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GC Application Note

Determination of iodoform in drinking water by PAL SPME Arrow and GC/MS

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Peter Egli, Beat Schilling, BGB Analytik AG, Adliswil, Switzerland
Guenter Boehm, CTC Analytics AG, Zwingen, Switzerland

Short summary

With PAL SPME Arrow detection limits for iodoform in tap water of 15 ng/L (S/N > 3) have been achieved in immersion mode and 2 ng/L in headspace mode (S/N > 3), with DVB as sorption phase. At 50 ng/L a standard deviation of 3.8% (n=5) was achieved. This is sufficiently low to reliably detect iodoform well below the odor threshold of 30 ng/L.

Introduction

Chlorine is frequently used to disinfect drinking water. Despite the benefits of this procedure there are also a number of important disadvantages to it. The process of chlorination leads to disinfection byproducts (DBPs), such as chloroform and other trihalomethanes. These compounds are formed from the interaction of aqueous free chlorine with natural organic matter present in the raw water. Many of these DBPs are suspected carcinogens and are regulated by the U.S. Environmental Protection Agency (EPA) as well as other agencies worldwide.
Iodinated trihalomethanes (ITHMs) can also be formed as a consequence of this process when iodide (i.e., from natural sources, seawater, or brines) is present. ITHMs are usually associated with characteristic pharmaceutical or medicinal odors and tastes in drinking water. The taste and odor threshold concentrations (ref.2, 3) of iodoform of 0.02 - 5 µg/L, is significantly lower than that of chloroform or bromoform, 100 and 300 µg/L, respectively. Odors and tastes in drinking water are a matter of concern for water suppliers and a frequent source of complaints from consumers. The EEC Drinking Water Directive (European Council Directive 80/778 EE), related to the quality of water intended for human consumption, includes taste and odor parameters. Hence water suppliers have to monitor iodoform levels quantitatively.

Analytics

Older methods for the analysis of chlorination and iodination DBPs are based on solvent extraction. These methods are time- and labor-intensive and require the use of hazardous organic solvents. Solid-phase microextraction (SPME) presents a simple, fast, and sensitive method of sample preparation that is also solvent-free. Currently there is no published standard analytical method for iodinated DBPs like iodoform.
Here we describe the quantitative analysis of iodoform in tap water by PAL SPME Arrow extraction combined with GC/MS. Immersion as well as headspace SPME has been performed on two different fiber types. The PAL SPME Arrow is a new technology for microextraction, combining trace level sensitivity with high mechanical robustness. The PAL SPME Arrow has an outer diameter of 1.1 or 1.5mm, resulting in large sorption phase surfaces and volumes (fig.1). The arrow-shaped tip allows smooth penetration of vial and injector septa. In contrast to traditional SPME fibers, the Arrow design fully protects the sorptive material, minimizing adverse influences and loss of analytes during transfer processes.

		Sorption phase surface	Sorption phase volume
a		62.8 mm^2	11.8 µL
b		44.0 mm^2	3.8 µL
c		9.4 mm^2	0.6 µL

Fig. 1: Dimension of a PAL SPME Arrow 1.5 mm (a), 1.1 mm (b) and SPME Fiber (c) in comparison

Experimental

Chemicals

Water:	Sartorius arium ultrapure with UV lamp (water according to ISO 3696)
Tap water:	Communal water supply from Adliswil, Switzerland
Iodoform, CHI_3:	puriss. p.a. Fluka CAS# 75-47-8
Toluol:	puriss Fluka 89681
Standard stock solution:	50 mg CHI_3 in 50 mL toluol
Standard working solution:	10 µL stock in 10 mL toluol (equivalent to 1 ng), solutions have to be kept at 4°C in the dark, working solutions were prepared freshly every day

Procedure

Sampling SPME Arrow:	PAL SPME Arrow Tool with PDMS 20 mm x 100 µm, or DVB 20 mm x 120 µm fibers, 1.1 mm diameter
Sampling SPME:	PAL SPME Tool with DVB 10 mm x 65 µm Supleco fiber (PN 57311)
Immersion extraction:	19 mL water in 20 mL headspace vials
Incubation temp:	25°C
Agitation:	PAL Heatex Stirrer Module @ 1600 rpm (200 cycloidal loops)
Extraction time:	60 min
Desorption:	200°C ; 2min
Headspace extarction:	10mL water in 20 mL headspace vials with 4 g Na_2SO_4
Pre conditioning:	0:30 min
Pre incubation time:	1:00 min
Incubation temp:	70°C
Agitation:	PAL Agitator Module @ 250 rpm
Needle penetration:	22 mm
Fiber penetration :	30 mm
Extraction time:	60 min
Desorption:	200°C ; 2 min
GC:	Varian 3400
MS:	Varian Saturn Ion Trap
Column:	30 m x 0.25 mm; 0.25 µm BGB-5
Carrier gas:	Hydrogen 2.0 psi
Temperature program:	50°C for 1min, then 10°C/min -> 280°C
Injector:	200°C
Mass range:	100 - 300 m/z

Results

Selection of sorption phase material

In the literature PDMS as well as DVB have been described as sorption phase materials. Based on the results depicted in Fig 2 and Fig 3 DVB has been selected as sorption phase.

