DETERMINATION OF C2-C12 ALDEHYDES IN WATER BY SPME ARROW ON-FIBER DERIVATIZATION AND GC/MS

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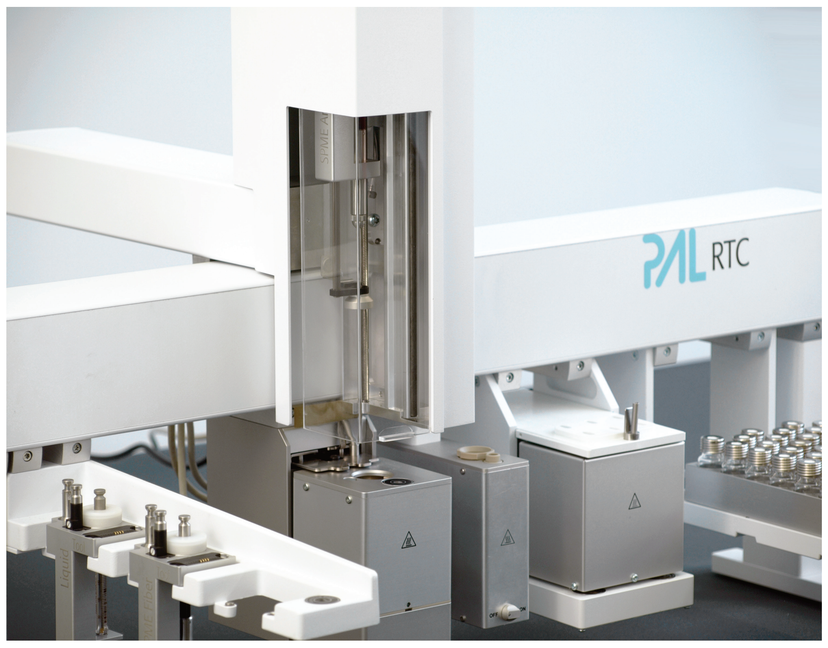


Introduction

Aldehydes are widely found in nature. Natural sources for aldehydes are, e. g., the alcoholic fermentation, lipid oxidation or atmospheric processes. Total aldehyde concentrations in drinking water disinfected with ozone range from less than 5 µg/L to 300 µg/L, depending on the TOC concentration and the applied ozone to organic carbon ratio. Primary aldehydes are formaldehyde, acetaldehyde, glyoxal, and methyl glyoxal, but aldehydes with higher molecular weights have also been reported (Glaze et al., 1989b).

Although no legislation has been established for their control, the World Health Organisation has published a drinking-water guideline value of 900 µg/L for formaldehyde.

PAL SPME Arrow, a new fiber type with drastically increased phase surface and phase volume were compared against published conventional SPME fibers. Besides the greatly improved mechanical stability PAL SPME Arrows feature a much larger surface area/sorption phase volume which is beneficial for achieving good sensitivities and increased extraction speed.

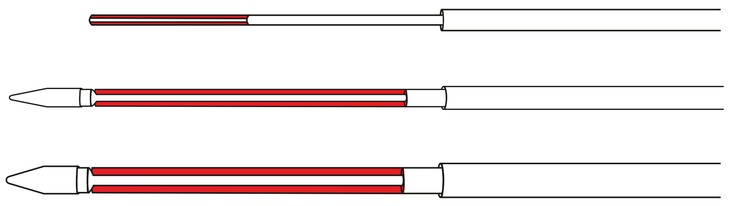
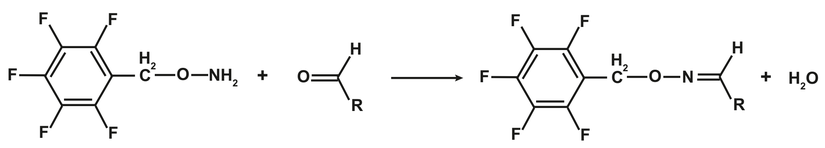


Figure 1: Comparison of conventional 100µm PDMS SPME fiber against 100µm PDMS SPME Arrow and 250µm PDMS SPME Arrow offering 5-7 times larger phase surface.

SPME on-fiber Derivatization

For comparison we used the SPME fiber derivatization (ref. 1-3) and subsequent analysis of a number of aldehydes with O-(2,3,4,5,6-pentafluorobenzyl)- hydroxylamine hydrochloride (PFBHA) in aqueous solution to form pentafluorobenzyl oxime derivatives.



