Robustness of SPME Arrow Immersion Sampling: Polycyclic Aromatic Hydrocarbons in Drinking Water

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PAL SYSTEM
Ingenious sample handling

Abstract

Analyzing polycyclic aromatic hydrocarbons (PAHs) in drinking water becomes challenging especially for hard water (high mineral content water) and/or when sodium thiosulfate being added for treating chlorine content in drinking water during analysis. In this article, repeatability for determination of PAHs in drinking water using SPME Arrow (PDMS) immersion technique with gas chromatography mass spectrometer (GC/MS) was carried out. Single SPME Arrow had been used in this experiment to determine its durability. The repeatability (n=100) which characterized as %RSD was less than 10.93% for all analytes, ranged between 1.74 % - 10.93 %. The relative peak area of the 100th injection against the 1st injection peak area for all analytes ranged between 0.600 to 0.947; indicating SPME Arrow fiber is dutiful for at least 100 injections with immersion technique. In conclusion, fully automated SPME Arrow immersion technique with GC/MS analysis is an excellent option to analyze PAH compounds in drinking water; with higher throughput and robustness.

Keywords

Polycyclic aromatic hydrocarbons (PAHs), solid phase micro-extraction (SPME), SPME Arrow, immersion, PDMS

Introduction

Robustness of SPME and SPME Arrow used for immersion sampling is much lesser compared headspace sampling. During immersion extraction, SPME Arrow phase is fully contacted with sample matrix; e.g. drinking water and tap water which containing minerals and residual chlorine. This will affect SPME and SPME Arrow performance. In this poster, repeatability for determination of PAHs in drinking water using SPME Arrow immersion technique with GC/MS was carried out. Automated SPME Arrow workflow was optimized and one (1) SPME Arrow (PDMS) was used throughout the analysis to determine SPME Arrow durability.

Chemicals

- Pak-Mix 16 in Cyclohexane (Neochema GmbH)
- Internal Standards Mix 25 in Acetone (Dr. Ehrenstorfer GmbH)
- Benzo[a]pyrene D12 in Cyclohexane (Dr. Ehrenstorfer GmbH)
- Sodium Thiosulfate (Sigma Aldrich)
- Acetone (> 99.5% Reagent grade) (Sigma Aldrich)
- Water (HPLC grade) (J.T. Baker)

Test Solution

Switzerland tap water (drinkable, 250mg/L total minerals) spiked with

- 16 PAH compounds (100.8306 pg/mL for each PAH)
- 4 deuterated PAH compounds (136.4374 pg/mL for each deuterated PAH)

Instrumentations

- PAL RTC 120 system with 1.1 mm Ø 100 µm PDMS SPME Arrow (ARR11-P-100/20-P1)
- Shimadzu GC-2010 with Restek Rtxi-5MS Column (30 m X 0.25 mmID X 0.25 µm)
  - Inlet Temperature: 280ºC
  - GC Carrier: Helium at 1.0 mL/min (Splitless)
  - GC Oven: Initial 35ºC (5 minutes); 40ºC/min to 150ºC; 20ºC/min to 250ºC; 10ºC/min to 305ºC (22 minutes)
- GCMS-QP2010
  - Interface Temperature: 310ºC
  - Source Temperature: 250ºC
  - Mode: EI with SIM

