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THE QUEEN'S AWARDS FOR ENTERPRISE: INTERNATIONAL TRADE 2015

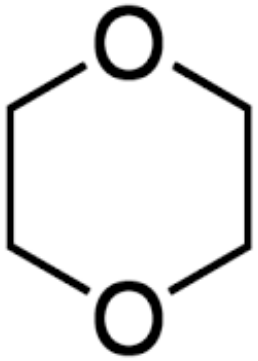
Increasing the sensitivity for 1,4-dioxane analysis in drinking water

Jan Peter Mayser
Rebecca Cole
Nicola Watson
Rachael Szafnauer

1,4-dioxane

Importance

- 1,4-dioxane is an emerging contaminant
- The US-EPA acknowledges that people may be exposed to 1,4-dioxane via drinking water, as well as from ambient air and soil
- Toxic Substances Control Act (TSCA) manages the exposure from water
- The 1,4-dioxane is one of the first 10 high-priority chemical assessments the EPA conducted under 2016 revisions to TSCA.

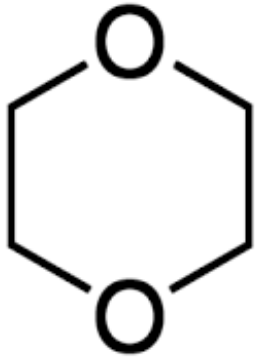


1,4 Dioxane

1,4-dioxane

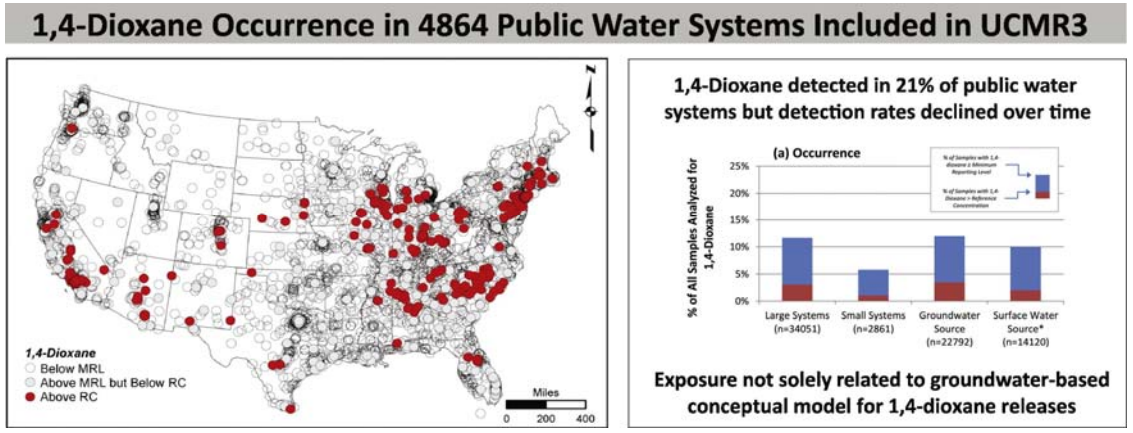
Toxicity

- Classified by US EPA as "likely to be carcinogenic to humans" by all routes of exposure.
- 1,4-Dioxane is frequently present at sites with TCA contamination



1,4 Dioxane

- Why so important in drinking water?
  - It is short-lived in the atmosphere, with an estimated 1- to 3-day half-life due to photooxidation



Adamson, D. T. *et al.* 1,4-Dioxane drinking water occurrence data from the third unregulated contaminant monitoring rule. *Sci. Total Environ.* **596**–**597**, 236–245 (2017).

1,4-dioxane

Where can it be found?

As a solvent stabilizer for TCA and other chlorinated solvents

As a solvent in lacquers paints, paints, pharma, etc.