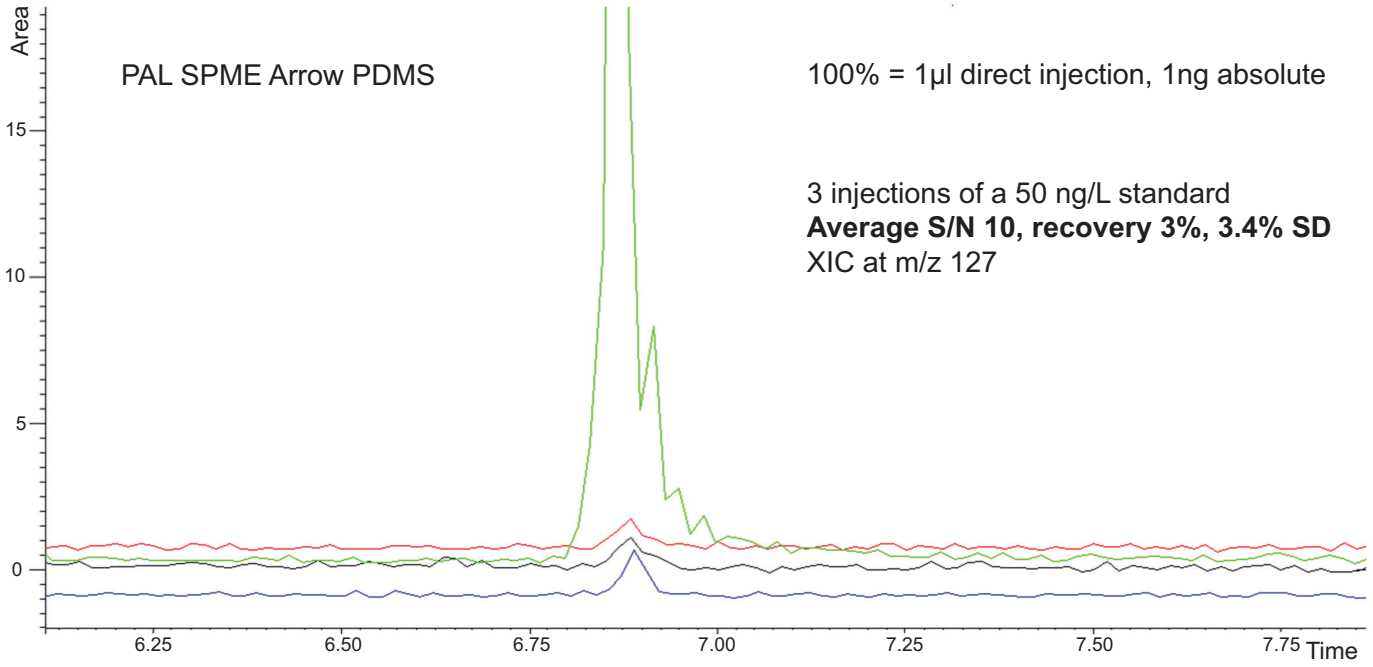

Fig. 2 : Immersion extraction of water spiked with 50 ng/L, immersion extracted with PDMS SPME Arrow