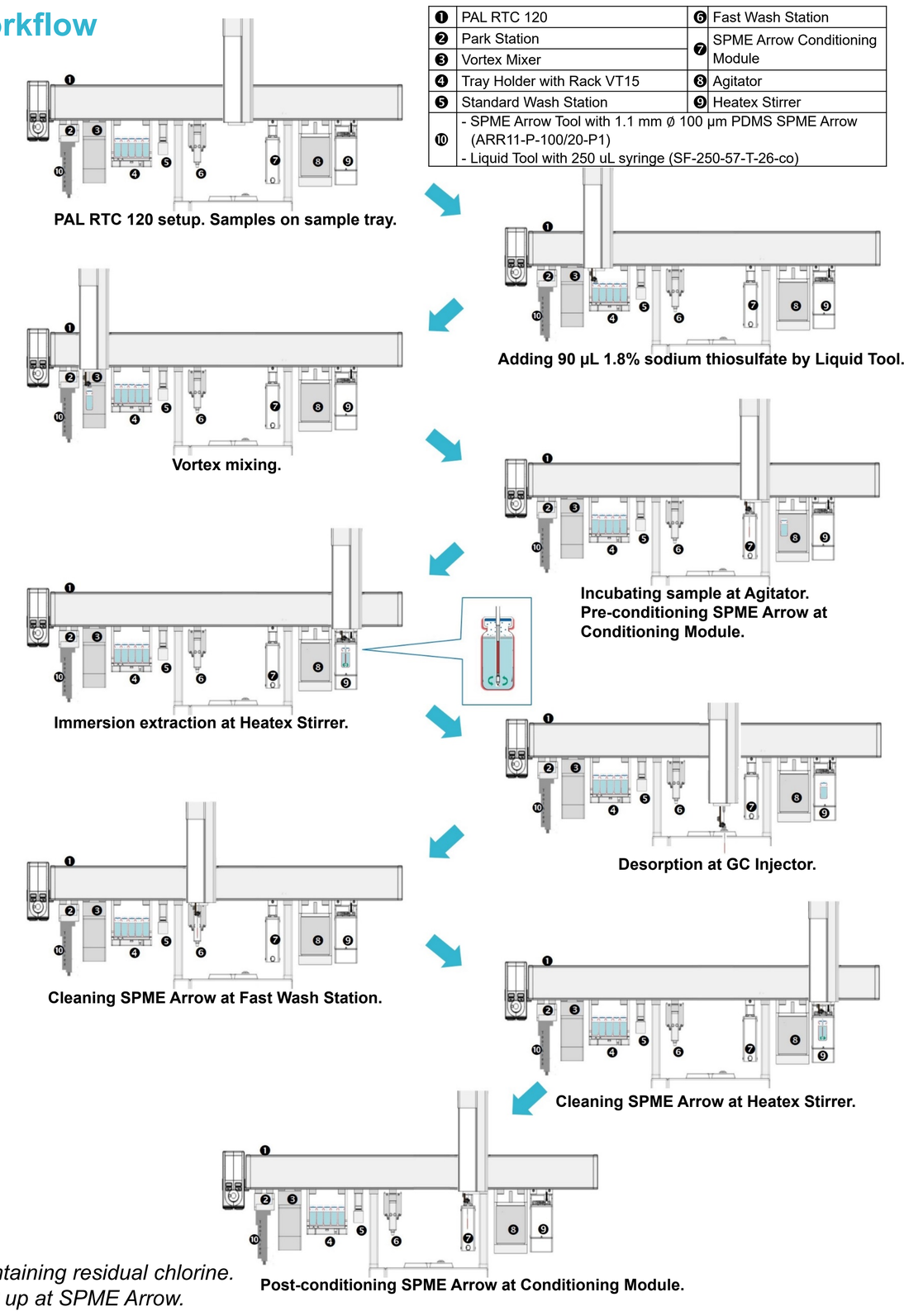
Table 1: Analytes details includes compound name, retention time and quantify ion.

Compound Name	Abbrev.	Target/ ISTD	Group	Retention Time, minutes	Quant. Ion, m/z
Naphthalene	N	Target	1	9.241	128
Acenaphthylene	Acy	Target	1	10.688	152
Acenaphthene-d10	Ace-d10	ISTD	1	10.832	164
Acenaphthene	Ace	Target	1	10.863	153
Fluorene	F	Target	1	11.418	166
Phenanthrene-d10	P-d10	ISTD	2	12.482	188
Phenanthrene	P	Target	2	12.508	178
Anthracene	Ant	Target	2	12.569	178
Fluoranthrene	Fl	Target	3	14.004	202
Pyrene	Pyr	Target	3	14.326	202
Benz(a)anthracene	BaAnt	Target	3	16.258	228
Chrysene-d12	Chr-d12	ISTD	3	16.275	240
Chrysene	Chr	Target	3	16.320	228
Benz(b)fluoranthene	BbFl	Target	4	18.204	252
Benz(k)fluoranthene	BkFl	Target	4	18.252	252
Benz(a)pyrene-d12	BaPyr-d12	ISTD	4	18.762	264
Benz(a)pyrene	BaPyr	Target	4	18.803	252
Indeno(1,2,3-cd)pyrene	Ipyr	Target	4	21.349	276
Dibenz(a,h)anthracene	DBahAnt	Target	4	21.436	278
Benzo(g,h,i)perylene	BghiPer	Target	4	22.043	276

Automated SPME Arrow Workflow

15 mL sample in 20 mL vial
⇓
① Add 90 µL 1.8% sodium thiosulfate
⇓
Vortex Mixing for 20 seconds
⇓
Sample vial transferred to Agitator. Incubating at 35ºC for 10 minutes.
⇓
SPME Arrow moves to Conditioning Module. Pre-conditioned at 250ºC for 10 minutes.
⇓
Sample vial transferred to Heatex Stirrer
⇓
Sample extraction: SPME Arrow immersed in sample solution at 35ºC for 30 minutes with 1500 rpm stirring.
⇓
SPME Arrow desorption at GC inlet for 5 minutes
⇓
Sample vial transferred back to Sample Tray
⇓
SPME Arrow being cleaned with distilled water at Fast Wash Station for 2 minutes.
⇓
② SPME Arrow being cleaned with distilled water at Heatex Stirrer for 2 minutes.
⇓
SPME Arrow being rinsed with distilled water at Fast Wash Station for 30 seconds.
⇓
SPME Arrow moves to Conditioning Module. Post-conditioned at 250ºC for 5 minutes.