Method

Chemicals:

Water	Sartorius arium ultrapure with UV lamp (water according to ISO 3696), further purified by heating to 90°C for 60 min
Aldehydes analyzed	Acetaldehyd (C2), propanal (C3), butanal (C4), hexanal (C6), heptanal (C7), octanal (C8), nonanal (C9), decanal (C10), undecanal (C11), dodecanal (C12), (Fluka, puriss. purity > 99%)
Internal Standard	10 µl 2,3,5,6-Tetrafluorobenzaldehyd (Fluka 328936, purity > 97%) in 10 ml methanol (Carlo Erba HPLC Grade, 412383)
Derivatization reagent	100 mg PFBOA O-(2,3,4,5,6-Pentafluorobenzyl)hydroxylamin hydrochlorid (Fluka 76735, purity > 99%) dissolved in 10 ml 0.05 M H2SO4 (Fluka, purity > 90%), further purified by heating to 90°C for 60 min

Procedure:

5 mL water sample in a 20 mL headspace vial
1.5 g NaCl (optional)
100 µL PFBOA reagent

Extraction/derivatization Conditions:

Sampling Tool:	PAL SPME Arrow 1.15 mm diameter, PDMS, 20 mm x 100 µm
Pre conditioning:	0:30 min
Pre incubation time:	1:00 min at 250°C
Incubation temp:	60°C
Agitation speed:	500 rpm
Needle penetration:	22 mm
Fiber penetration:	30 mm
Extraction time:	30:00 min
Desorption time:	2:00 min at 250°C

Analytical Conditions:

GC:	Varian 3400
MS:	Varian Saturn Ion Trap
Column:	30 m x 0.25 mm 0.25 µm BGB-5
Carrier gas:	Hydrogen 5.0 psi
Temp program:	70°C for 1min, then 5°C/min > 280°C
Injector:	SPI 250°C, isothermal
Mass range:	75 - 230 m/z (Fragment: 181)

Results

Reaction Conditions:

After dipping the Arrow/fiber into the derivatizaion reagent the extraction/derivatization was performed at 60°C on the Arrow/fiber exposed to the headspace. An extraction time of 30 min was chosen because longer times showed no further increase of the extraction yield (see fig. 2).

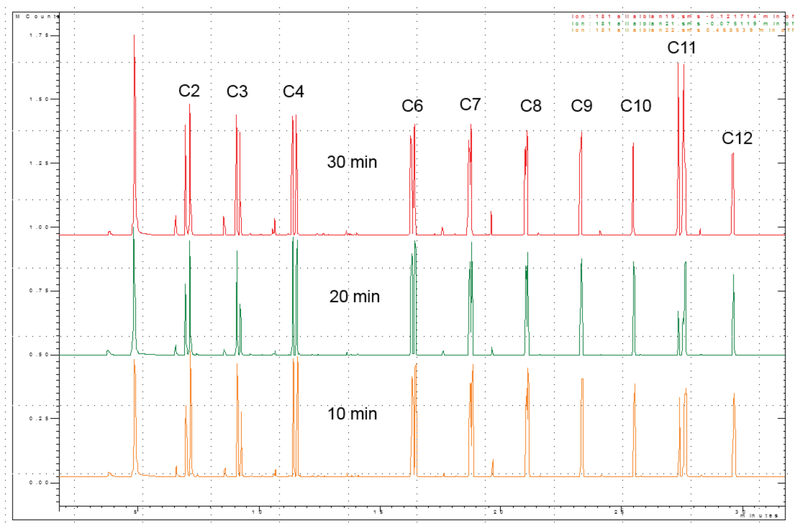


Figure 2: Optimiztion of extraction/reaction time, reaction temperature was 60°C. Note that the reaction yields stereoisomers, hence the doublets in the chromatogram.

Salting out with 1.5 g of NaCl/10 mL showed a small increase of signals for the smaller aldehydes (C2-C4), as would be expected. However, since the effect was limited salting out was not used for further experiments.