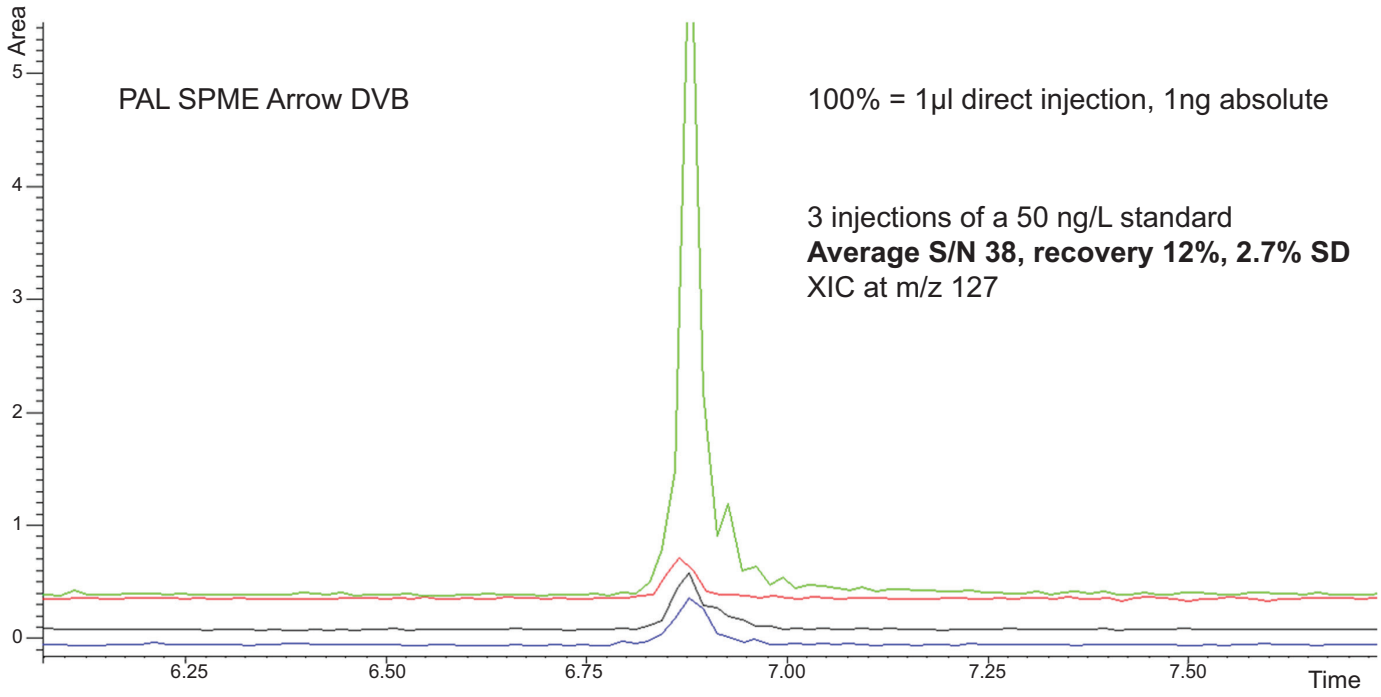

Fig. 3: Immersion extraction of water spiked with 50 ng/L, immersion extracted with DVB SPME Arrow

Optimization of extraction parameters

Based on the results depicted in fig. 4 the extraction time for immersion was set to 60 min.

With desorption temperatures between 160°C and 220°C little decomposition of iodoform has been observed (fig. 5,). A desorption temperature of 200°C has been selected for all experiments. Frazey et al. (ref. 1) report noticeable decomposition above 160°C.

