desorption System (TDS). The Twisters are individually heated in a flow of inert gas and analytes are thermally desorbed and quantitatively transferred to the GC/MS system for determination.”

## Experimental setup facilitates material testing

To determine the identity and concentration levels of compounds that could potentially leach out of polymer pipes tested for use in water supply systems, Veolia scientists have developed an experimental setup, which is beautiful in its simplicity: A piece of the water pipe to be analyzed is cut off and sealed at one end. The sealed piece of polymer pipe is placed in the upright position on a magnetic stir plate and an aqueous solution containing the disinfectant is added for a specified period of time. The solution is stirred and extracted using a Twister, and any DBPs formed and extracted are subsequently determined by TD-GC/MS. The Twister is used as described above, without the use of toxic solvents, which could dilute the extract and mask peaks of

in Paris are routinely using SBSE to test polymer materials before they are accepted for use in the immense drinking water supply systems of Veolia, just in France. The main beneficiary in the end is the consumer, who can be sure that the water that comes out of the tap in his or her home is clean, safe to drink, and free from unpleasant odors.

## Literature

- [1] Controlling Disinfection By-Products and Microbial Contaminants in Drinking Water, US EPA, [www.epa.gov/sites/production/files/2015-09/documents/dwstandards2012.pdf](http://www.epa.gov/sites/production/files/2015-09/documents/dwstandards2012.pdf)
- [2] National Primary Drinking Water Regulations, [www.epa.gov/your-drinking-water/table-regulated-drinking-water-contaminants](http://www.epa.gov/your-drinking-water/table-regulated-drinking-water-contaminants)
- [3] <https://en.wikipedia.org/wiki/Trihalomethane>
- [4] Disinfections and Disinfection By-Products, [www.who.int/water\\_sanitation\\_health/dwq/S04.pdf](http://www.who.int/water_sanitation_health/dwq/S04.pdf) and [www.who.int/water\\_sanitation\\_health/dwq/fulltext.pdf](http://www.who.int/water_sanitation_health/dwq/fulltext.pdf)
- [5] M. J. Cardador, M. Gallego, Haloacetic Acids in Swimming Pools: Swimmer and Worker Exposure. *Environ. Sci. Technol.* 45 (2011) 5783-5790
- [6] Determination of haloacetic acids and dalapon in drinking water by liquid-liquid micro extraction, derivatization, and gas chromatography with electron capture detection, <https://nepis.epa.gov/Exe/ZyPDF.cgi/901V0400.PDF?Dockey=901V0400.PDF>
- [7] Poster Presentation, DBP 2014: Efficient Monitoring of Regulated By-Products using automated, miniaturized, green techniques. David Benanou and Dalel Benali-Raclot, Veolia Environnement, R&D Centre for Water, Maisons Laffitte (Paris), France
- [8] Poster Presentation, DBP 2014: Characterization of emerging Disinfection By-Products from Polymeric Materials by in situ Stir Bar Sorptive Extraction-GC/MS. David Benanou and Dalel Benali-Raclot, Veolia Environnement, R&D Centre for Water, Maisons Laffitte (Paris), France