1,4-Dioxane in drinking water: Increasing the sensitivity for trace-level analysis

Environmental Measurement Symposium 2022

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World-leaders in thermal desorption

SCHAUENBURG Analytics

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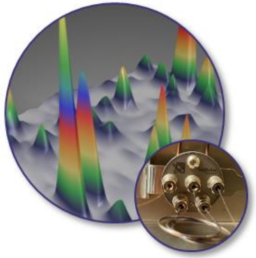
SepSolve Analytical

Sample extraction & enrichment

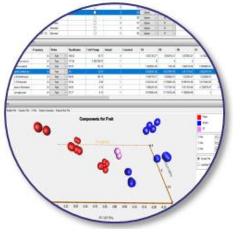
Thermal desorption

Sampling technologies



GC×GC separation

Time-of-flight mass spectrometry



Data mining & chemometrics

1,4-Dioxane: What is it and where can it be found?

As a solvent stabilizer for TCA and other chlorinated solvents

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

As a contaminant in ethoxylated products (surfactants, detergents)

In cosmetics as a stabilizer

1,4-Dioxane: Should we be worried?

PERSISTENT POLLUTANTS

New York restricts 1,4-dioxane in cle and personal care products

State is first in US to limit level of this persistent pollutant in consumer goods

by Cheryl Hogue

December ... 2019

POLLUTION

1,4-Dioxane: Another forever chemical plagues drinking-water utilities

Highly miscible in water, the likely carcinogen is challenging to remove

by Cheryl Hogue

November 8, 2020 | A version of this story appeared in Volume 98, Issue 43

1,4-Dioxane in Cosmetics: A Manufacturing Byproduct

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The FDA has received questions about 1,4-dioxane, a contaminant that may occur in trace amounts in certain cosmetics. The following information is from responses to those questions, scientific literature, and other public sources.

CAMPAIGN for SAFE COSMETICS

A PROJECT OF BREAST CANCER PREVENTION PARTNERS

Regulations Chemicals of Concern Health & Science Reports Safer Cosmetics Companies

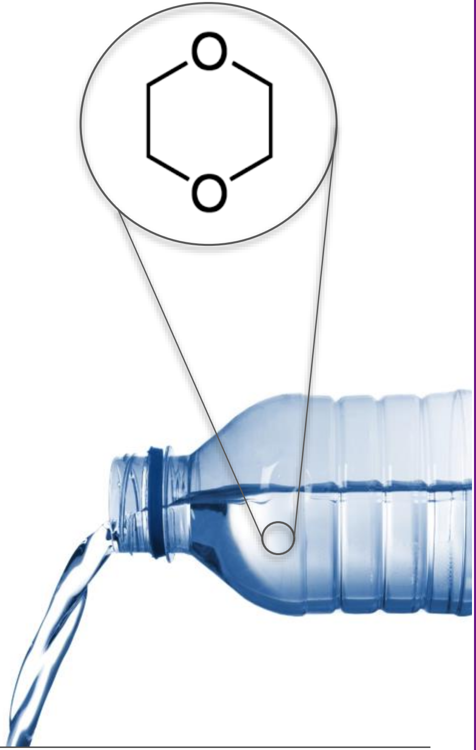
Home / Get the Facts / 1,4-dioxane

1,4-DIOXANE

1,4-Dioxane: An emerging contaminant of concern

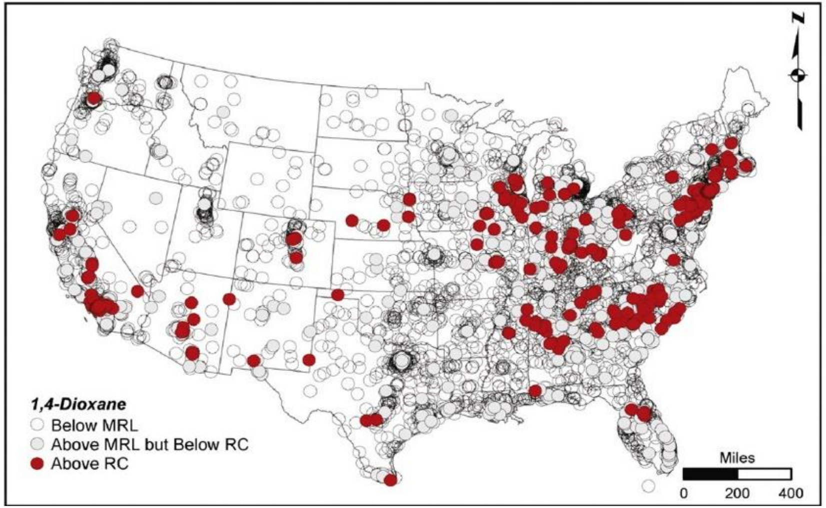
- The USEPA acknowledges that people may be exposed to 1,4-dioxane via drinking water, as well as from ambient air and soil
- Toxic Substances Control Act (TSCA) manages the exposure from water
- 1,4-Dioxane is one of the first 10 high-priority chemical assessments the EPA conducted under 2016 revisions to TSCA
- Classified as “likely to be carcinogenic to humans” by all routes of exposure: US EPA, 2019