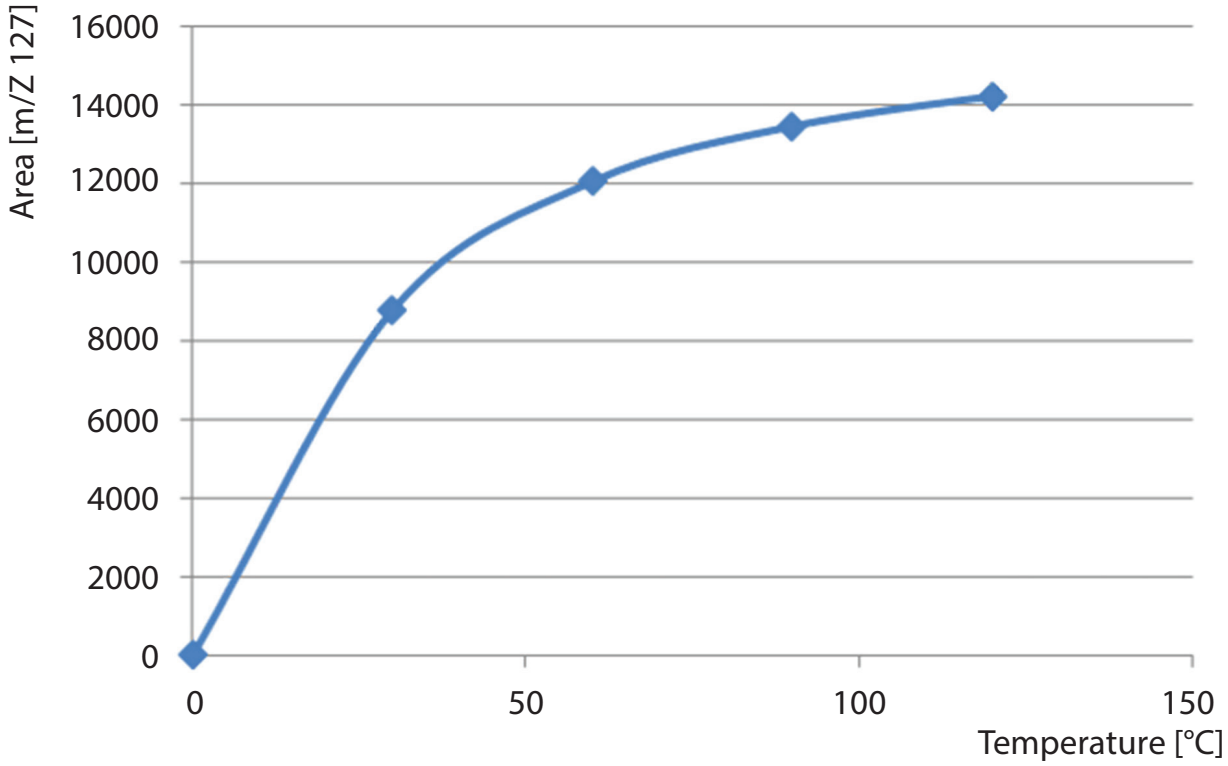

Fig. 4 : Immersion extraction time course for a 100 µm DVB SPME Arrow : water spiked @ 50 ng/L

