PAL SYSTEM
Ingenious sample handling

Issue 1
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Ingenious News

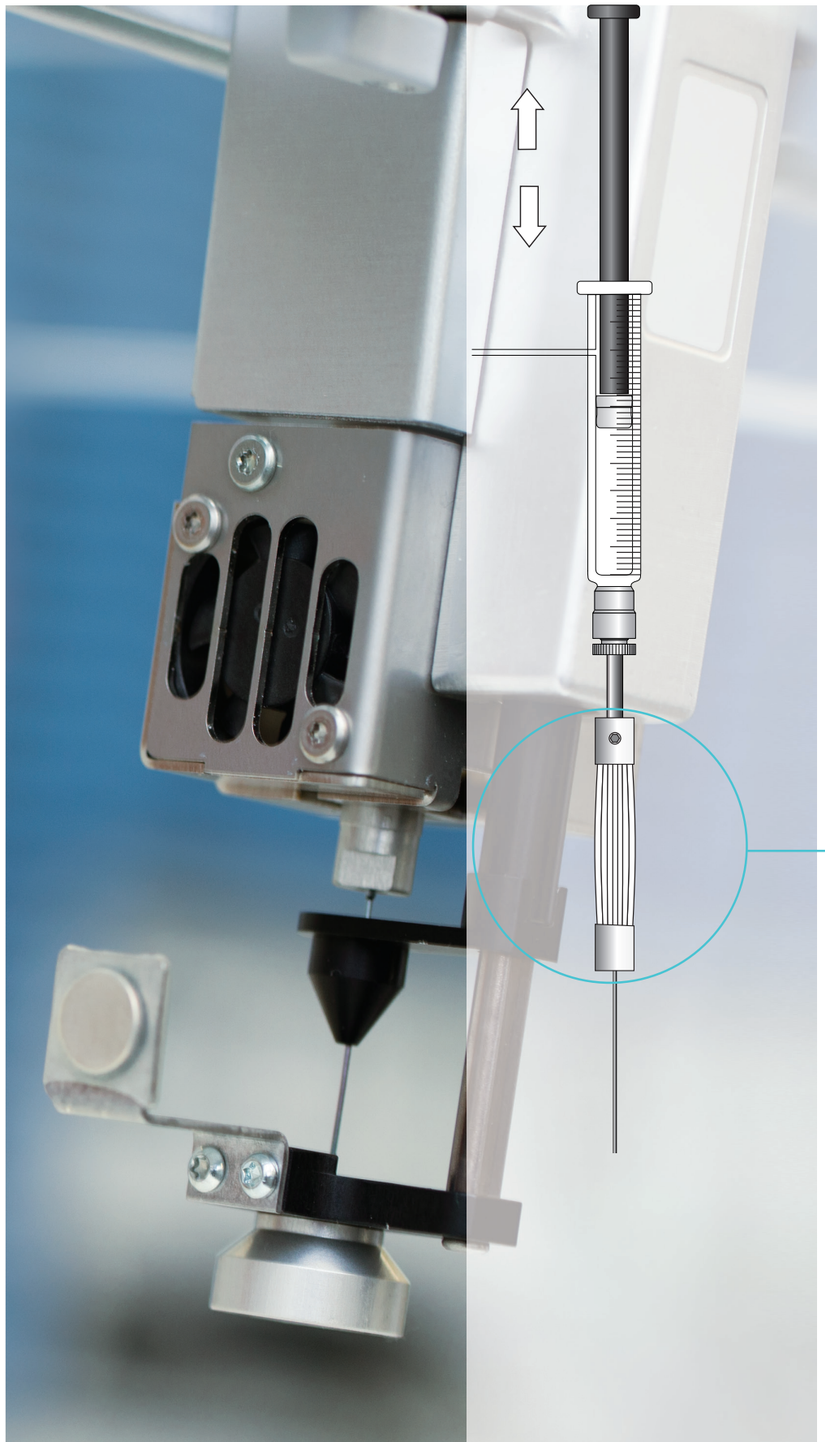
PAL SYSTEM

www.palsystem.com

CHEMICAL CLINICAL ENVIRONMENTAL FOOD SAFETY

ITEX (In-tube extraction) Dynamic Heaspace Tool ng/L-sensitivity without the pitfalls of P&T Systems

- Rapid and efficient enrichment of volatile and semi-volatile compounds from solid, liquid and gaseous samples
- In-tube extraction and thermal desorption using industry standard adsorbents
- Syringe-only concept: no sample loops, transfer lines, or switching valves that could be contaminated
- Active cooling allows for rapid sample preparation and short cycle times
- No modifications of the GC injector needed
- PAL Robotic Tool Change enables head space, SPME and ITEX-sampling within the same sequence on one system



ITEX Dynamic Headspace high sensitivity, no hassle

Typical application areas include:
(see pages 6-9 for more details):

- Drinking and waste water
- Food, additives, flavors
- Chemical
- Clinical

ITEX Dynamic Headspace Extraction Procedure

The sample is heated and / or agitated in a sealed vial.