1,4 Dioxane

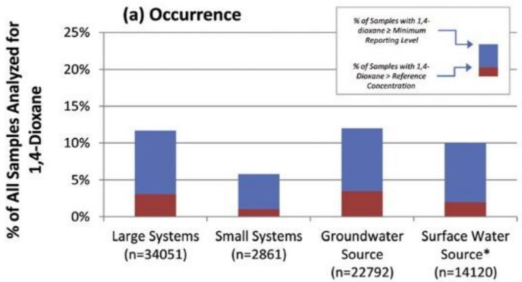


Why a focus on drinking water?

1,4-Dioxane Occurrence in 4864 Public Water Systems Included in UCMR3



1,4-Dioxane detected in 21% of public water systems but detection rates declined over time

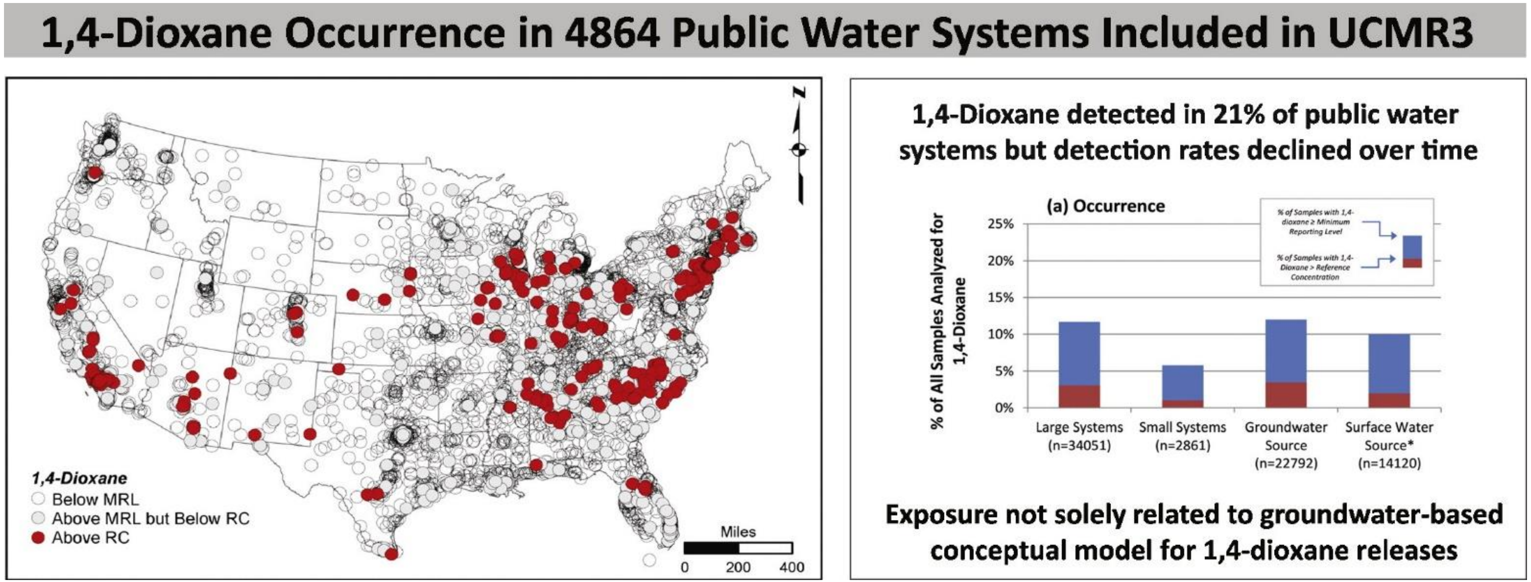


Exposure not solely related to groundwater-based conceptual model for 1,4-dioxane releases

- 1,4-Dioxane has been detected at many public water sites > 0.35 µg/L (red, reference concentration, RC) and even more sites > 0.07 µg/L (blue, min. reporting level, MRL)

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).