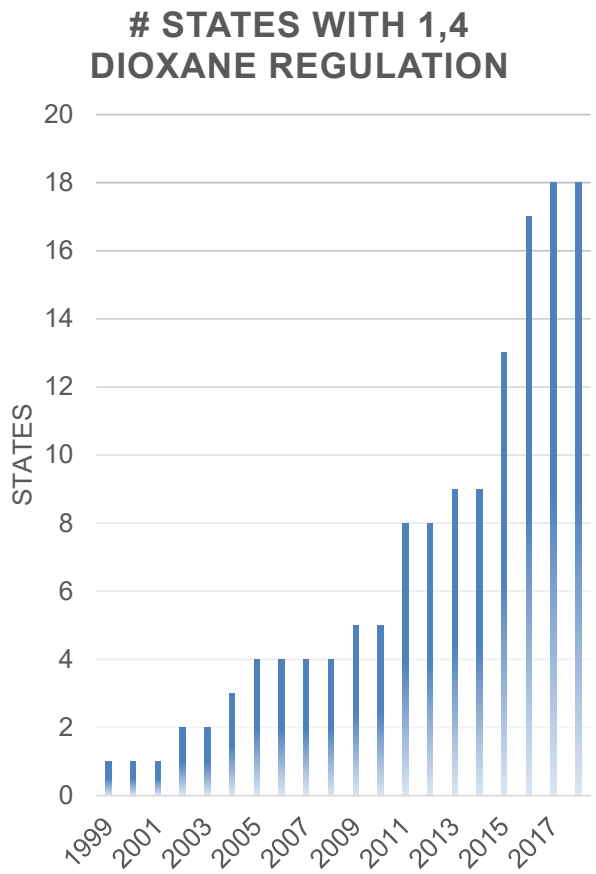
As a contaminant in ethoxylated products (surfactants, detergents)

In cosmetics as a stabilizer

Guidelines in the US

by the various US states

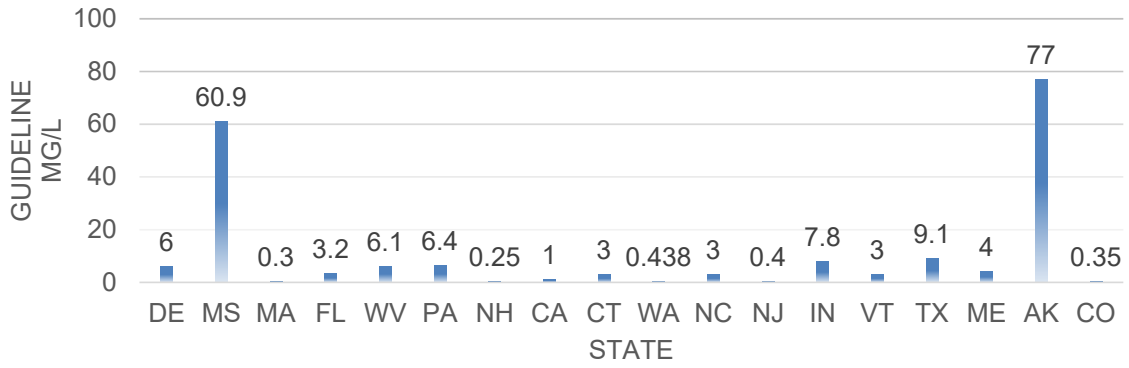
- Number of States with specific 1,4 dioxane regulations have increased
- EPA has established non-enforceable screening levels for residential water use at 0.67 µ/L.

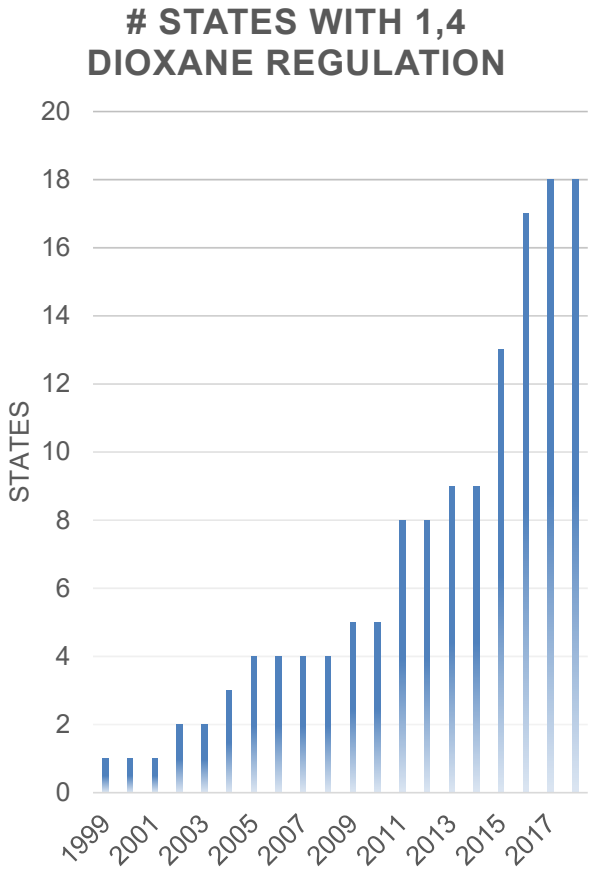


Guidelines in the US

by the various US states

- Number of States with specific 1,4 dioxane regulations have increased
- EPA has established non-enforceable screening levels for residential water use at 0.67 µ/L.
- Various guideline limits from the 18 states with guidelines

