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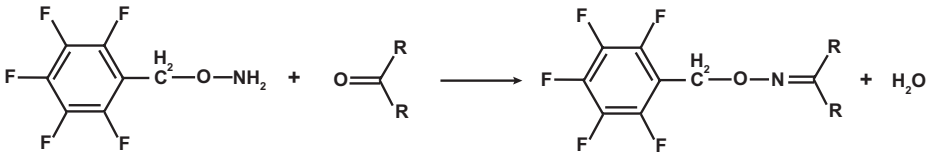

Figure 1: Reaction of O-(2,3,4,5,6-pentafluorobenzyl)- hydroxylamine hydrochloride (PFBHA) with aldehydes and ketones in aqueous solution

Aldehydes

Aldehydes are widely found in nature. Natural sources for aldehydes are, e. g., the alcoholic fermentation, lipid oxidation or atmospheric processes. Aldehydes have also been identified as by-products of drinking water disinfection, particularly ozonation. The primary aldehydes that have been measured are formaldehyde, acetaldehyde, glyoxal, and methyl glyoxal, but aldehydes with higher molecular weights have also been reported. Total aldehyde concentrations in drinking water disinfected with ozone range from less than 5 µg/L to 300 µg/L.

Some aldehydes are important flavor compounds, in some cases undesirable off flavors. The formation of aldehydes is a major contributor to the deterioration in flavor of beer upon storage. Certain aldehydes have extremely low odor thresholds, such as (E)-alkenals or (E,E)-alkadienals. The means to detect the presence of such compounds is therefore important for a large variety of food samples as they contribute considerably to flavor quality or cause off-flavors, such as the known cardboard note in beer or packaging materials.

A non-natural source of aldehydes in food, particularly beverages is the widespread use of polyethylene terephthalate (PET) containers. It is assumed that aldehydes are formed during the production of the PET container and then slowly released into the food.

Furthermore, aldehydes are considered as markers for enhanced oxidative stress in biological systems, and have also been proposed as a diagnostic marker of cancer status.

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.

In order to monitor treatment practices, assess exposure to consumers, and control health risks that might be associated with this class of by-products, a reliable and sensitive monitoring method is required.

SPME with on-fiber derivatization

Since a publication by Martos and Pawliszyn in 1998 (ref.1) a significant number of publications on this topic have appeared, dealing with environmental, clinical, flavor, and chemical topics. Procedures for a wide range of analytes have been established applying both headspace and immersion derivatization.

Here we describe the on SPME fiber derivatization 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 (Fig. 1). PFBHA reacts quantitatively, even with conjugated aliphatic aldehydes.

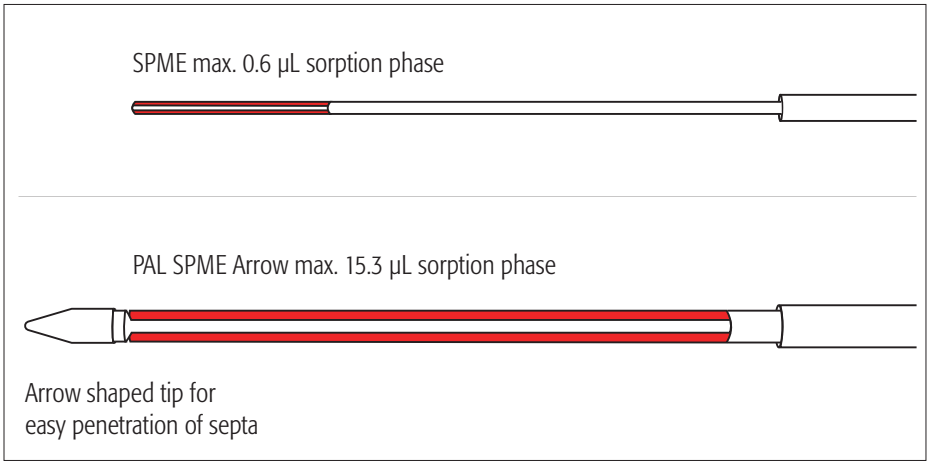

Figure 2: PAL SPME Arrow compared to a conventional SPME fiber. Size and position of the sorptive phases are shown in red.

The resulting oximes (E- and Z-isomers) do not decompose at elevated temperatures, neither do they require a time-consuming clean-up step and can easily be resolved by GC. The detection is achieved by either electron capture, thermionic or mass-selective detection. EPA method 556 is based on this reaction, but applying derivatization in solution rather than on-fiber.