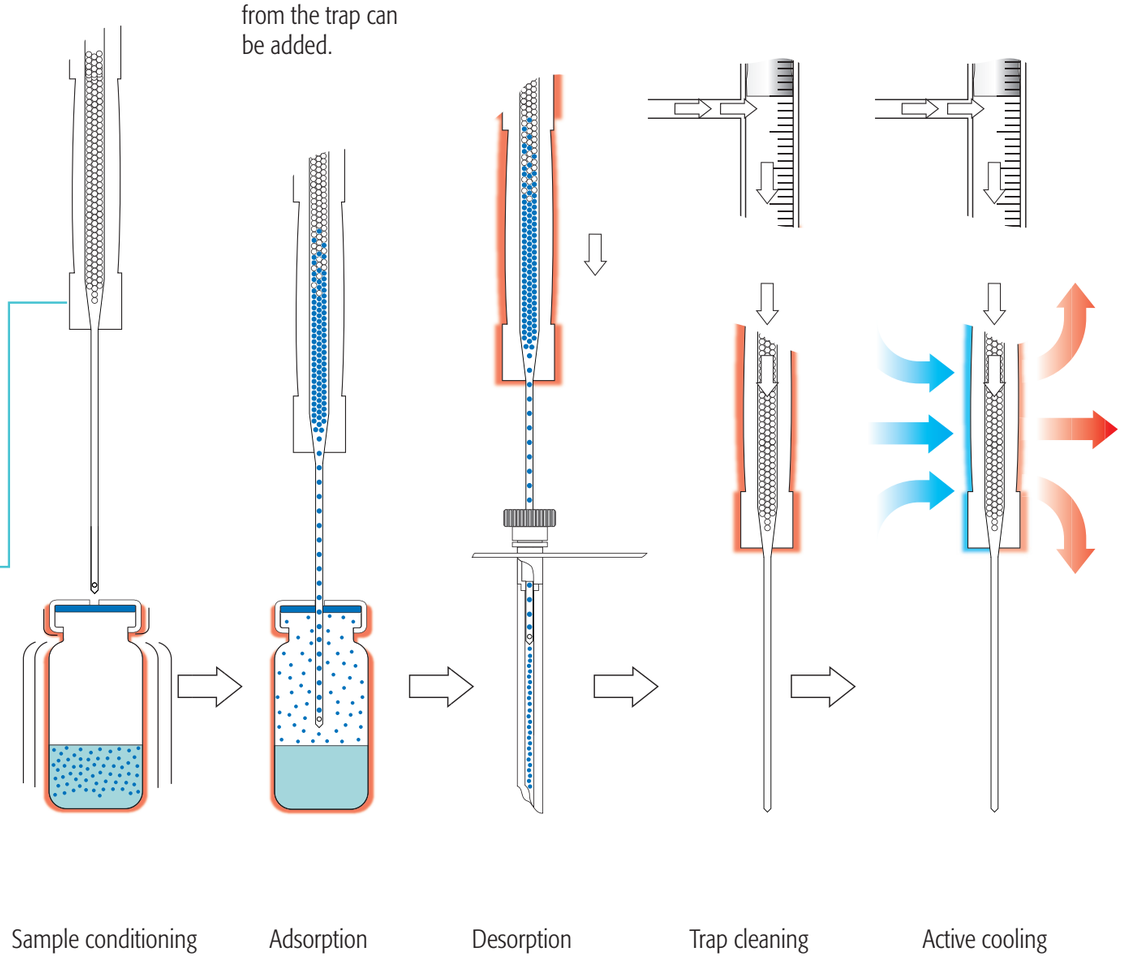
The ITEX needle pierces the sealed vial and the heated syringe pumps the the headspace gas through the cold trap.

An additional step to remove water from the trap can be added.

The loaded ITEX trap is flash heated up to 350°C and analytes are desorbed into the hot GC injector.

After thermal desorption the hot ITEX trap is cleaned with inert flush gas.

Active cooling allows for short cycle times.

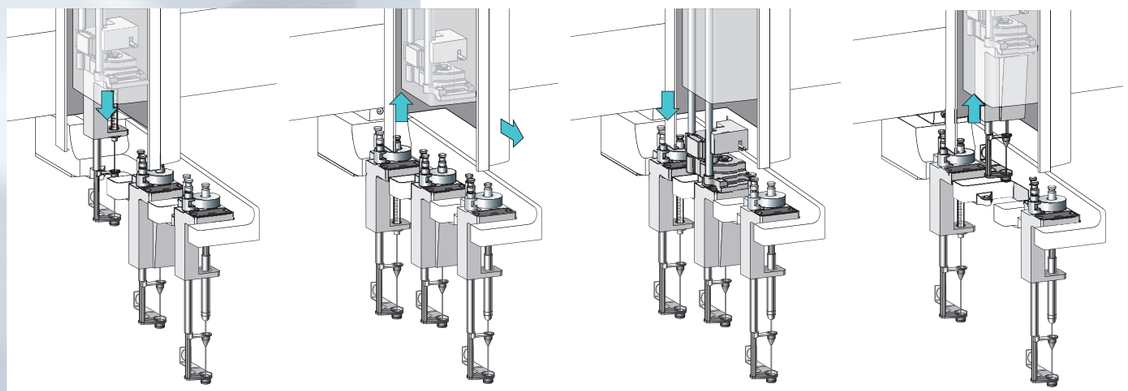


Powerful options for
ITEX Dynamic Headspace

The PAL RTC
(Robotic Tool Change)
takes productivity to
new levels

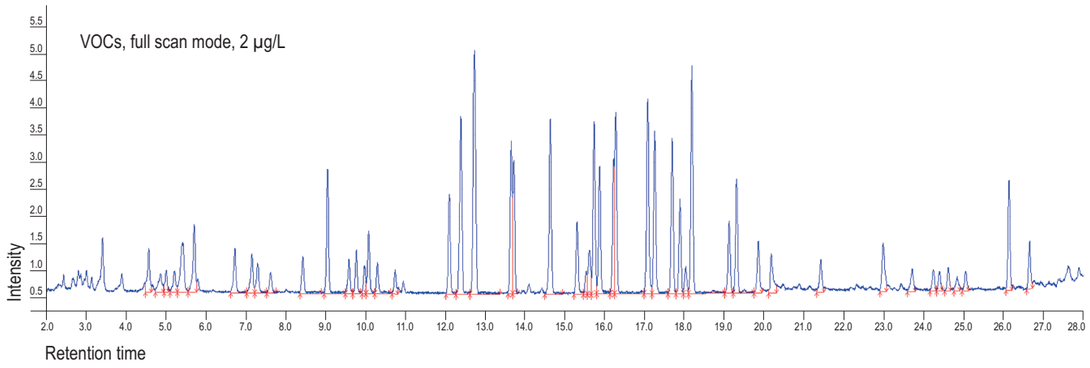
Robotic Tool Change and ITEX Dynamic Headspace, ingeniously productive.