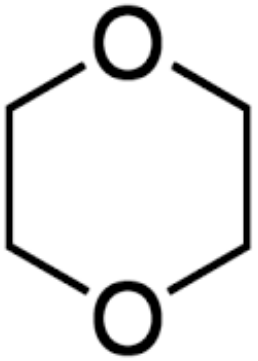




Analytical challenges

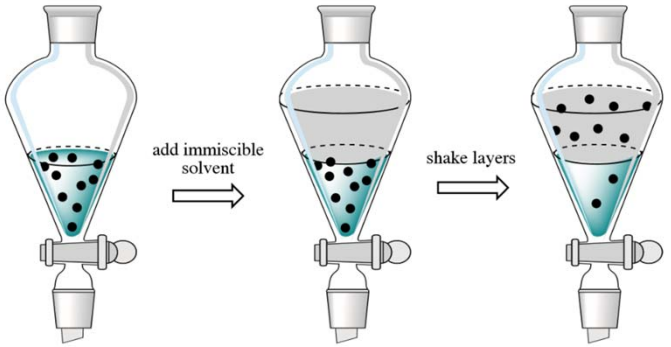
1,4-dioxane

- High water solubility
- High SVOC vapor pressure
  - ➢ poor liquid/liquid extraction



1,4 Dioxane

- 1,4-dioxane has a 50-100x lower RRF (Relative Response Factor) than other compounds in the 8260 compound mix



Centri®

Automated extraction and enrichment

HiSorb™ high-capacity sorptive extraction

Fully automated immersive or headspace sampling of liquids and solids.

SPME–trap

Fast and sensitive sample extraction, with a range of selective fiber types.

Headspace–trap

Versatile sampling from solids and liquids contained in regular headspace vials.

Thermal desorption and direct thermal extraction

The ideal option for analysis of trace VOCs and SVOCs.

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SPME and SPME–trap on Centri

- A simple solvent-free technique for extracting and concentrating VOCs and SVOCs, SPME is often used for headspace extraction, concentration and injection.

- SPME workflows are highly automated and can be used for analytes with a wide boiling point range, including volatiles and semi-volatiles

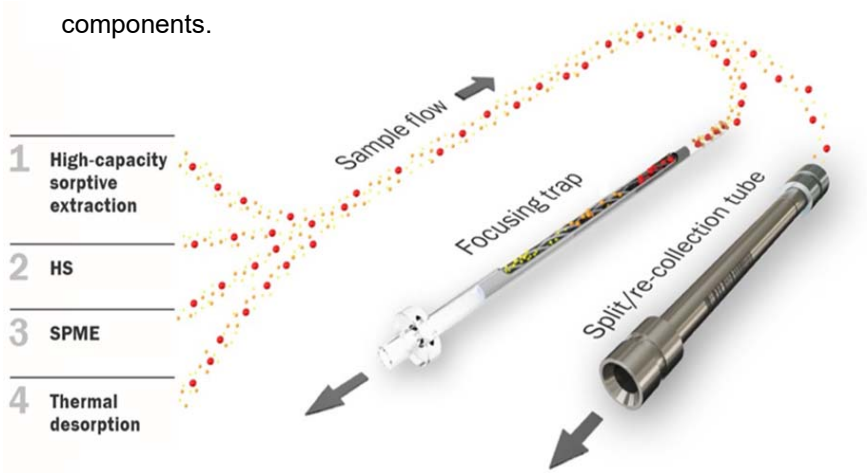
- With Centri, for the first time, SPME fibers can be desorbed to the cold focusing trap for:
  - Optimisation of VVOC peak shape
  - Increased sensitivity, through multiple samplings and desorptions to the focusing trap prior to GC–MS injection
  - Further selectivity-tuning by selecting sorbents for the focusing trap

Innovation at the heart of Centri

Discover more. Deliver more: with advanced cryogen-free focusing

Stage 1: Focusing and enrichment

- All techniques benefit from use of the focusing trap at the heart of Centri.
- Up to 1000-fold sensitivity enhancement using cryogen-free focusing.
- Ability to load multiple sample extractions, increasing sensitivity further.
- Selective elimination of water & volatile interferences reveals trace components.