The fibers used in this work are PAL SPME Arrow 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 (Fig. 2,4).

Experimental

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 (Int Std):
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 H_2SO_4 (Fluka, purity > 90%), further purified by heating to 90°C for 60 min

Procedure:

The PAL SPME Arrow fiber is dipped into the derivatizating reagent (s. above). Then the fiber is exposed for 30 min to the headspace of a 5 mL water sample (60°C) in a 20 mL headspace vial.

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
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

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:	PI 250°C, isothermal
Mass range:	75 - 230 m/z

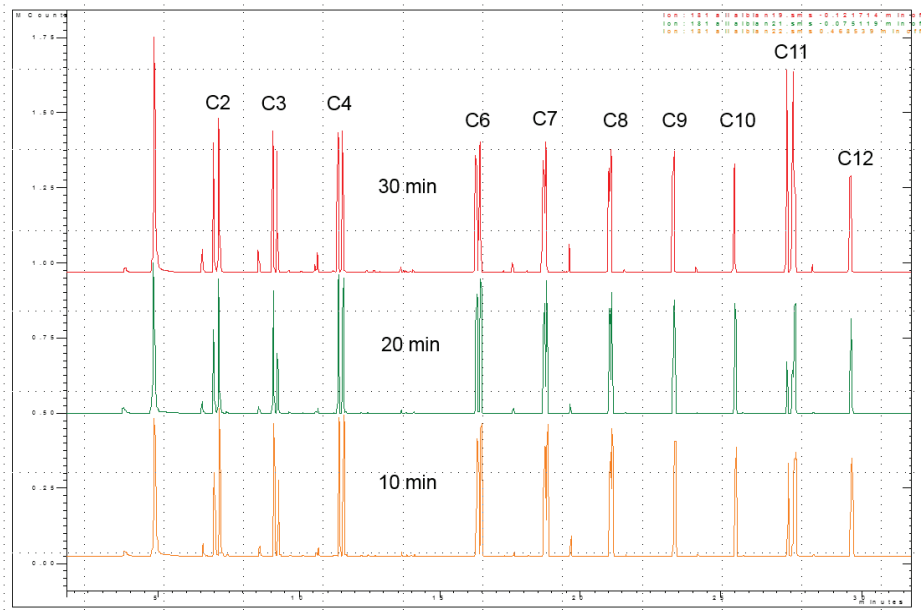

Figure 3: Optimization of extraction/reaction time, reaction temperature was 60°C. Note that the reaction yields stereoisomers, hence the doublets in the chromatogram.

Figure 4: PAL SPME Arrow Tool for PAL RTC and PAL RSI.

Results:

Reaction conditions:

After dipping the fiber into the derivatizaion reagent the extraction/derivatization was performed at 60°C on the 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. 3).

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.

Conclusions:

The method employing a PAL SPME Arrow fiber allows for the quantitation of water samples down to 50 ng/L for most of the described aldehydes with good precision. 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. 3).
Blank water samples as well as the samples of the higher aldehydes contain C2 (acetaldehyde) and other contaminants in amounts high enough to hamper the analysis at levels below 50 ng/L.
The sensitivity of the method could be increased further by applying selected reaction monitoring (SIM).
The robustness of the PAL SPME Arrow allowed for the uninterrupted analysis of several hundred samples with one single fiber.

Reproducibility and calibration data:

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.