Why a focus on drinking water?



- 1,4-Dioxane has been detected at many public water sites > 0.35 µg/L (red, reference concentration, RC) and even more sites > 0.07 µg/L (blue, min. reporting level, MRL)
- **Since all routes of exposure are dangerous, why the huge focus on drinking water?**

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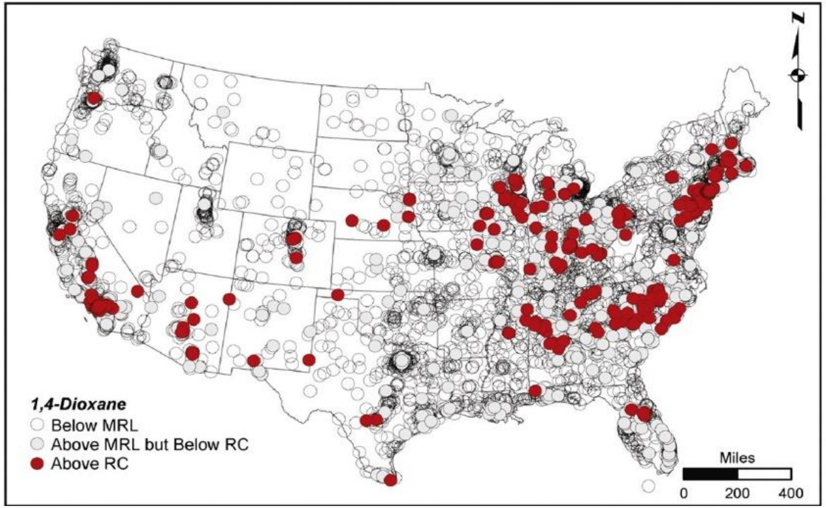

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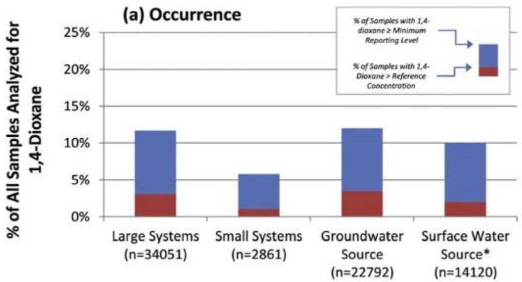

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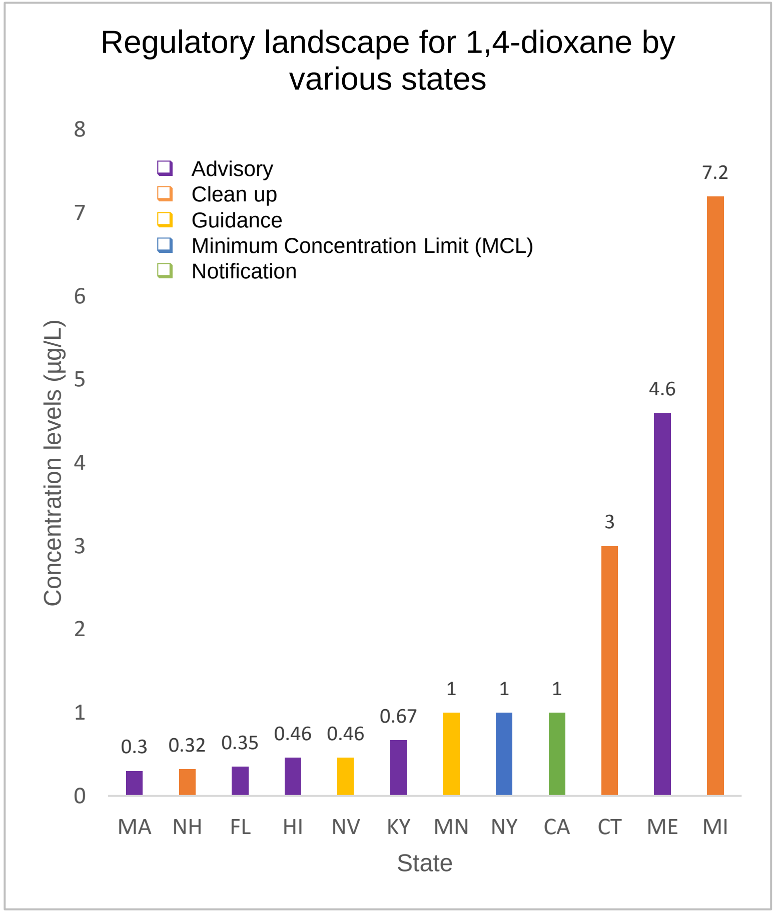
- 1,4-Dioxane has been detected at many public water sites > 0.35 µg/L (red, reference concentration, RC) and even more sites > 0.07 µg/L (blue, min. reporting level, MRL)
- Estimated 1- to 3-day half-life due to photooxidation, short-lived in the atmosphere, while this is not the case when present in water

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).