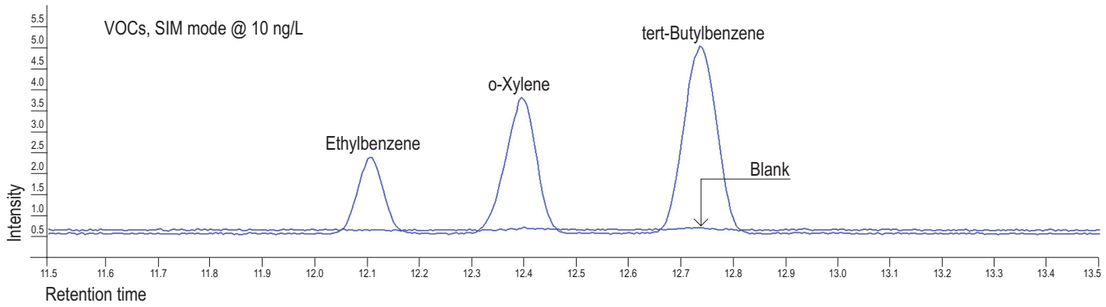
- Headspace, SPME and ITEX sampling within the same sequence
- Automatic selection of the syringe with optimal accuracy, e.g. for adding standards or preparing serial dilutions
- Automated optimization of methods e.g. by selecting the most suitable ITEX trap and conditions
- Derivatization reactions performed without manual intervention for productivity, process safety and protection against hazardous chemicals
- Possibility to permanently configure several workflows on one system for a walk-up prep station, e.g. Liquid/ Liquid Extraction and Solid Phase Extraction (SPE)



For more information about
Robotic Tool Change

Environmental application
VOCs, BTEX in water at ppt levels, EPA 502.2





Sample preparation:

Full scan data: 2 µg/L MegaMix® Standard, 524.2 73 components), Restek PN 30601

SIM scan data: 10 ng/L MegaMix® Standard, 502.2 (54 components), Restek PN 30432

10mL water + standard, filled into 20 mL headspace vial, + 3g NaCl

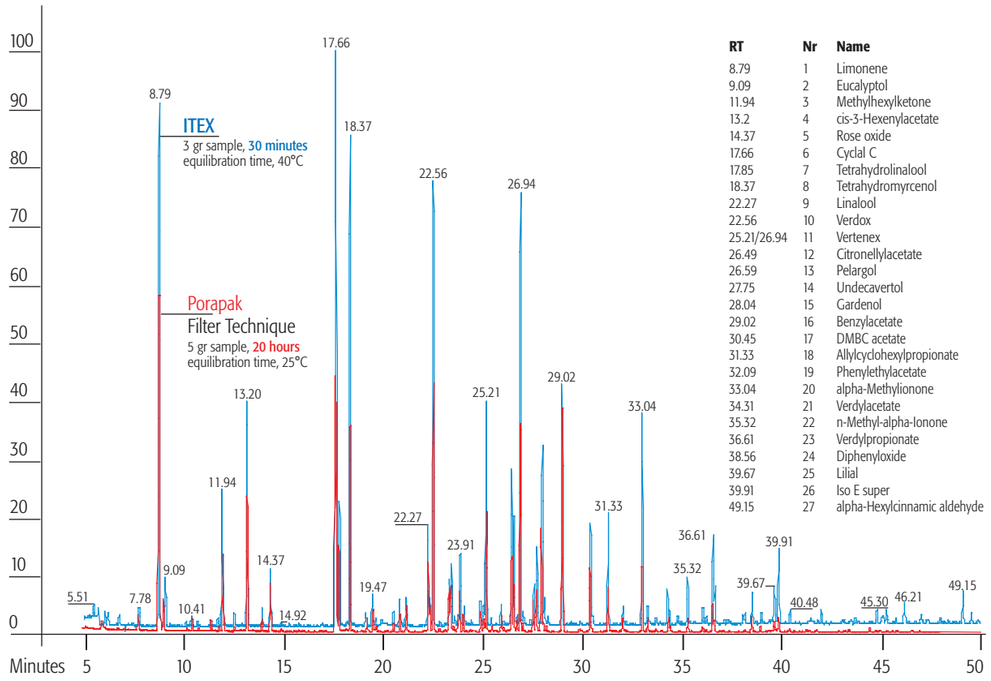
Chromatography (Shimadzu GC-2010 Plus):

Column:	Rxi® 624 Sil MS, 30 m x 0.32 mm, 1.8 µm df
Carrier gas:	helium, 93.2 kPa
Temperature program:	40°C for 1 min, 5°/ min to 250°C, 2 min hold
Injector:	split/split less @ 225°C
Liner	Restek catalog # 23321.1, 3.5 mm Splitless Single Tpr Gsnk
GC:	Shimadzu GC-2010 Plus
Detector:	Shimadzu GCMS-Q2010 SE

ITEX Dynamic Headspace conditions

Incubation temp.	40°C
Incubation time	3 min
Syringe temp.	50°C
Extraction strokes	30 x 1 mL @ 40°C (12 min)
Extraction speed	100 µL/s
Desorption	200°C with 1 mL headspace,
ITEX trap material:	Tenax TA