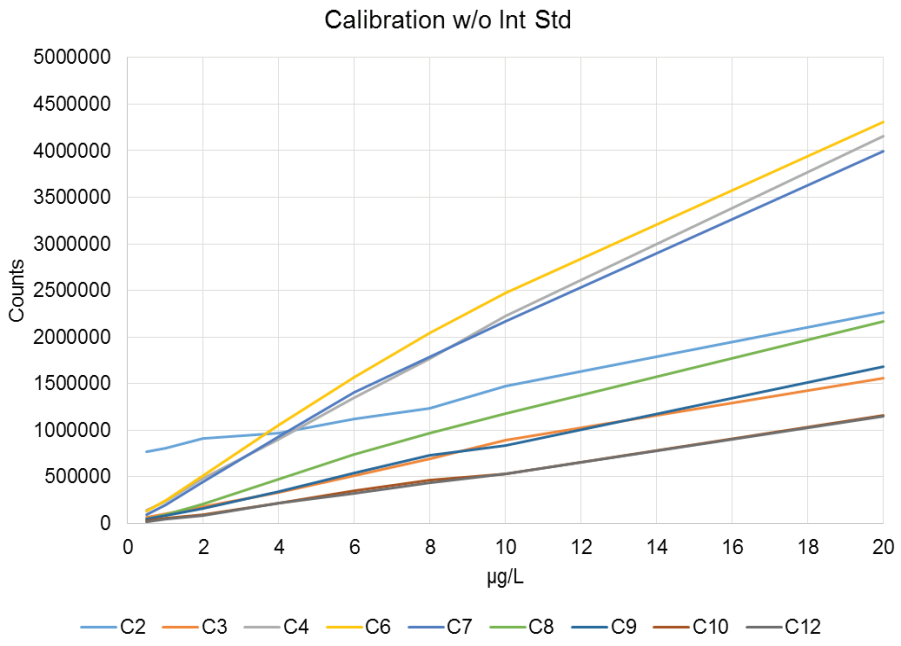

Figure 5: Calibration without Int Std. It can be seen that the background level of C2 (acetaldehyde) is rather high and could not be eliminated. The values for C11 are not included because of co-eluting compounds.

	20 µg/L	10 µg/L	8 µg/L	6 µg/L	4 µg/L	2 µg/L	1 µg/L	0.5 µg/L	R^2
C2	2266627	1476145	1232841	1118940	966230	911115	803863	769740	0.996
C3	1559080	895465	694653	509554	335235	183452	106914	60730	0.995
C4	4153541	2229706	1764289	1347615	903684	486444	239342	142822	0.992
C6	4310253	2475526	2047288	1567859	1053491	512852	248795	131511	0.992
C7	3991048	2165753	1786319	1402977	930288	448971	198072	97556	0.994
C8	2171225	1181341	966167	741344	469938	208754	92831	48914	0.994
C9	1685269	835834	727871	540683	344514	158269	81931	45430	0.997
C10	1163606	529545	465284	349988	221618	92857	50759	22330	0.997
C12	1148210	532635	437879	317742	219795	87271	43249	20597	0.998

Table 2: Calibration data: good linearity was achieved.