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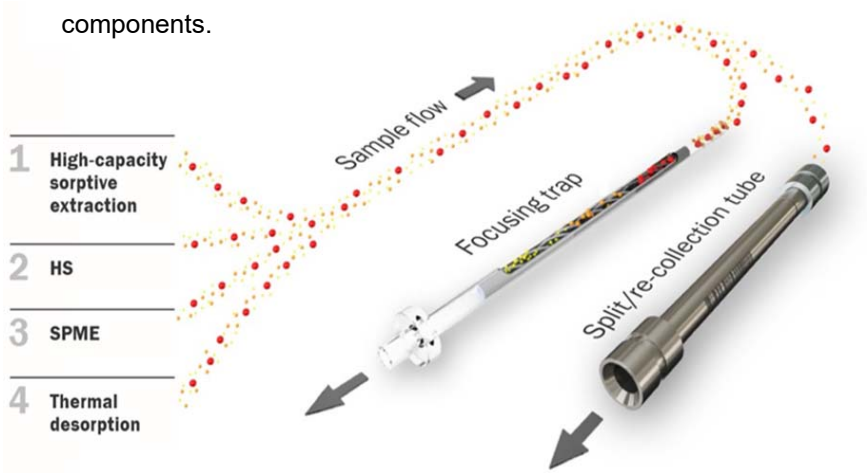
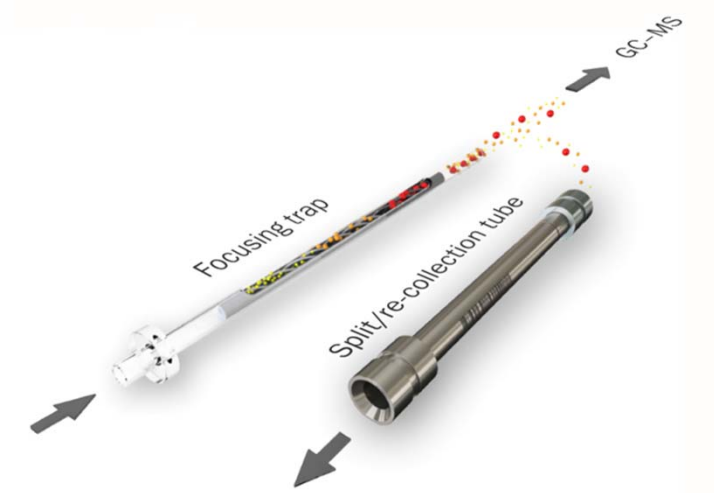