Food application
Comparison of flavors/softeners
ITEX Dynamic Headspace vs. Poropak Filter



RT	Nr	Name
8.79	1	Limonene
9.09	2	Eucalyptol
11.94	3	Methylhexylketone
13.2	4	cis-3-Hexenylacetate
14.37	5	Rose oxide
17.66	6	Cyclal C
17.85	7	Tetrahydrolinalool
18.37	8	Tetrahydromyrcenol
22.27	9	Linalool
22.56	10	Verdox
25.21/26.94	11	Vertenex
26.49	12	Citronellylacetate
26.59	13	Pelargol
27.75	14	Undecavertol
28.04	15	Gardenol
29.02	16	Benzylacetate
30.45	17	DMBC acetate
31.33	18	Allylcyclohexylpropionate
32.09	19	Phenylethylacetate
33.04	20	alpha-Methylionone
34.31	21	Verdylacetate
35.32	22	n-Methyl-alpha-Ionone
36.61	23	Verdylpropionate
38.56	24	Diphenyloxide
39.67	25	Lilial
39.91	26	Iso E super
49.15	27	alpha-Hexylcinnamic aldehyde

Chromatography (Thermo TraceGC):

Column:	Stabilwax 30 m x 0.25 mmID x 0.25 mm film thickness
Oven:	35°C - 0.5 min. 15°C / min. 50°C - 0min. 5°C / min. 220°C / 1min.
SSL:	splitless with surge, surge pressure 20kPa/0.4 min. (0.5ml), split flow 100 mL /0.3 min.
Carrier:	He, 1 mL/min constant flow with vacuum compensation

MS conditions (Thermo Trace MS system):

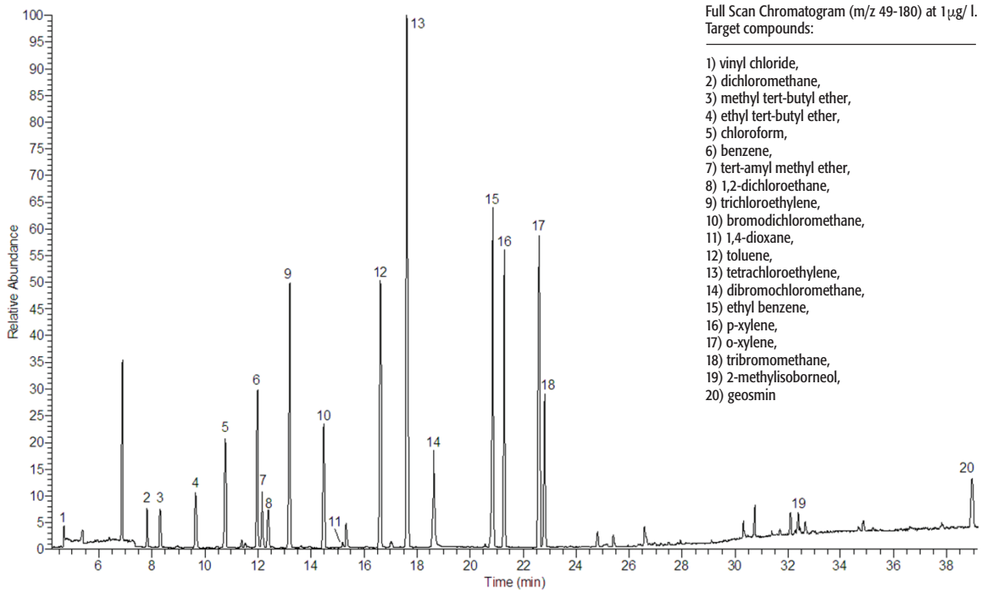
Ionisation mode:	EI+
Source temperature:	230°C
Interface:	220°C
Mass:	20-350 amu

ITEX Dynamic Headspace conditions:

Incubation temp:	40°C
Incubation time:	30 min.
Syringe temp:	45°C
Extraction volume:	1000 µL/stroke
Extraction strokes:	10
Extraction speed:	100 µL/sec.
Desorption temp:	200°C
Desorption speed:	100 µL/sec.
Flush time:	5 min.

Courtesy of: Givaudan Research Company,
CH-8600 Dübendorf, Zürich. Switzerland , H. Koch

Environmental application
Purgable organic compounds (VOCs) in water by GC/MS, EPA 524.2



ITEX ppt sensitivity for volatile or semi-volatile compounds

Instrumentation		Conditions
GC	Thermo Trace GC Ultra	40°C for 1 min., 4°C/ min. to 130°C, 10°C/ min. to 200°C for 10 min.
MS	Thermo DSQII	El 70ev, Scan mode m/z 49-180
Injector	AtasGL Optic 3 with cryfocusing unit	280°C Cryotrap – 165°C for 30 sec., 30°C/ sec. to 250°C
GC Column	Restek VMS 60 m x ,0.32 mm i.d., 1.8 µm film	1.5 mL/ min. constant flow
Autosampler	PAL RTC with ITEX Dynamic Headspace, Tenax GR/Carbosieve S3 trap	10 ml sample in 20 ml headspace vial

ITEX Dynamic Headspace, extraction parameters

Sample storage in tray cooler:	25°C	Extraction volume:	1000 µL
Tray temp:	40°C	Extraction flow rate:	100 µL/sec.
Syringe temp:	60°C	Desorption volume:	500 µL
Incubation time:	5 min.	Desorption flow rate:	10 µL/sec.
Agitator speed:	500 rpm	Desorption temp:	300°C
Extraction temp:	60°C	Trap cleaning temp:	350°C
Extraction stroke:	60	Trap cleaning time:	5 min.