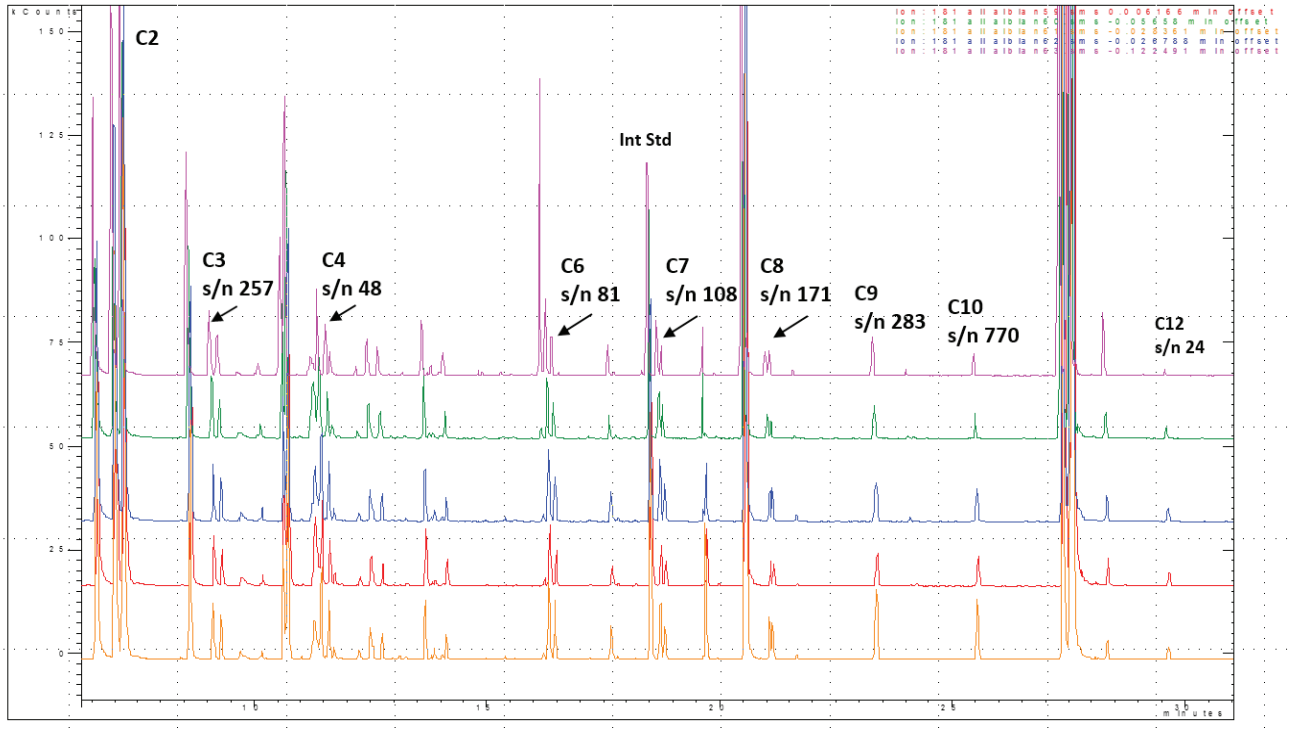

Figure 6: Reproducibility and siganl/noise (s/n) ratios of the different aldehydes at 160 ng/L

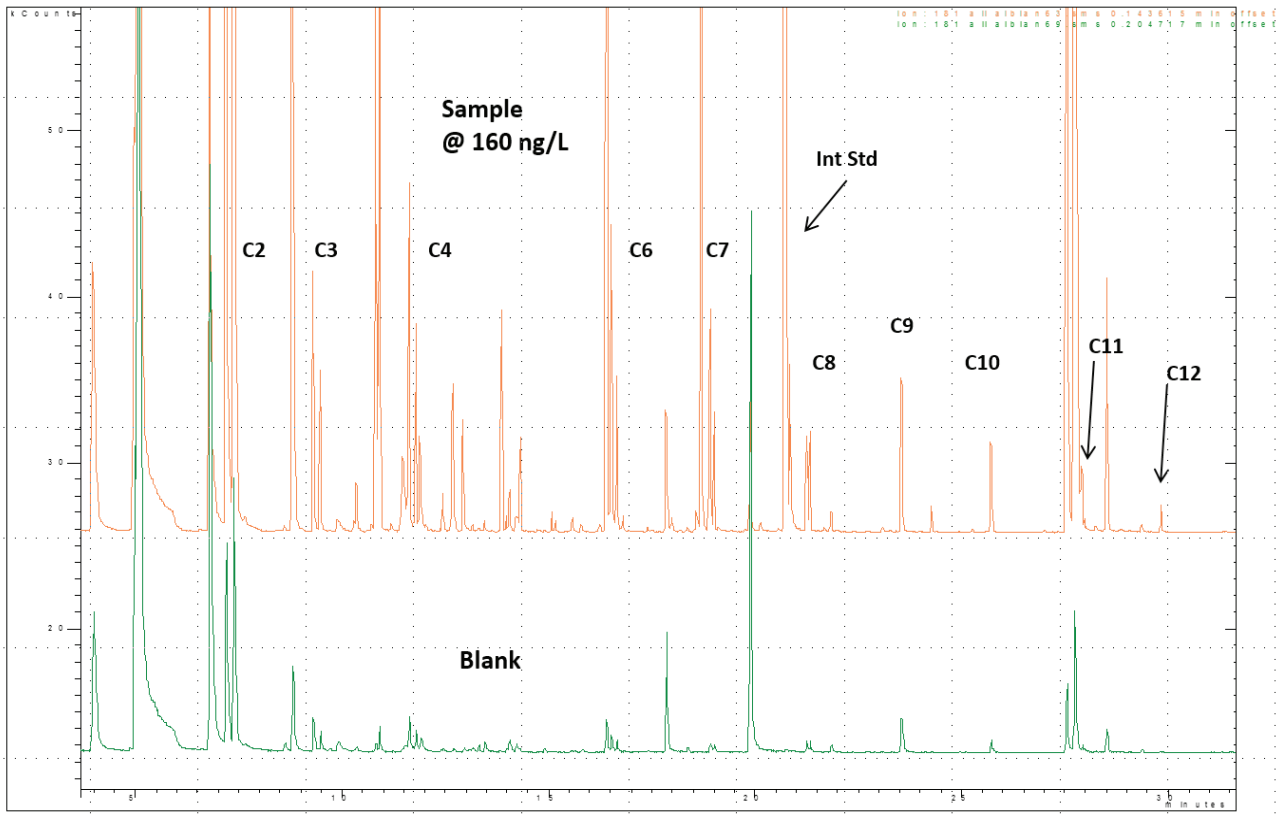

Figure 7: Sample @ 160 ng/L (orange) compared to a blank water sample (green).

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[4] 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.

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