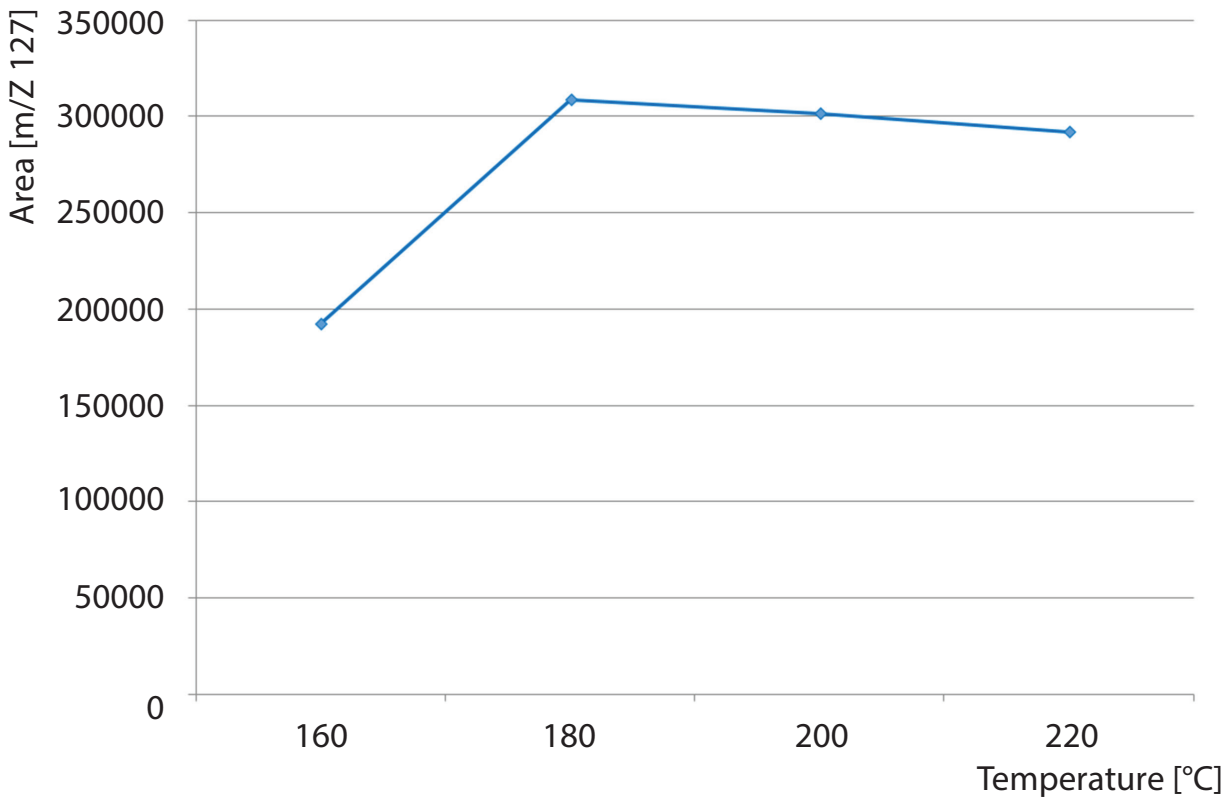

Fig. 5: Optimization of desorption temperature for a 100 µm DVB SPME Arrow

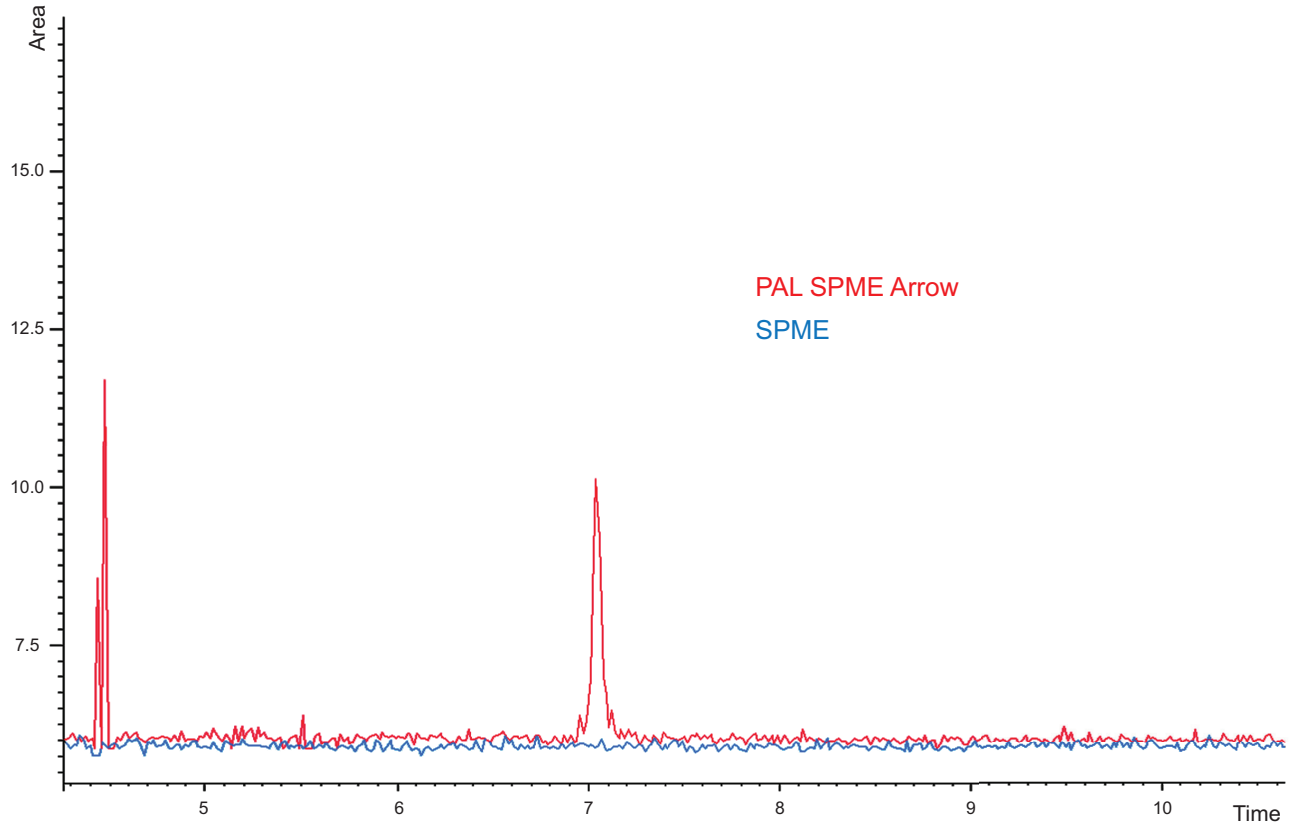

Fig. 6 : Comparison SPME Arrow DVB /SPME DVB fibers for the immersion extraction of water spiked @ 50ng/L after 60 min