Guidelines in the US

- No enforceable federal drinking water standard for 1,4-dioxane
- Many states have started regulating[1] (right), but these vary as do the types of reporting required
- EPA has established non-enforceable screening levels for residential water use at 0.46 µg/L
- Intended to provide technical information to state agencies and public health officials
- US EPA Method 522 developed for determination of 1,4-dioxane in drinking water by SPE



1 State-by-State Regulation of 1,4-Dioxane in Drinking Water | Bryan Cave Leighton Paisner - JDSupra

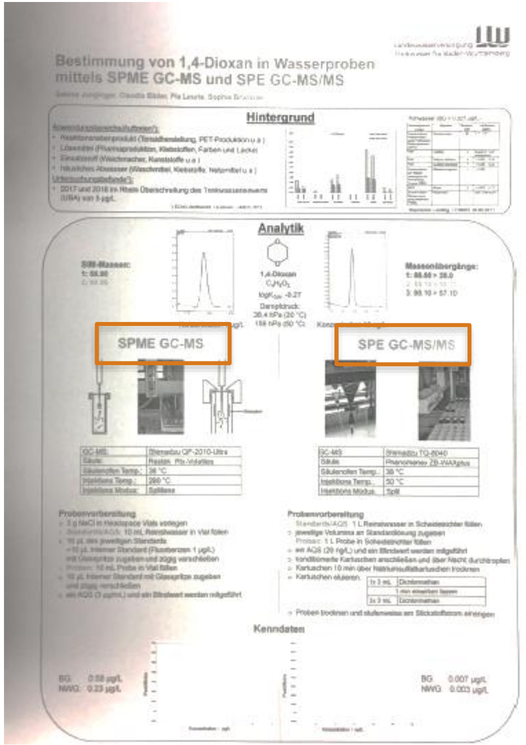
A global issue: Guidelines in Germany

Regulation: Anfrage an Bayerischen Landtag 17/16517 26.06.2017

LOQ: 0.58 µg/L
- SPME method HS–SPME–GC–MS

LOQ: 0.025 µg/L
- German water regulation change (LOQ in surface water)

LOQ: **0.007 µg/L**
- LWV has change to new SPE GC-MS/MS method



German body for the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

Challenges with existing analytical techniques

Determination of 1,4-dioxane in drinking water

- A variety of techniques used
  - Headspace solid-phase microextraction (HS–SPME)
  - Purge-and-trap (P&T)
  - Solid phase extraction (SPE)

- HS–SPME and P&T
  - ✓ Use smaller sample volumes (10s of mLs) and can be automated
  - ✗ Can suffer with limited sensitivity and carryover issues due to sample foaming

- SPE
  - ✓ Can reach much lower detection limits thanks to improved preconcentration, with GC–MS in SIM or triple quad MS
  - ✗ Manual, lengthy extraction process using hazardous solvents such as dichloromethane (DCM)
  - ✗ Potential for matrix interferences

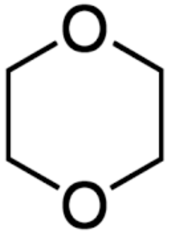
Need a method which is:

- Short
- Automated
- Reproducible

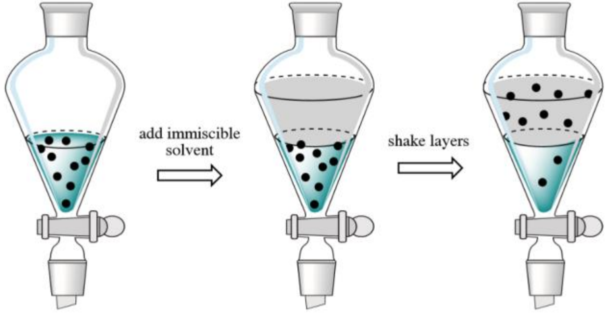
1,4-Dioxane: A challenging compound

- Polar, leading to high water solubility
- Similar boiling point to water, 101ºC
- Poor liquid/liquid extraction

- Has a 50-100x lower RRF (Relative Response Factor) than other, similar volatility compounds
- Sensitivity levels are inherently lower



1,4-Dioxane



How do we tackle this?

