Revisiting Disinfection Byproducts with Supercritical Fluid Chromatography-High Resolution-Mass Spectrometry: Identification of Novel Halogenated Sulfonic Acids in Disinfected Drinking Water

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Analytical Question

Is supercritical fluid chromatography an effective technique to identify and characterize unknown disinfectant byproducts?

Analyte Details

- Disinfectant by-products (DBPs)
- 15 new halogenated sulfonic acids
- Unstable in presence of quenching agent
- Currently unregulated in drinking water
- Poses possible health risks
- Based on 3 chemical structures
  - See figs 1-3

Matrix Details

- Groundwater
- Surface water
- Riverbank filtrate
- Tap water
- Swimming pool water

Analytical Techniques

- Supercritical fluid chromatography-high resolution mass spectrometry with quadrupole time-of-flight
- Electrospray ionization
- NMR spiked with ^{13}C-urea
- Chlorination of standards
- Pure water method blank used

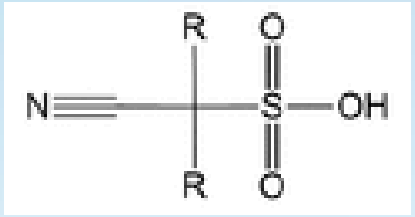

Figure 1: Base structure for haloacetonitrilesulfonic acids

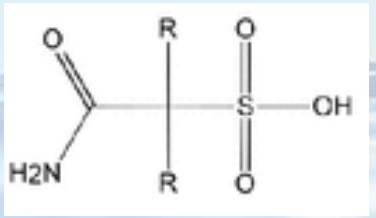

Figure 2: Base structure for haloacetamidesulfonic acids

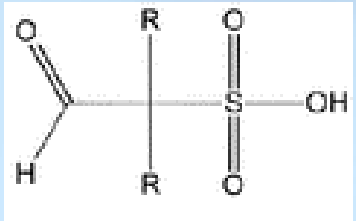

Figure 3: Base structure for haloacetaldehydesulfonic acids

Sampling Plan Information

- Judgmental sampling plan
- Grab samples from 3 types of locations
- Tap water from 8 cities in Europe
- Swimming pool samples from 3 pools in Germany
- 6 drinking water treatment plants (DWTPs) before and after disinfection
  - 5 sets of repeat samples every 2 weeks from DWTP 1-2, Germany
  - 3 sets of repeat samples every 2 months from DWTP 3-5, Hungary
  - 1 set of samples from DWTP 6, Spain
- Collected in 100 mL borosilicate brown glass bottles
- Transported in a Thermobox set at 10-12°C
- Enriched with ^{13}C within 24 hours
- Freeze-dried at 15°C and 1.65mbar
- Centrifuged
- Stored at -20 °C until analysis

Results

15 new halogenated sulfonic acids were identified and characterized. These sulfonated DPBs were detected at all the DWTPs. At least 1/15 sulfonated DBPs were detected in all tap samples. They were also detected in higher concentrations in swimming pool water.

Conclusion

With the detection and identification of 15 novel sulfonated DBPs, it is confirmed that supercritical fluid chromatography is an effective technique to identify and characterize unknown DBPs when paired with NMR spectroscopy.

Justification

By using a judgmental plan, they researched locations of DWTPs across Europe and swimming pools across Germany. As DWTPs and tap water would affect a greater population, they collected more of those two types of samples than the pool water samples.

With grab samples, the change in DBP concentrations over time could be measured in the DWTPs. Also, as there were many different locations, there is no certainty that a composite sample would properly represent all of the sample locations.

Of Interest?

This article caught my eye with the mention of pool water analysis, as I have a minor background in the civilian applications of pool water analysis and DBPs, especially those related to chlorine. Supercritical fluid chromatography interested me as we had not yet covered it in class, and I was interested to see how it differed from more common varieties of chromatography.

Article Reference

Nihemaiti, M.; Icker, M.; Seiwert, B.; Reemtsma, T. Revisiting Disinfection Byproducts with Supercritical Fluid Chromatography-High Resolution-Mass Spectrometry: Identification of Novel Halogenated Sulfonic Acids in Disinfected Drinking Water. Environmental Science & Technology 2023, 57 (9), 3527–3537. DOI:10.1021/acs.est.2c05536.
https://pubs.acs.org/doi/10.1021/acs.est.2c05536