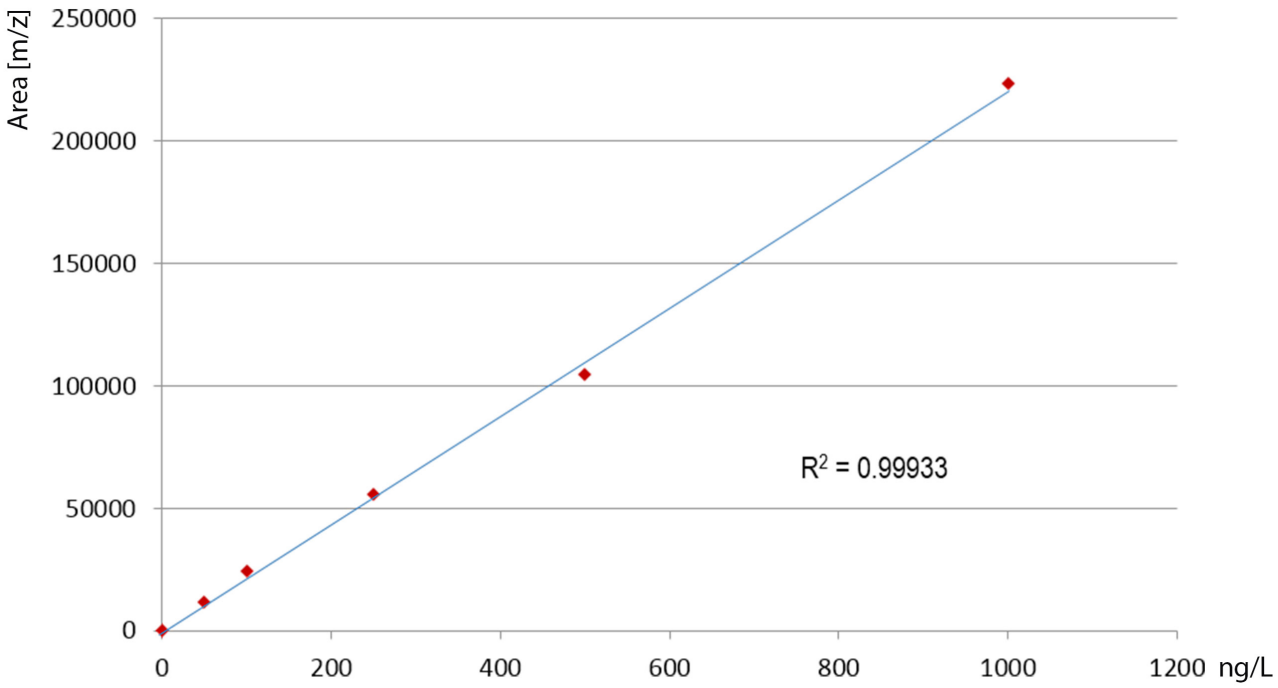

Fig. 7: Calibration curve of iodoform in water 50-1000 ng/L , immersion extraction

Immersion vs. Headspace Extraction

In the literature both immersion (e.g. stir bar extraction) and headspace extraction have been applied for iodoform. Based on the results described in fig. 6 headspace extraction has been chosen. Interestingly the difference between headspace and immersion extraction is much less pronounced for the SPME fiber.
As shown in fig. 8 and 9 SPME Arrow shows a 26x higher recovery in headspace mode than the corresponding SPME fiber.

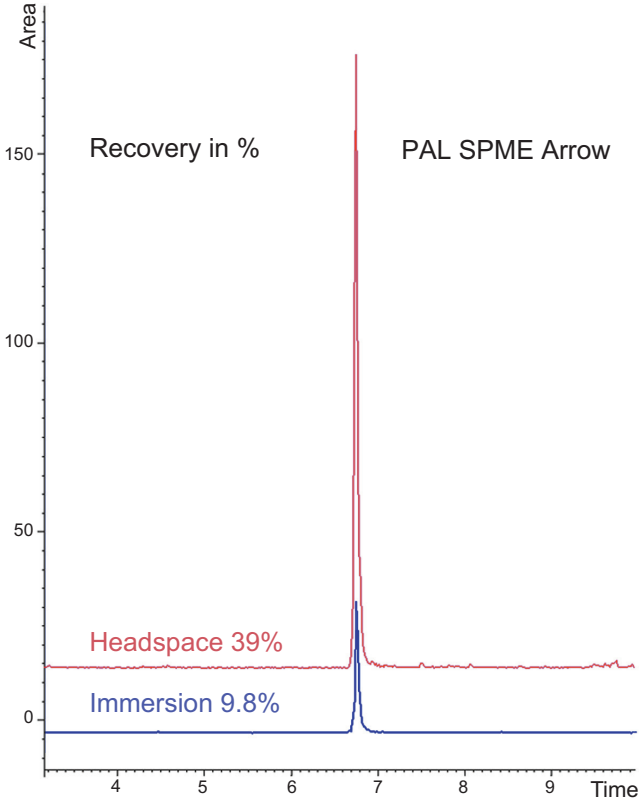

Fig. 8 : Comparison of immersion extraction vs. headspace extraction for DVB SPME Arrow @ 1 µg/L