Sensitivity comparison between ITEX Dynamic Headspace and Purge & Trap

Sensitivity Comparison of ITEX with Purge & Trap

	ITEX Dynamic Headspace					Purge & Trap	
Compound	MDL [µg L^{-1}]	Linear range [µg L^{-1}]	R^2	RSD [%]	Recovery [%]	MDL [µg L^{-1}]	RSD [%]
Vinylchloride	0.008	0.02-2.0	0.999	5.3 (n=63)	103	0.008	
Dichloromethane	0.01	0.03-2.7	0.999	5.5 (n=63)	97		
MTBE	0.004	0.01-1.5	0.999	6.1 (n=63)	88	0.001	4.7
ETBE	0.001	0.004-1.5	0.998	6.6 (n=77)	94	0.009	5.1
Chloroform	0.004	0.007-2.9	0.999	5.4 (n=77)	99	0.008	
Benzene	0.001	0.002-1.8	0.999	5.4 (n=84)	89	0.002	5
TAME	0.001	0.004-1.5	0.999	5.8 (n=77)	95	0.01	3
1,2-dichloroethane	0.002	0.006-2.5	0.999	5.3 (n=77)	97		
Trichloroethylene	0.001	0.007-2.9	0.999	5.2 (n=77)	95	0.003	5.3
Bromodichloromethane	0.001	0.002-4.0	0.999	6.1 (n=91)	97	0.007	5.2
1,4-Dioxane	0.07	0.1-2.1	0.998	8.9 (n=49)	59		
Toluene	0.005	0.009-1.7	0.998	7.3 (n=70)	96	0.001	4.5
Tetrachloroethylene	0.001	0.003-3.2	0.999	5.7 (n=84)	97	0.004	7.3
Dibromochlormethane	0.005	0.02-4.9	0.999	5.8 (n=70)	98	0.001	4.1
Ethylbenzene	0.002	0.009-1.7	0.999	8.7 (n=70)	93	0.001	5.5
p-Xylene	0.004	0.009-1.7	0.999	8.9 (n=70)	117	0.001	4.9
o-Xylene	0.005	0.02-1.7	0.999	6.9 (n=63)	90	0.002	4.7
Bromoform	0.002	0.006-5.8	0.999	5.7 (n=84)	94		
2-Methylisoborneol	0.03	0.1-2.0	0.999	5.5 (n=49)	94	0.001	5.6
Geosmin	0.06	0.1-2.0	0.999	5.1 (n=49)	88	0.002	6.1

MDL: Method detection limit
Ref: Laaks J, Jochmann MA, Schilling B, Schmidt TC ; Anal. Chem. 2010, 82, 7641-7648

Further application examples

Environmental

In-Tube Extraction of Volatile Organic Compounds from Aqueous Samples: An Economical Alternative to Purge and Trap Enrichment

Jens Laaks,† Maik A. Jochmann,*,†
Beat Schilling, and Torsten C. Schmidt†
Anal. Chem. 2010, 82, 7641–7648

Clinical

Headspace In-Tube Extraction Gas Chromatography–Mass Spectrometry for the Analysis of Hydroxylic Methyl-Derivatized and Volatile Organic Compounds in Blood and Urine

Ilpo Rasanen, Jenni Viinamäki, Erkki Vuori, and Ilkka Ojanperä*
J Analytical Toxicology, 34, 2010, 113-121

Food

In-tube Extraction and GC–MS Analysis of Volatile Components from Wild and Cultivated sea buckthorn (Hippophae rhamnoides L. ssp. Carpatica) Berry Varieties and Juice

Sonia A. Socaci,a Carmen Socaciu,a* Maria Tofan,a Ioan V. Ratib and Adela Pinteaa - Phytochem. Anal. 2013, 24, 319–328

Automated and quantitative headspace in-tube extraction for the accurate determination of highly volatile compounds from wines and beers

Julián Zapata, Laura Mateo-Vivaracho, Ricardo Lopez, Vicente Ferreira*
J. Chromatography A, 1230 (2012) 1– 7

Chemical

Microwave-assisted nonionic surfactant extraction of aliphatic hydrocarbons from petroleum source rock

A. Akinlua[a],*, M.A. Jochmann[b], J. Laaks[b], A. Ewert[b], T.C. Schmidt[b] - Analytica Chimica Acta 691 (2011) 48–55

ENVIRONMENTAL FOOD SAFETY

PAL SPME Arrow - New Dimension for SPME Analysis

Since its development by Belardi and Pawliszyn in 1989, Solid-Phase Microextraction (SPME) has become one of the most popular extraction technologies for environmental, food and health analyses. However, the technique remained almost unchanged with some significant drawbacks, such as the limited mechanical stability and small phase volumes of the fibers. All attempts to overcome these limitations have until now been a trade-off between versatility and labor-intense handling.

With the PAL SPME Arrow we present a new technology for micro-extraction, offering trace level sensitivity combined with high mechanical robustness.
The PAL SPME Arrow features an outer diameter of max. 1.5mm, which allows the enclosure of a large sorption phase volumes with a highly resistant and stabilizing inner rod.
The arrow-shaped tip allows smooth penetration of vial septa and injector. In contrast to traditional SPME fibers, the Arrow design fully protects the sorptive material, minimizing adverse influences and loss of analytes during transfer processes. With the PAL RTC and RSI the Arrow SPME microextraction is fully automated.