Using focusing trap technology and multi-step enrichment (MSE)

LOQ: 0.58 µg/L

- SPME method HS–SPME–GC–MS

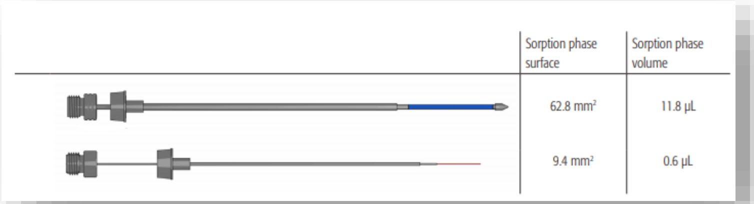
LOQ: 0.025 µg/L

- German water regulation change (LOQ in surface water)

LOQ: **0.007 µg/L**

- LWV has change to new SPE GC-MS/MS method

- Can we modify the ‘old’ HS–SPME method with **cryogen-free sample enrichment**?
- Recent advances of SPME
  - SPME Arrow technology provides **increased phase capacity** to sample more of each analyte



Automated sample extraction and enrichment

Headspace–trap
(& classical headspace)

Centri®

SPME (Arrow)–trap
(& classical SPME)

Automated sample extraction and enrichment

Headspace–trap
(& classical headspace)

HiSorb high-capacity
sorptive extraction

Centri®

SPME (Arrow)–trap
(& classical SPME)

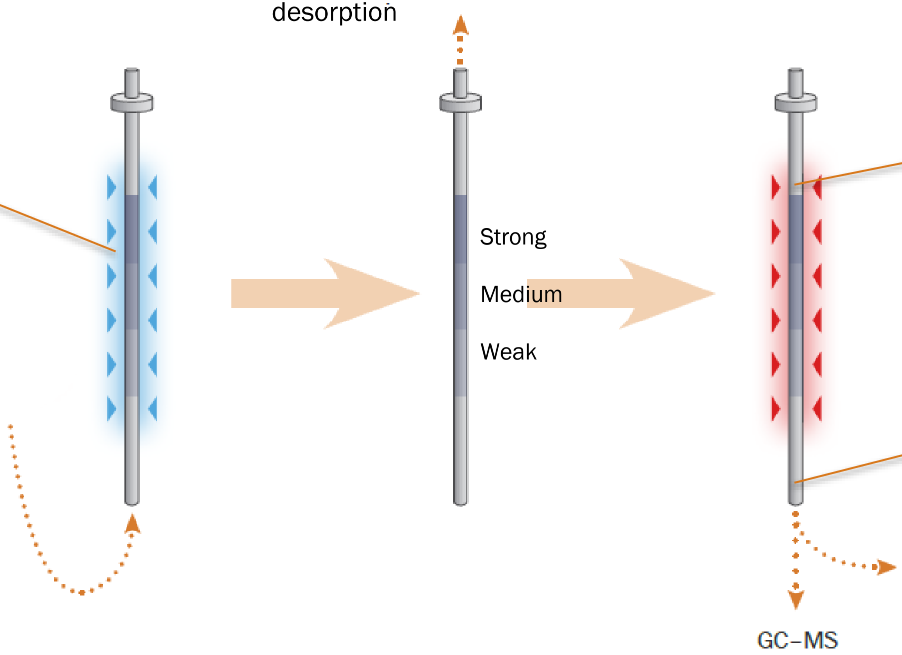
Tube-based thermal
desorption (TD)

How does the trap work?