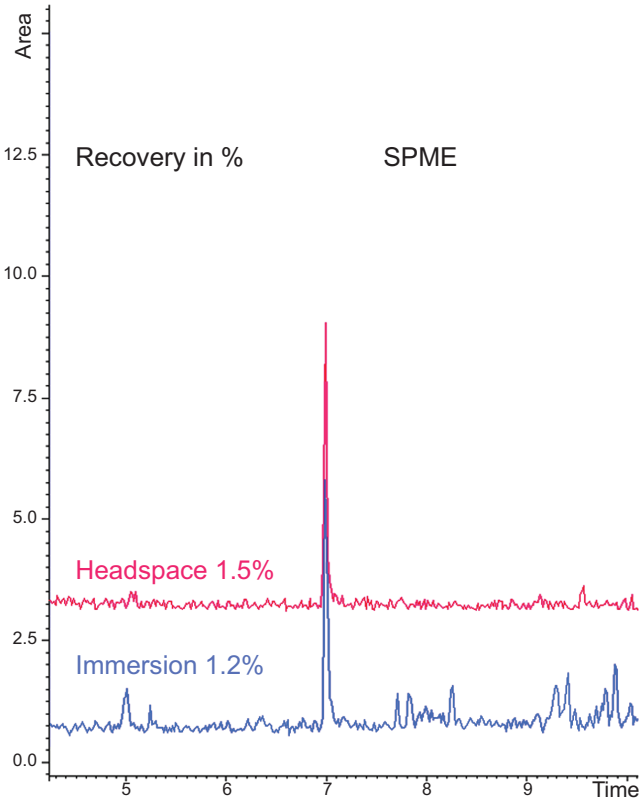

Fig. 9 : Comparison of immersion extraction vs. headspace extraction for DVB SPME fiber @ 1 µg/L

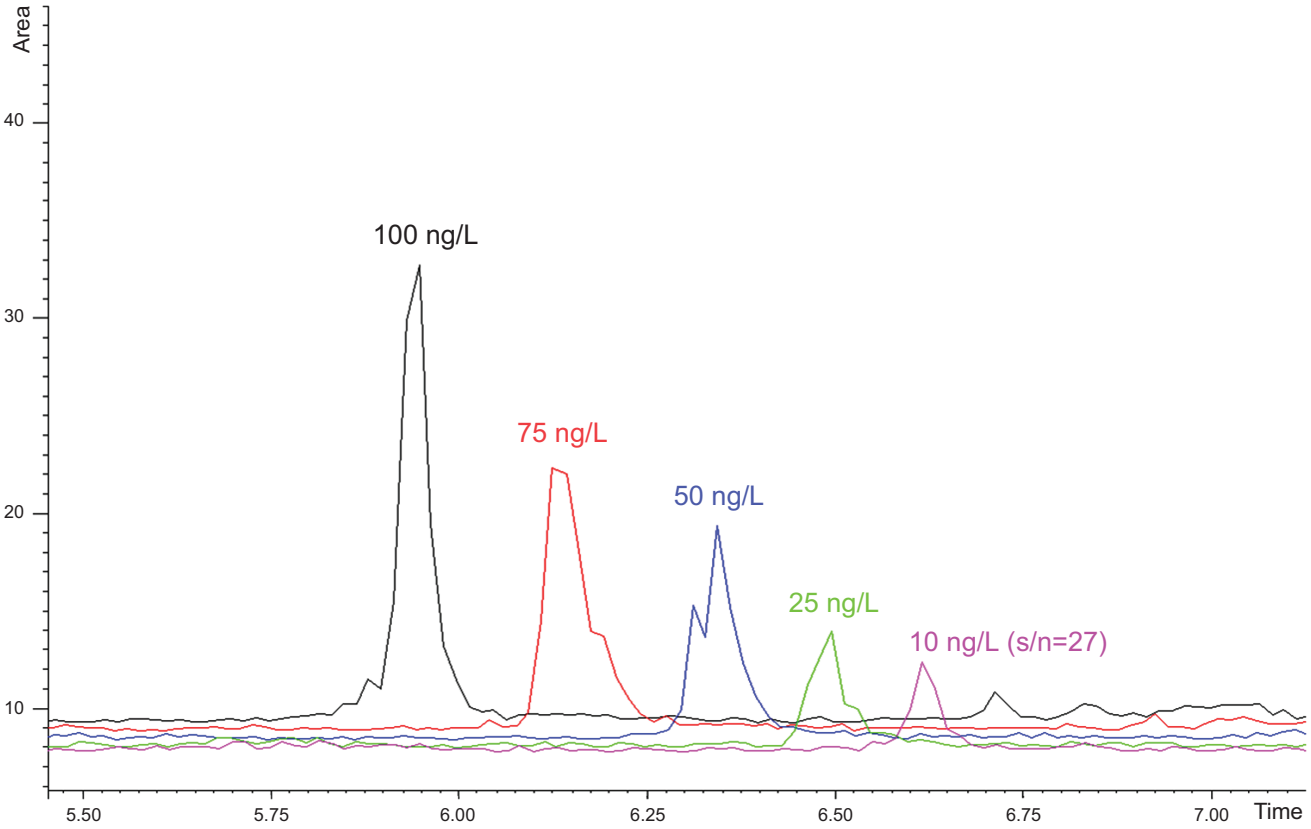

Fig. 10: Chromatograms of of iodoform in water, headspace extraction wit a DVB SPME Arrow, at different concentrations