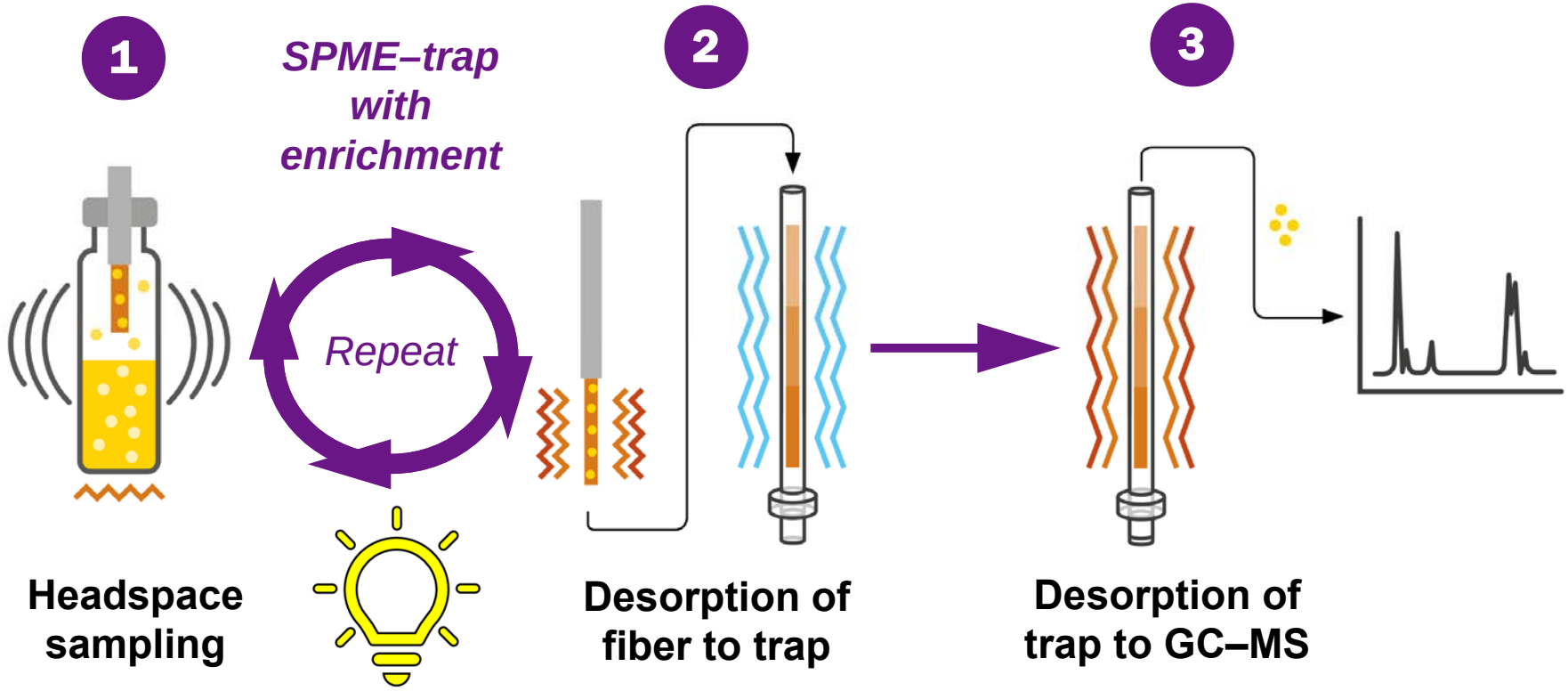
Stage 2: Desorption & GC injection

- Backflush operation allows simultaneous analysis of VVOC/VOC/SVOCs.
- Narrow-bore design and rapid heating rates for fast injection, providing sharp chromatographic peaks.
- Quantitative re-collection, taking a snap-shot of the sample for repeat analysis and more stable sample archiving.



MSE-SPME-trap®

Multi-step-enrichment solid-phase-micro-extraction with trap



Method parameters

Dynamic SPME sampling

- 1,4-dioxane in water, saturated with NaCl
- SPME extractions from headspace
  - Triple phase PDMS/CWR/DVB fibre

- Incubation temperature: 40˚C
- Sampling time per extraction: 15 mins
- Stacked 6 extraction on to the trap

Increasing productivity

Maintaining automated workflow

SPME-workflows are easily automated

With MSE-SPME-trap we can

- use the existing and proven method
- increase the extraction yield

Workflow:

Sampling | Desorption | Pre-concentration

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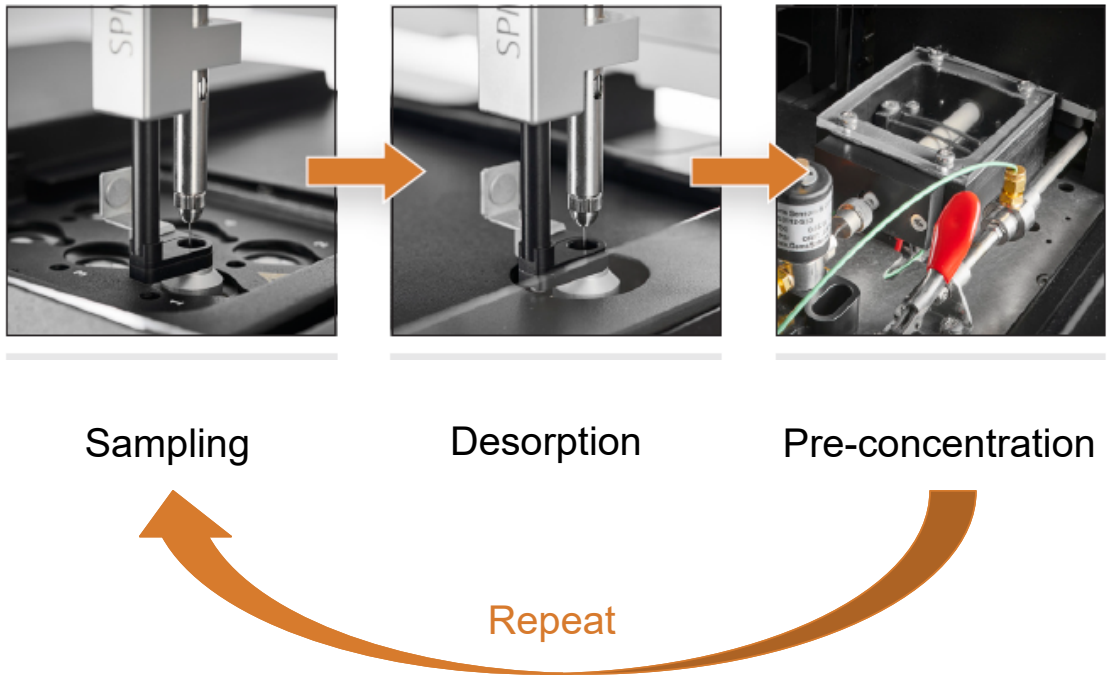
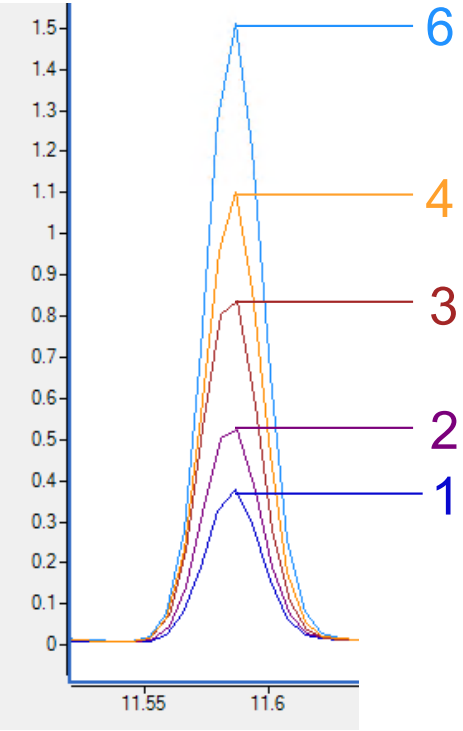