Interferents such as water and air can be selectively purged prior to trap desorption

Trapping uses **electrical cooling** rather than cryogen

SPME fiber/Arrow is heated and analytes desorbed onto a sorbent packed focusing

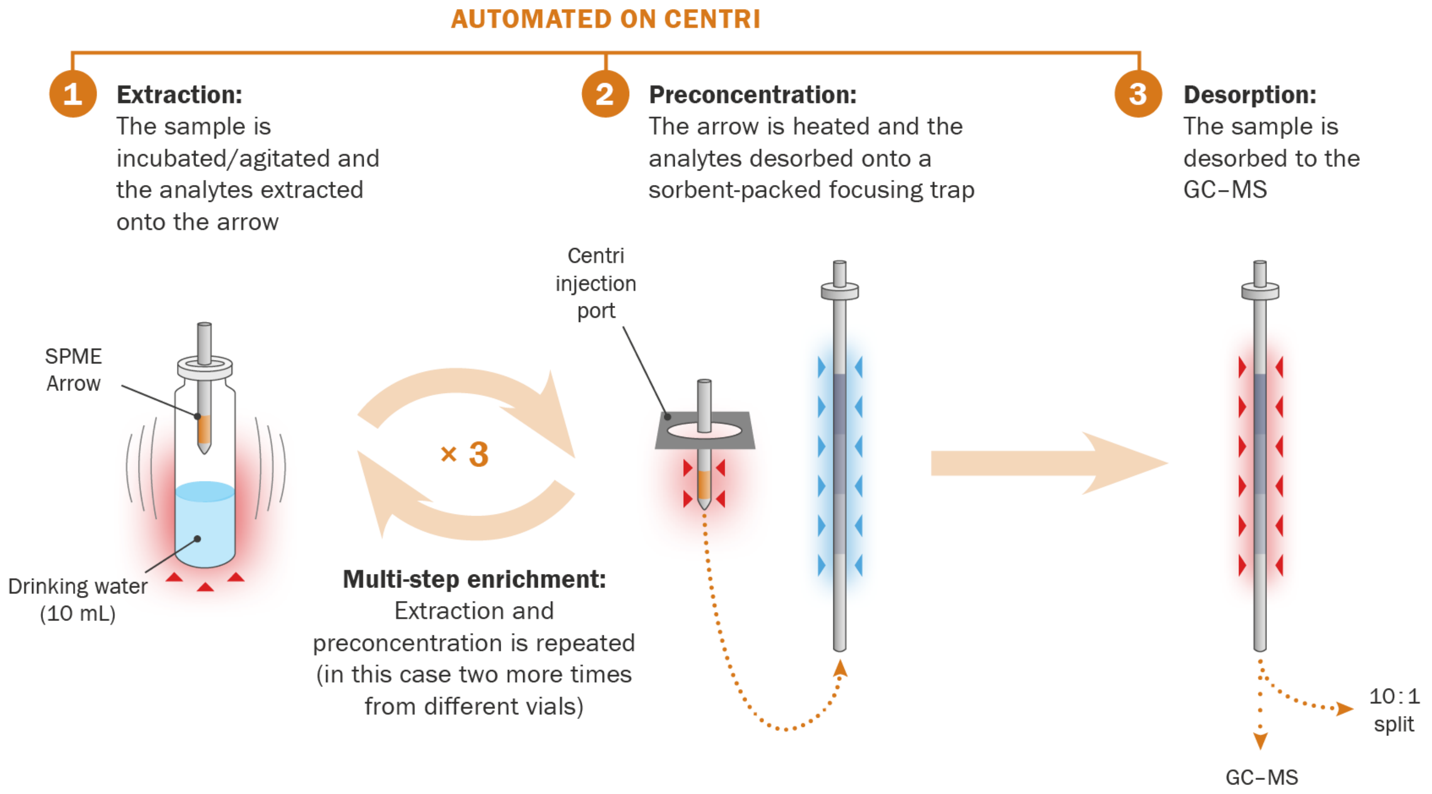


The trap is heated rapidly, up to 100°C/s, during desorption

Analytes enter and leave the trap at the same end **('backflush desorption')**

Optional split – quantitative re-collection of split flow for sample archiving or re-analysis

Multi-step enrichment (MSE®) SPME Arrow–trap

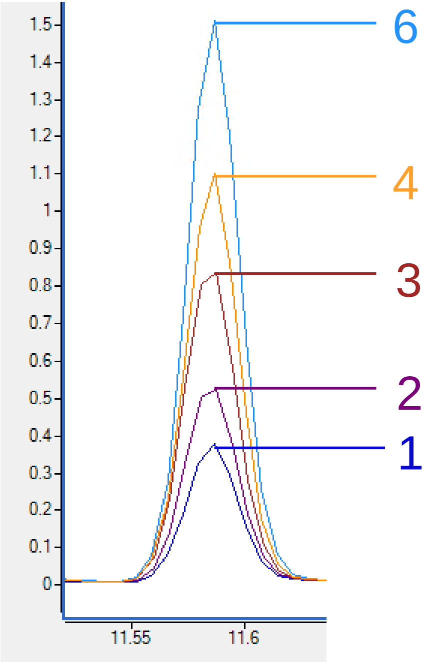


Increasing sensitivity: Experiments with SPME fiber

MSE–SPME–trap

- Using the ‘old’ HS-SPME GC-MS methodology
- Increased the extraction yield using enrichment
- However:
  - 6 enrichments meant that one sample took >2h
  - Not a commercially viable option for high-throughput lab