Aldehyde	#1	#2	#3	#4	#5	Mean	Std. Dev.	%RSD
C2	1368761	1410756	1512509	1432007	1476145	**1440036**	**45749.51**	**3.17**
C3	684295	801885	806476	875981	915465	**816820**	**72022.9**	**8.81**
C4	1980129	2026277	1950798	2125312	2129706	**2042444**	**67113.44**	**3.28**
C6	2108728	2143327	2080365	2161982	2175526	**2133986**	**31910.76**	**1.49**
C7	1940569	1953331	1930925	2044924	1965753	**1967100**	**37104.58**	**1.88**
C8	1144195	1192141	1185666	1262568	1181341	**1193182**	**35147.13**	**2.94**
C9	820606	852812	824028	903949	835834	**847446**	**27763.91**	**3.27**
C10	501254	528851	529842	562818	529545	**530462**	**17813.1**	**3.35**
C11	2459892	1566813	1478380	1857195	2522259	**1976908**	**400358.3**	**20.25**
C12	506797	507374	559419	571990	532635	**535643**	**24244.17**	**4.52**

Table 1: Reproducibility and standard deviation at 10 µg/L. Note that the signals for C11 are disturbed by co-eluting compounds.

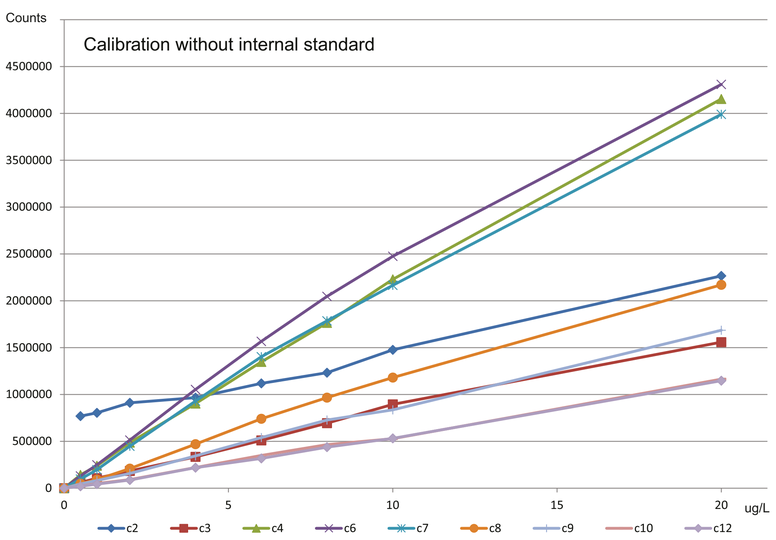


Figure 3: Calibration without Internal Standard. It can be seen that the background level of C2 (acetaldehyde) is rather high and could not be eliminated. The values for C11 are not included because of co-eluting compounds.

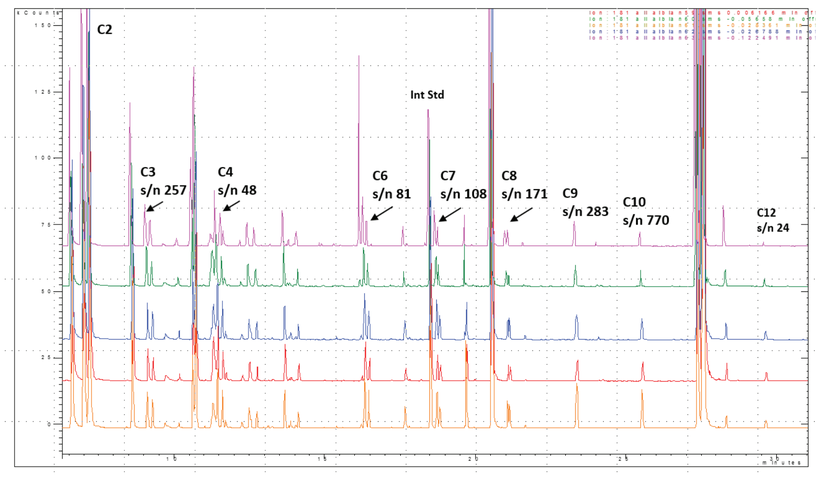


Figure 4: Reproducibility and signal/noise ratios of the different aldehydes at 160 ng/L.