Increasing Sensitivity

multiple extractions



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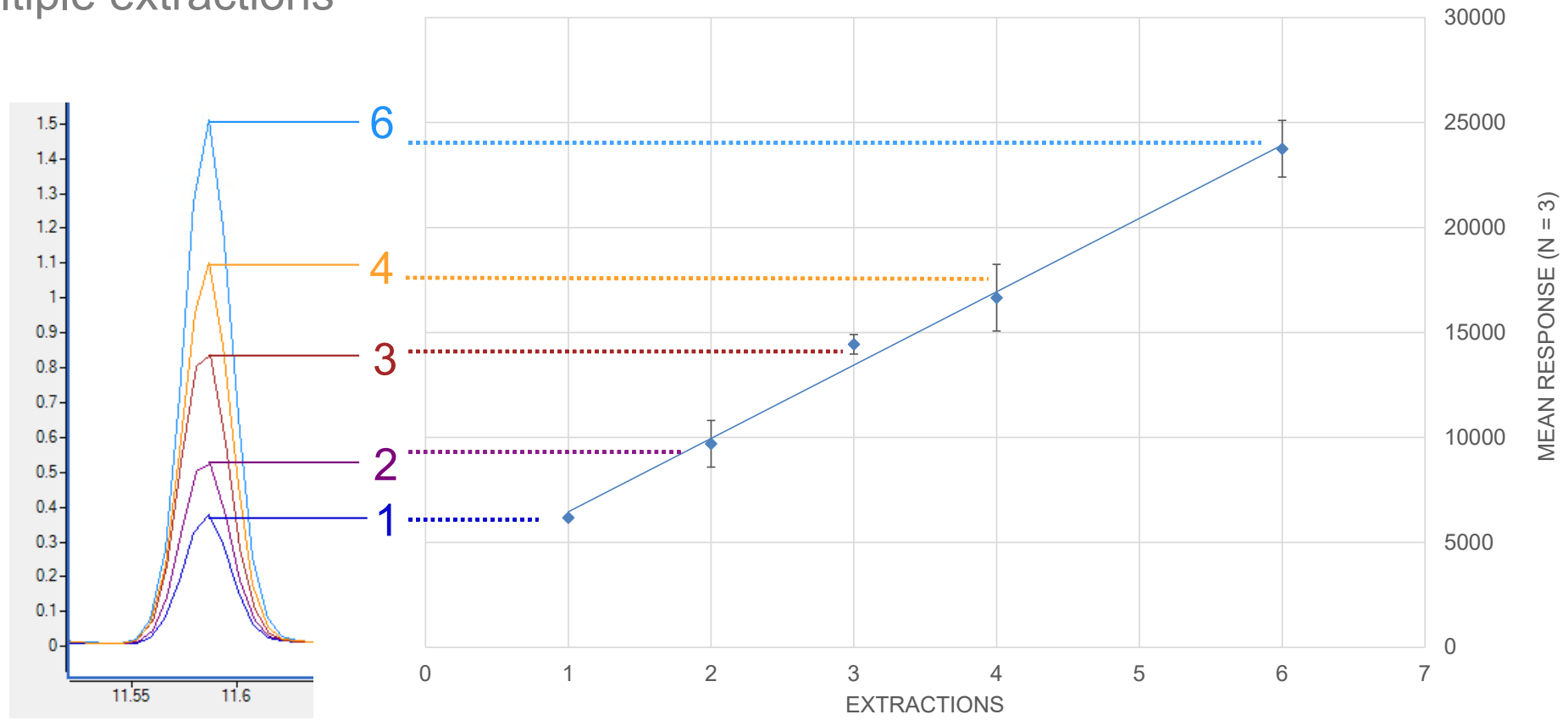
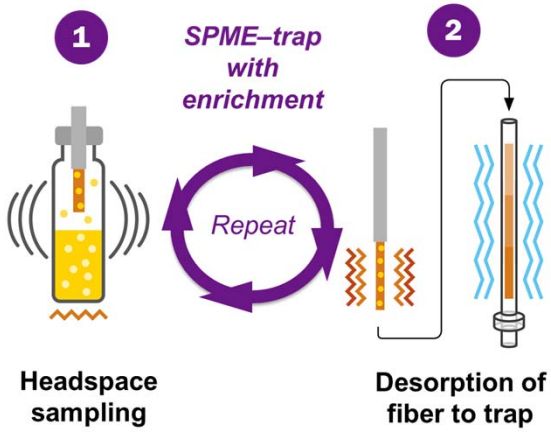