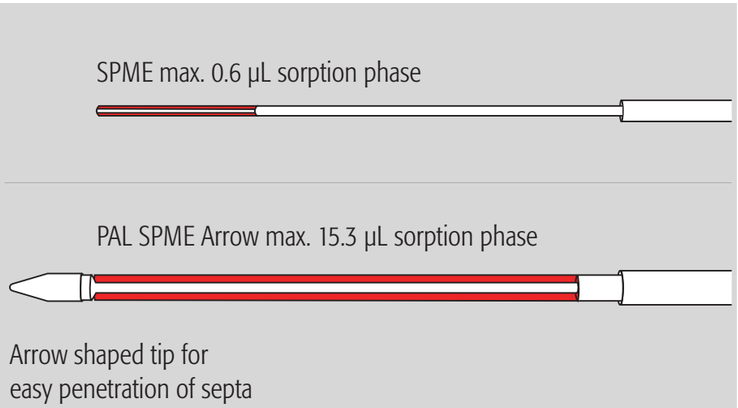


Figure 1: PAL SPME Arrow compared to a coventional SPME fiber: Size and position of the sorptive phases are shown in red.

The PAL SPME Arrow outperforms conventional SPME Fibers

SPME immersion extraction, detection limits

Limits of detection (DIN) (ng L^{-1})

	Naphthalene	Acenaphthylene	Acenaphthen	Anthracene	Pyrene	Benzo(ghi)perylene
Fiber 100/10	3.2	2.6	2.2	3.8	3.2	4.6
Arrow 250/15	0.03	0.04	0.05	0.02	0.02	0.5

Table 1: Limits of detection for six typical polyaromatic hydrocarbons (PAHs) in water, measured by immersion extraction with PAL SPME Arrow or a conventional SPME fiber. PAL SPME Arrow achieves a roughly 40 - 100 x better sensitivity compared to a conventional SPME fiber.

*Conditions:
PAL SPME Arrow, 250 µm PDMS, 15 mm length, 7.7 µL sorption phase
Commercially available SPME fiber, 100 µm PDMS, 10 mm length, 0.6 µL sorption phase
Determined according to German DIN 32645

Aroma analysis of white wines

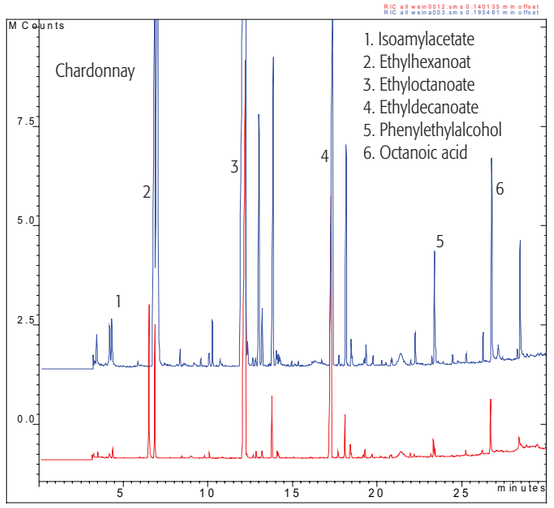


Figure 2: Analysis of Chardonnay aromas:
PAL SPME Arrow (blue 100 µm PDMS 20 mm 0.80 mm OD) compared to a **conventional SPME fiber** (red 100 µm PDMS 10 mm 0.30 mm OD)

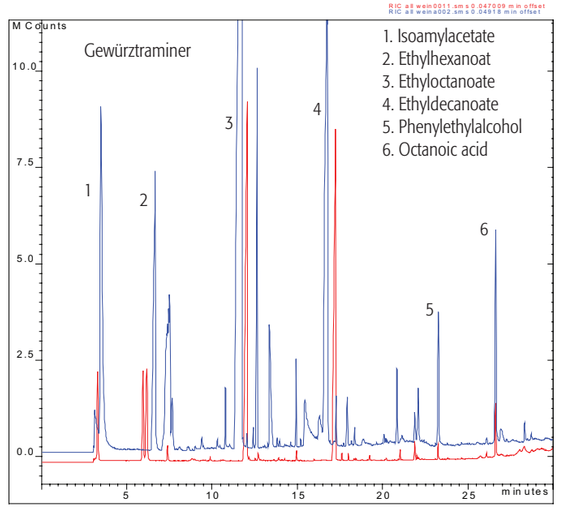


Figure 3: Analysis of Gewürztraminer aromas:
PAL SPME Arrow (blue 100 µm PDMS 20 mm 0.80 mm OD) compared to a **conventional SPME fiber** (red 100 µm PDMS 10 mm 0.30 mm OD)

Analysis of VOCs, EPA 502.2

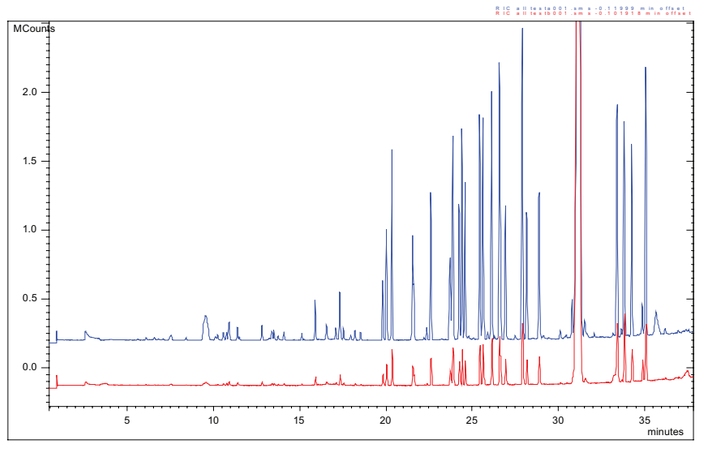


Figure 4:
Analysis of VOCs in water, analogue to EPA 502:
PAL SPME Arrow (blue 100 µm PDMS 20 mm 0.80 mm OD) compared to a **conventional SPME fiber** (red 100 µm PDMS 10 mm 0.30 mm OD)