❶	PAL RTC 120	❻	Fast Wash Station
❷	Park Station	❼	SPME Arrow Conditioning Module
❸	Vortex Mixer		
❹	Tray Holder with Rack VT15	❽	Agitator
❺	Standard Wash Station	❾	Heatex Stirrer
❿	- SPME Arrow Tool with 1.1 mm ø 100 µm PDMS SPME Arrow (ARR11-P-100/20-P1) - Liquid Tool with 250 uL syringe (SF-250-57-T-26-co)		



① Adding reducing agent for water samples containing residual chlorine.
② Intensive cleaning to eliminate minerals build up at SPME Arrow.

Figure 1: Automated SPME Arrow workflow modified for PAHs in water analysis.

Analysis

- 15 mL Test Solution in 20 mL vial
- Replicates of 100 samples analyzed using one (1) SPME Arrow

Results

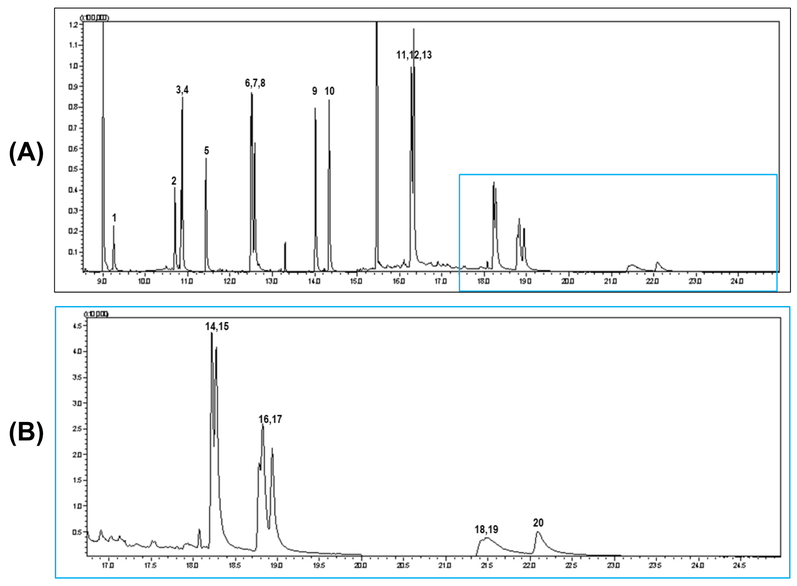


Figure 2: TIC Chromatogram.

(A) Full TIC chromatogram.
(B) Zoom in TIC chromatogram at 17.5 minutes to 25.0 minutes.

***1**-N **2**-Acy 3-Ace-d10 **4**-Ace **5**-F **6**-P-d10 **7**-P **8**-Ant **9**-Fl **10**-Pyr **11**-BaAnt **12**-Chr-d12 **13**-Chr **14**-BbFl **15**-BkFl **16**-BaPyr-d12 **17**-BaPyr **18**-Ipyr **19**-DBahAnt **20**-BghiPer*

Conclusions

SPME Arrow is robust to be used for immersion sampling technique with fully automated workflow. In PAHs in drinking water analysis, adequate cleaning procedures for SPME Arrow ensure good reproducibility results with satisfaction GC-MS response obtained for 100 sample injections.

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Table 2: Reproducibility (%RSD) of relative peak area (corrected with corresponding ISTD) for each analyte (n=100).

Analyte Name/ISTD	%RSD of Relative Peak Area	Analyte Name/ISTD	%RSD of Relative Peak Area
N/Ace-d10	4.68	BaAnt/Chr-d12	2.27
Acy/Ace-d10	3.35	Chr/Chr-d12	2.15
Ace/Ace-d10	1.81	BbFl/BaPyr-d12	4.17
F/Ace-d10	2.86	BkFl/BaPyr-d12	4.45
P/P-d10	1.74	BaPyr/BaPyr-d12	2.35
Ant/P-d10	3.87	Ipyr/BaPyr-d12	9.54
Fl/P-d10	2.25	DBahAnt/BaPyr-d12	10.93
Pyr/P-d10	2.75	BghiPer/BaPyr-d12	7.60

Table 3: Ratio for Peak Area of the 100th injection against the 1st injection.

Compound	Ratio	Compound	Ratio	Compound	Ratio
N	0.832	Ant	0.854	BkFl	0.826
Acy	0.945	Fl	0.921	BaPyr-d12	0.700
Ace-d10	0.909	Pyr	0.921	BaPyr	0.724
Ace	0.839	BaAnt	0.846	Ipyr	0.678
F	0.858	Chr-d12	0.922	DBahAnt	0.600
P-d10	0.947	Chr	0.904	BghiPer	0.710
P	0.893	BbFl	0.772		

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