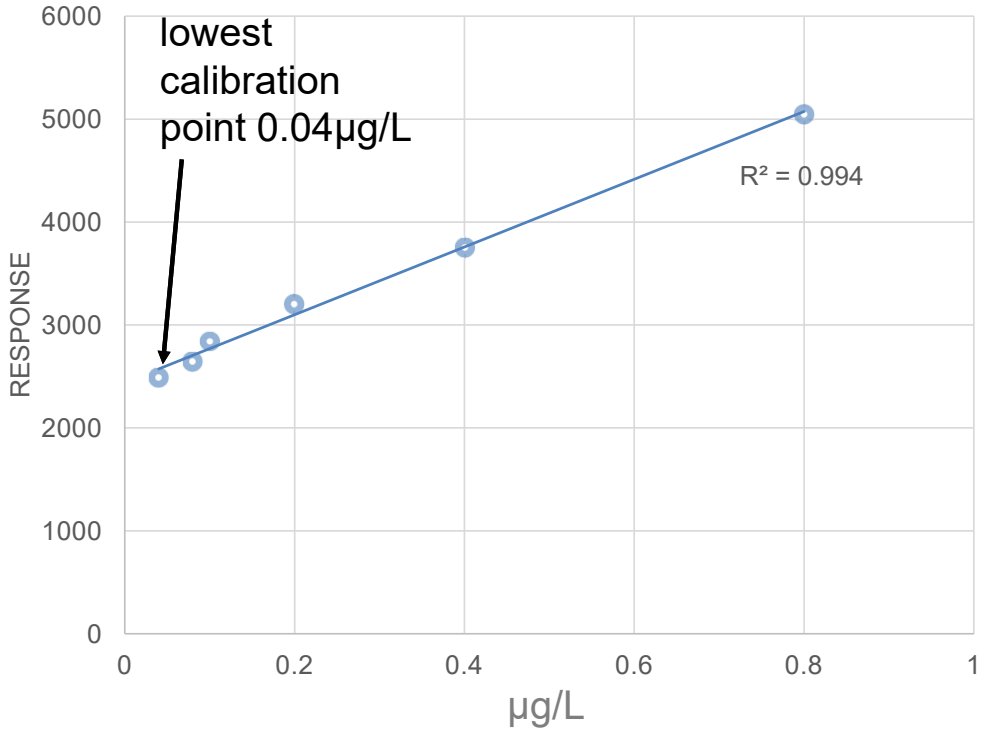
Calibration of 1,4-dioxane

using MSE-SPME-trap

- Six-point calibration curves and R^2 values
- for 6 times enrichment
- the dynamic process increases extraction efficiency