PAL SPME Arrow sorption materials

currently PDMS, Carbon WR (further materials under development)

The PAL SPME Arrow offers

- Superior SPME sensitivity: typically a 5-fold increase compared to conventional SPME
- Excellent mechanical stability through patented design
- Full protection of sorption phase material
- Highest process safety due to a fully automated SPME process with PAL Systems

PAL Heatex Stirrer - New Mixing and Heating Technology for Sample Preparation and SPME

The efficient mixing of reagents is required for many operations in the laboratory, like sample homogenization, the dissolving of solids or liquid/liquid extraction. For the efficient headspace analysis of liquid samples a rapid exchange between the liquid and the gas phase (headspace) is required. Often magnetic stirrers are applied to achieve mixing. However, especially at higher speeds stir bars tend to loose contact to the magnet and stop turning. This problem is aggravated when solids are added to the sample liquid which is common practice, e.g. the addition of salts to the liquid to shift the equilibrium. Furthermore stir bars make auto-sampling cumbersome since a bar has to be added to every sample vial manually. Vortex mixers offer effective stirring, but cannot be used for SPME sampling.

The powerful PAL Heatex Stirrer mixes samples rapidly applying cycloid shaped mixing pattern without the need for stir bars. For SPME headspace and immersion sampling the special design (pat. pending) ensures that the delicate fiber is not damaged (see fig. 3).

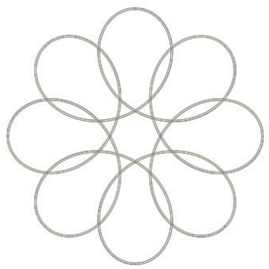


Figure 2: Flower power for stirring: cycloidal mixing patterns.

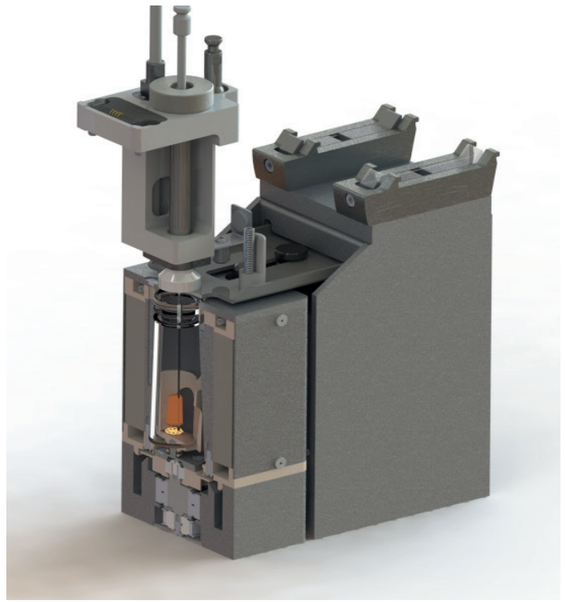


Figure 1: Cutaway view of the Heatex Stirrer Module with SPME tool.

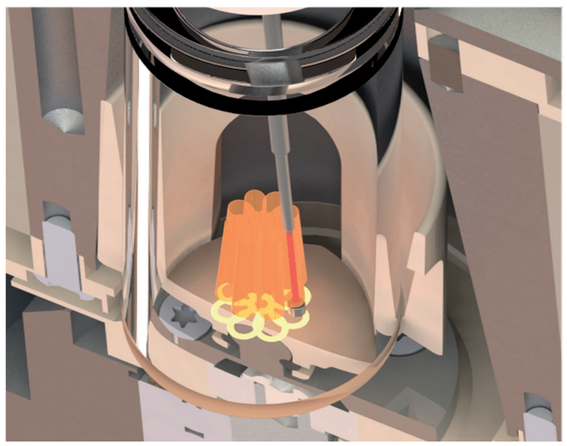


Figure 3: Motion of a liquid (orange) when applying a cycloidal mixing pattern (yellow). The entire volume of the liquid is mixed efficiently. The integrity of the SPME fiber (red) is not compromised.

Specifications of the PAL Heatex Stirrer Module

- Temperature Range 40 - 150 °C
- Stirring Speed 0 - 160 rpm (0-1370 cycloidal loops)
- Dimensions (L x W x H) 190 mm x 85 mm x 160 mm

The PAL Heatex Stirrer: Performance and unsurpassed handling

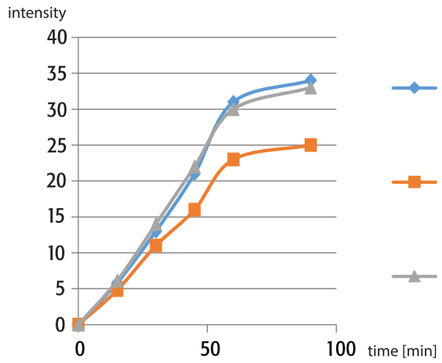


Diagram 1: Immersion SPME saturation curves of pyrene in water. The Heatex Stirrer at 160 rpm (blue curve) is as efficient as the magnetic stirrer at 1250 rpm.

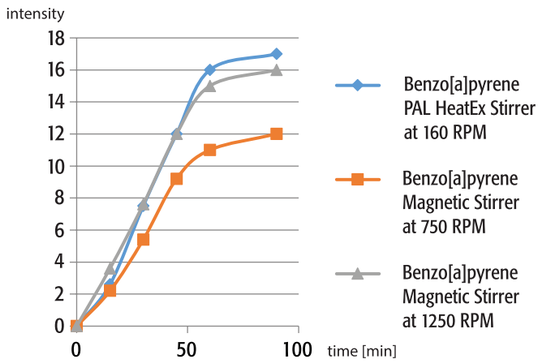


Diagram 2: Immersion SPME saturation curves of benzo[a]pyrene in water. The Heatex Stirrer at 160 rpm (blue curve) is as efficient as the magnetic stirrer at 1250 rpm.