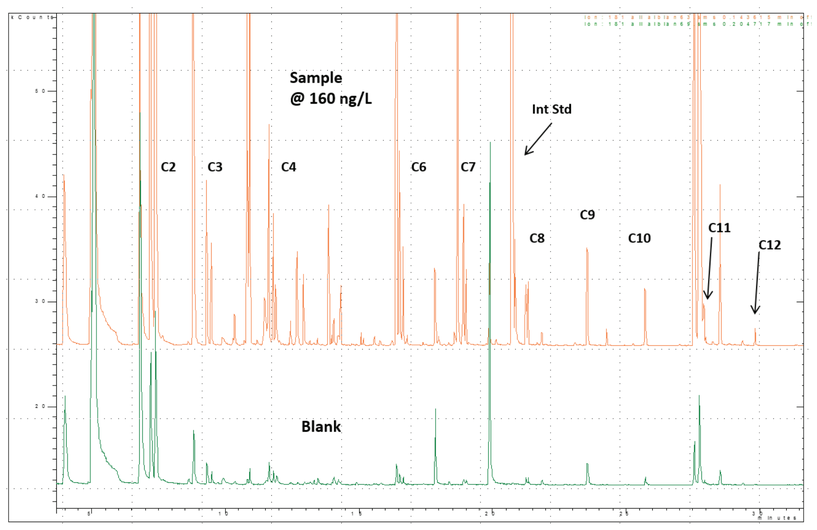


Figure 5: Sample at 160 ng/L (orange) compared to a blank water sample (green).

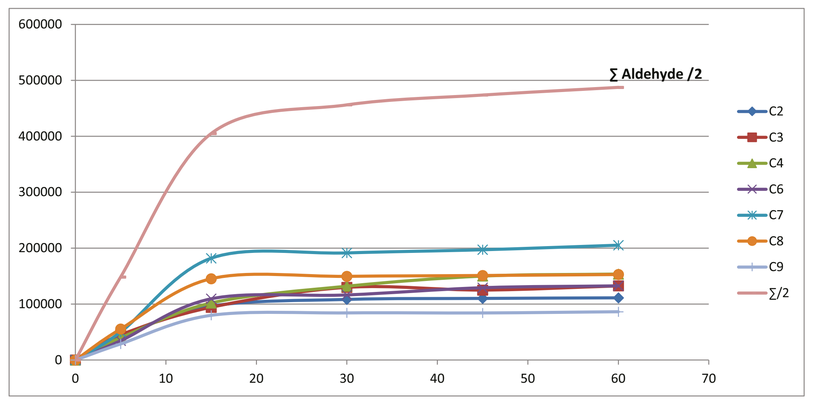


Figure 6: Extraction time dependence of SPME fiber.

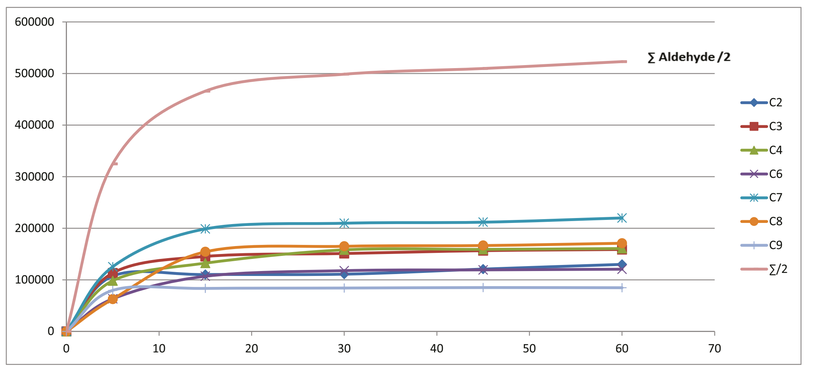


Figure 7: Extraction time dependence of SPME Arrow.

Conclusion

The method described employing a PAL SPME Arrow allows for the quantitation of water samples down to 50 ng/L for most of the described aldehydes. A previous publication applying standard SPME fibers and GC/MS achieved sensitivities down to 120-340 ng/L in spiked samples for C1, C3-C5 (ref. 2). Blank water samples as well as the samples of the higher aldehydes contain C2 (acetaldehyde) and other contaminations in amounts high enough to hamper the analysis at levels below 50 ng/L. The robustness of the PAL SPME Arrow allowed for the uninterrupted analysis of several hundred samples with one single SPME Arrow.

References

[1] Determination of aldehydes in drinking water using penta-fluorobenzylhydroxylamine derivatization and solid-phase microextraction. F.Ventura, B. Cancho, M. T. Galceran; J. Chromatogr. A. 2002, 943, 1-13.
[2] Analysis of aldehydes in water by solid-phase microextraction with on-fiber derivatization. S.W. Tsai, C.M. Chang; J. Chromatogr. A. 2003, 1015, 143.
[3] Evaluation of solid-phase microextraction methods for the determination of trace concentration aldehydes in aqueous solution. J. Beranek, A. Kubatova; J. Chromatogr. A. 2008, 1209, 44-54.