✷ Increase phase capacity with SPME Arrow



1,4-Dioxane peak with no. of SPME fiber enrichments (from same vial) noted

MSE–HS–SPME Arrow–trap sampling

1,4-Dioxane in drinking water

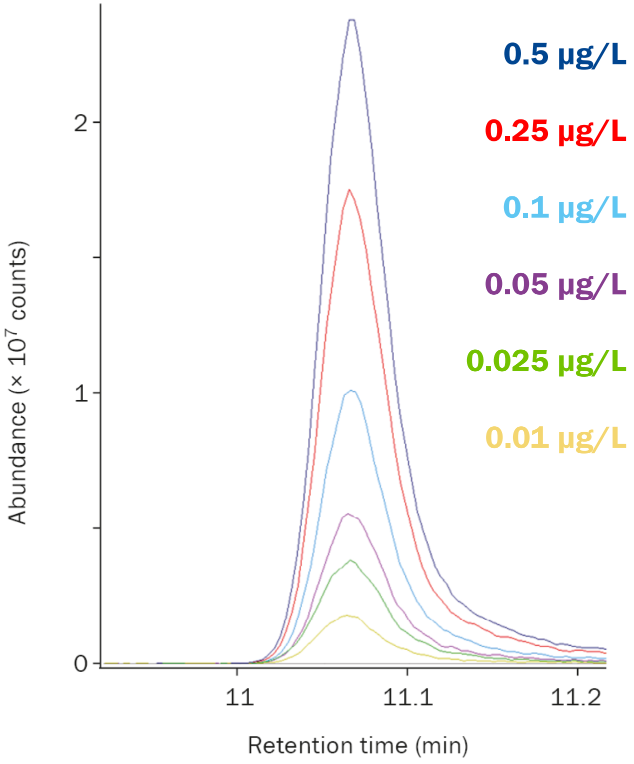
LOQ: 0.58 µg/L

LOQ: 0.025 µg/L

LOQ: **0.007 µg/L**

- Calibration: 0.01 – 0.5 µg/L (10-500 ppt) in water (10 mL) saturated with NaCl (2 g)
- Headspace–SPME Arrow extractions using PDMS/CWR/DVB phase
- Sampling: 3 extractions (same vial) for 10 mins each
- Real-world sample: Tap water from the Markes International Bridgend site