MSE-SPME-trap Calibration curve



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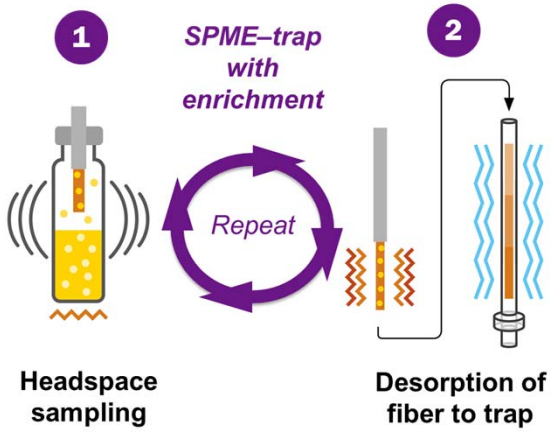

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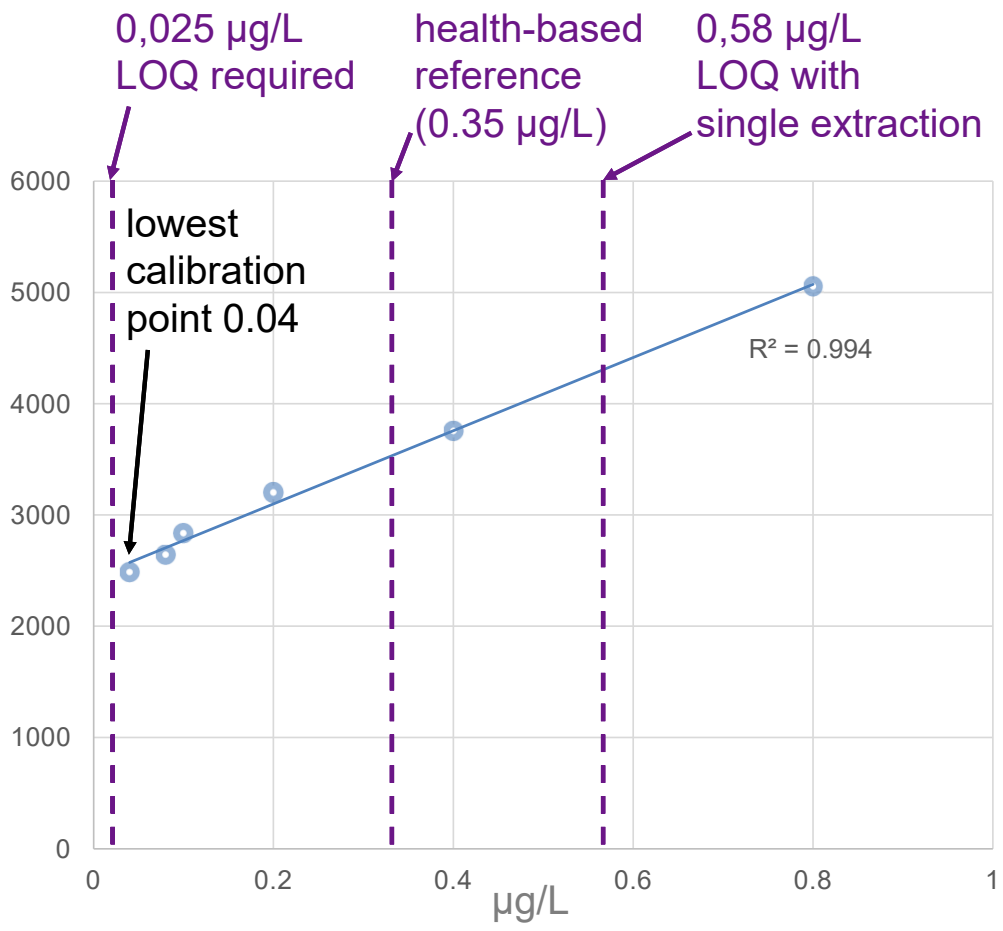

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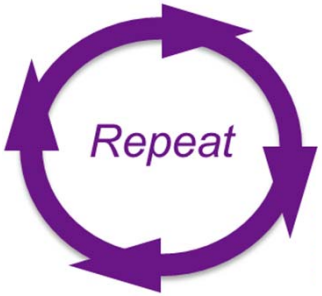
MSE-SPME-trap

Regulated compounds

with MSE-SPME-trap

- the sensitivity of SPME can be strongly enhanced
- other proven methods can easily be adapted to fit new regulations
- this process can be fully automated
- and combined with other methods



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