Figure 4: The PAL Heatex Stirrer (left) gives superior results for liquid/liquid extractions, i.e. smaller droplets and hence more intense exchange between organic and aqueous layer when compared to liquid/liquid extraction with a magnetic stirrer at 1000 rpm (right).

With better performance at lower stirring speeds compared to conventional magnetic stirrers, the PAL Heatex Stirrer offers full integration into the PAL3 Sytem. There is no need for magnetic stir bars or heating bathes making automated stirring of samples easy and convenient.

The PAL Heatex Stirrer offers:

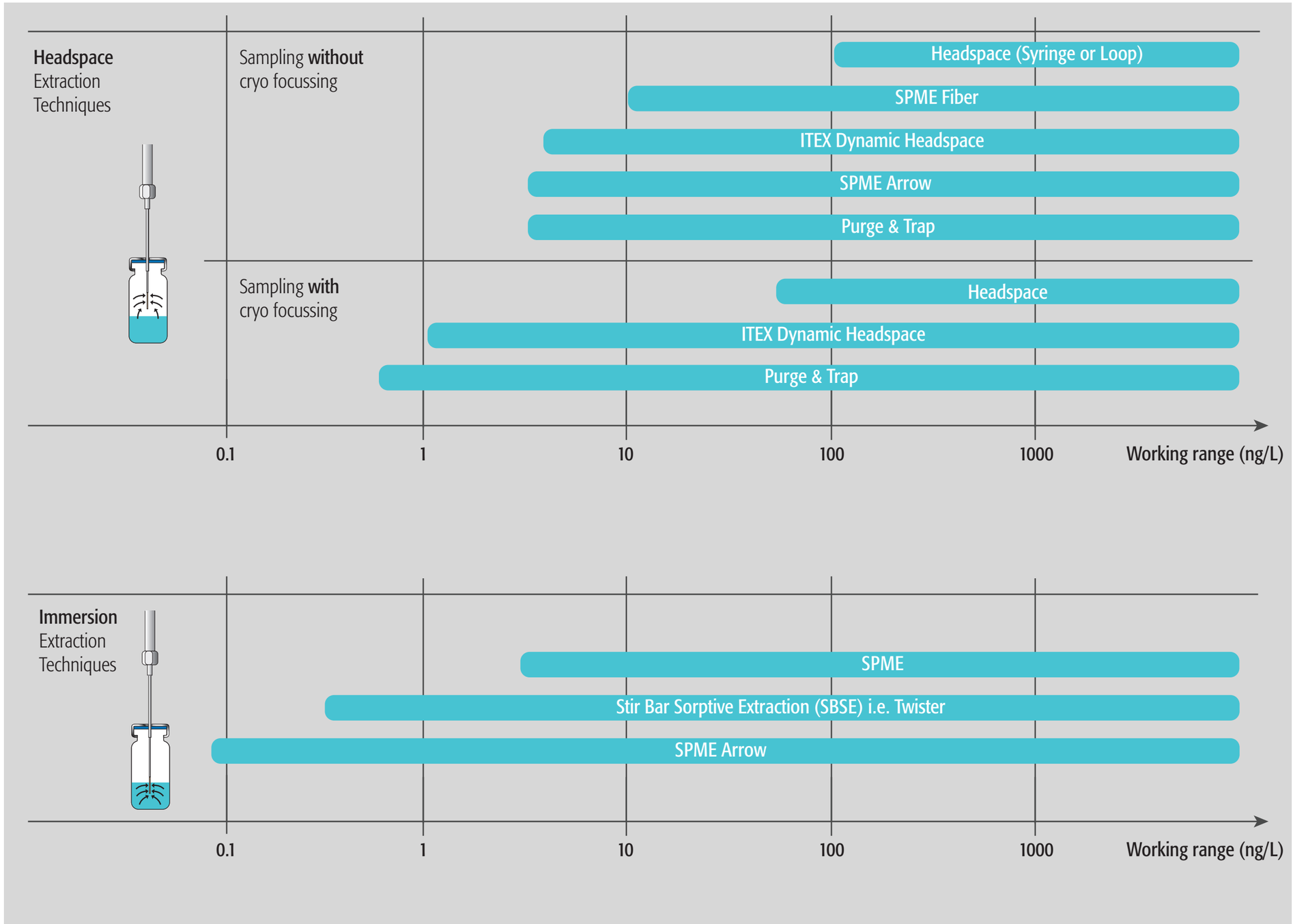
- Rapid equilibration through effective stirring for head-space and immersion SPME sampling while ensuring the integrity of the fiber
- Efficient dissolution of solids, temperature controlled
- Liquid/liquid extraction
- Stirring/heating for derivatization reactions
- No stir bar required, constant stirring also with samples containing solids
- Precise control of the equilibration temperature 40-150 °C
- Software controlled, temperature and stirring speed are logged
- Compact size

How do different GC extraction techniques compare?

The two diagrams on the right outline the working ranges of the different techniques for GC headspace (Fig.1) or immersion extractions (Fig 2).

For extractions and sample preparation PAL System offers the necessary tools to achieve the required sensitivities:

PAL Headspace Tool
PAL SPME Fiber
PAL SPME Arrow
PAL ITEX Dynamic Headspace Tool



For more information on PAL System Tools visit:
http://www.palsystem.com/index.php?id=284

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