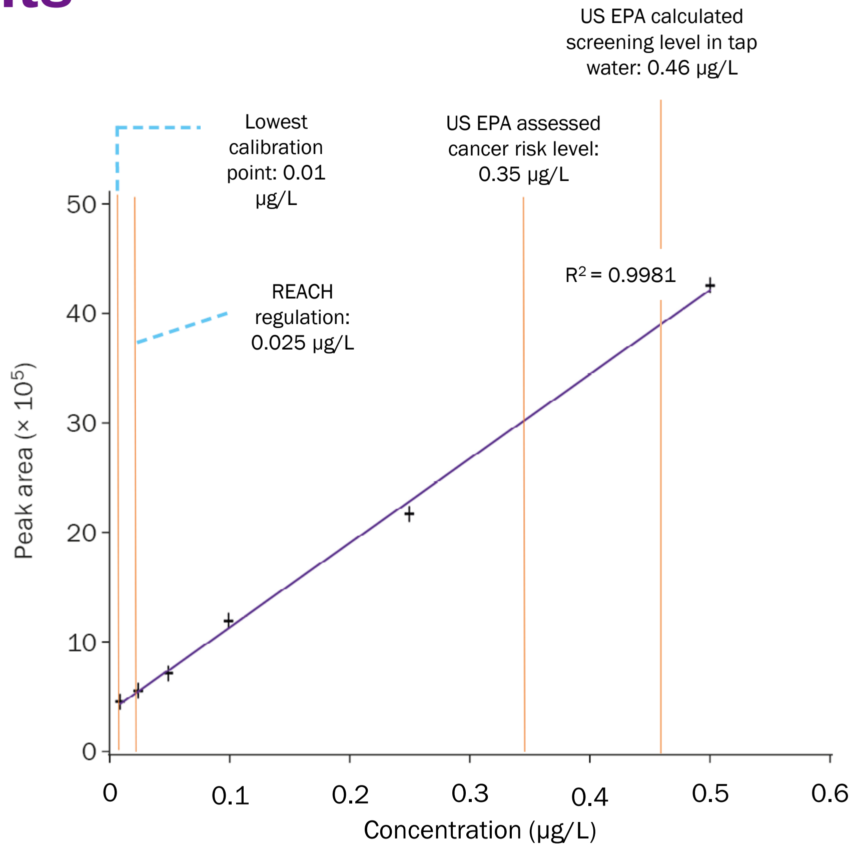
Calibration: 1,4-Dioxane



- 0.01 to 0.5 µg/L 1,4-dioxane (10 – 500 ppt)
- Extracted ion chromatograms (88 ion) overlaid

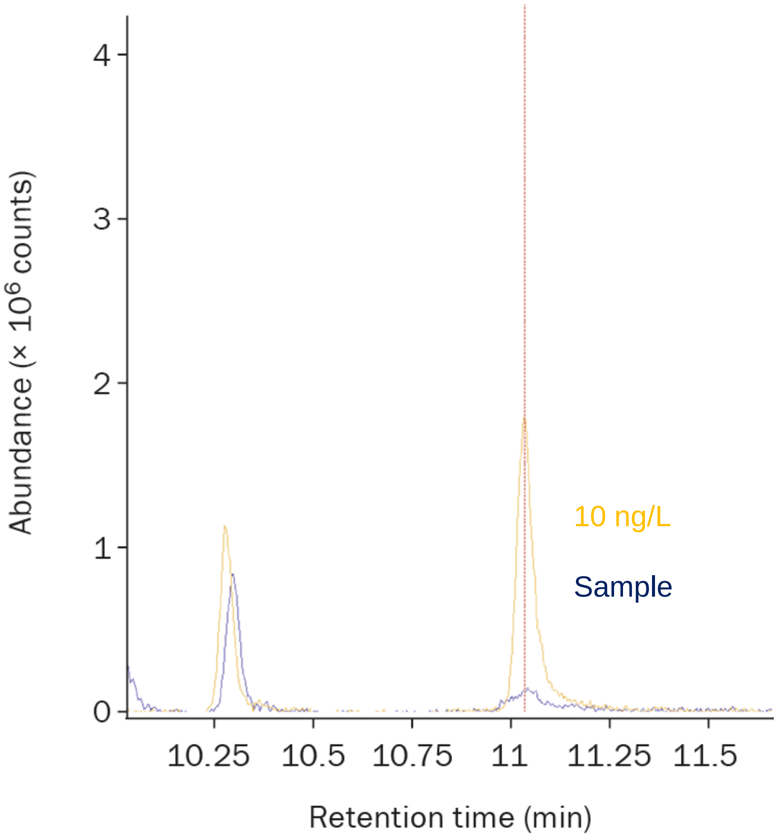
Going beyond regulatory limits

- Excellent linearity
  - 6-point calibration (n = 3 per level) R^2 >0.99
- Good reproducibility
  - Relative standard deviations (RSDs) 3 – 13%
  - US EPA Method 522 indicates < 20%
- Detection of lowest calibration point 10 ng/L below both regulations
- Sample and analysis time = <1 hour (overlap mode used to shorten this further)



Tap water sample

- Collected from Markes' UK site
- Little-to-no detection of 1,4-dioxane: < 10 ng/L calibration point
- Confirmed with replicates performed (*n* = 10)



Conclusions

MSE–SPME Arrow–trap analysis

- Low limits of quantification:
  - **46x lower** than the US EPA screening level for tap water (0.46 µg/L) and **35x lower** than the assessed cancer risk level (0.35 µg/L)[2]
  - **2.5x lower** than the more stringent German REACH regulation LOQ of 0.025 µg/L (25 ppt)

- Sample enrichment: *more* analyte extracted for detection enabling these lower limits to be reached with excellent peak shape and sensitivity

- Fully automated and solvent-free technique with potential for use in high-throughput laboratories
  - Time to result:

  >24h manual SPE (no analysis time) → <1h for MSE–SPME Arrow–trap

[2] https://www.epa.gov/sites/default/files/2014-03/documents/ffrro_factsheet_contaminant_14-dioxane_january2014_final.pdf

Thank you for your attention

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