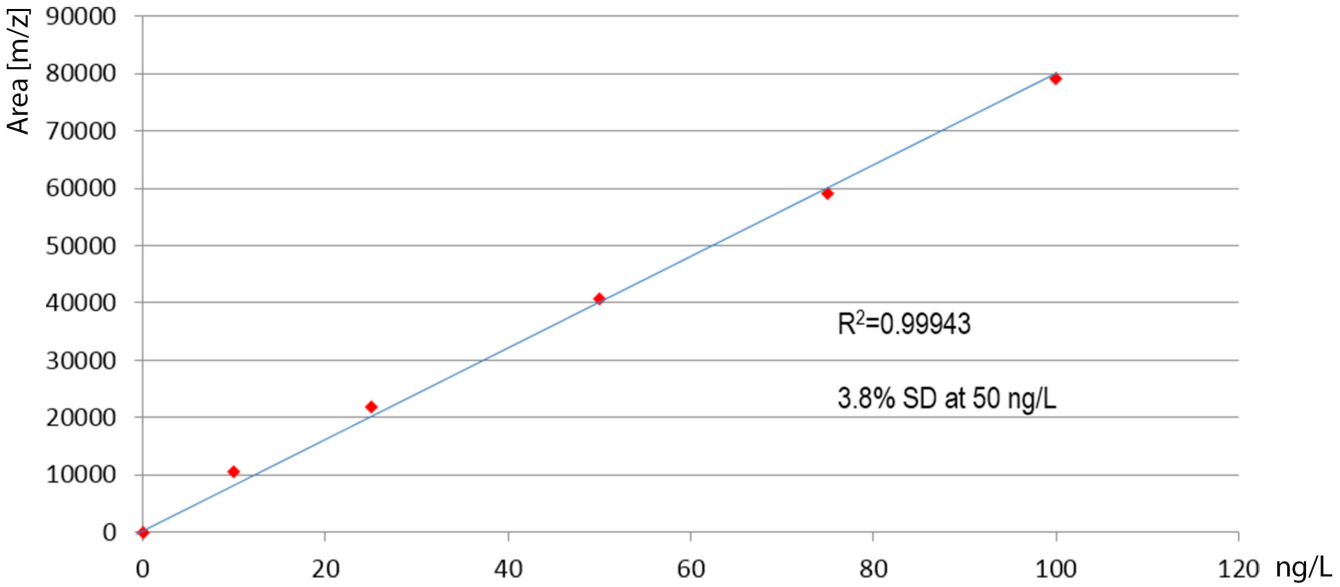

Fig. 11: Calibration curve of iodoform in water 10-1000 ng/L , headspace extraction

Conclusions

With a DVB PAL SPME Arrow detection limits of 15 ng/L (S/N > 3) have been achieved in immersion mode and 2 ng/L in headspace mode (S/N > 3). At 50 ng/L the standard deviation was 3.8% (n=5). This is sufficiently low to detect iodoform well below the odor threshold of 30 ng/L.

DVB as sorption phase shows roughly a 3 x better recovery for iodoform than PDMS.

With immersion extraction the recovery of iodoform is 8 x higher with the PAL SPME Arrow than with the corresponding SPME fiber. With headspace extraction the recovery for SPME Arrow is 26 x higher.

With desorption temperatures between 160°C and 220°C little decompositon of iodoform has been observed (ref. 1 reports noticeable decomposition above 160°C). A desorption temperature of 200°C has been selected for all experiments.

References

[1] Solid-Phase Microextraction with Temperature-Programmed Desorption for the Analysis of Iodination Disinfection Byproducts
Paul A. Frazey, Robert M. Barkley, and Robert E. Sievers
Anal. Chem. **1998**, 70, 638-644

[2] Determination of the Odor Threshold Concentrations Of Iodinated Trihalomethanes in Drinking Water
Beatriz Cancho, Cristina Fabrellas, Alfredo Diaz, and Francesc Ventura, Teresa Galceran
J. Agric. Food Chem. **2001**, 49, 1881-1884

[3] Simultaneous analysis of 10 trihalomethanes at nanogram per liter levels in water using solid-phase microextraction and gas chromatography mass-spectrometry
Sebastien Allard*, Jeffrey W.A. Charrois, Cynthia A. Joll, Anna Heitz
J. Chromatography A, 1238 (**2012**) 15– 21

[4] An Optimized Analytical Method for the Simultaneous Detection of Iodoform, Iodoacetic Acid, and Other Trihalomethanes and Haloacetic Acids in Drinking Water
Xiaolin Liu, Xiao Wei, Weiwei Zheng, Songhui Jiang, Michael R. Templeton, Gengsheng He, Weidong Qu*
PLoS ONE **2013**, 8(4) e60858. doi:10.1371/journal.pone.0060858

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CTC Analytics AG
Industriestrasse 20
CH-4222 Zwingen
Switzerland
T +41 61 765 81 00
Contact: info@ctc.ch