Analysis of Hexachlorocyclopentadiene and Chlorinated Pesticides by GC-MS with SPME Preconcentration of Sparged Samples
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Introduction
Hexachlorocyclopentadiene (HEX) has been used as a precursor or intermediate in the manufacture of insecticides, nonflammable resins, flame retardants, and shock-proofing plastics. HEX and related pesticides have been detected in water samples at various locations in the United States.

Role of HEX in Pesticide Synthesis

Overview of SPME

- Extraction modes
  - Direct immersion: most common method, not suitable for biological matrices.
  - Headspace: minimize background noise, protect the fiber from damage.
- SPME optimization
  - Fiber type, extraction time, ionic strength, pH, temperature of sample, agitation, fiber.

Conditions for GC-MS Analysis

- Detection limits for water and urine samples, respectively, using the SIM mode of GC-MS.
- SPME extraction time of 10 minutes at 95 °C is optimal which is best extracted at 80 °C.
- Addition of NH₄OH improves the sensitivity of analysis selected ion monitoring (SIM) mode of mass spectrometry.

Comparison of SIM Detection Limits for SPE and SPME

Comparison of SPE and SPE

SPME with polydimethylsiloxane-coated fiber

SPME/GC-MS Analysis of an Urine Sample Spiked with Chlorinated Pesticides

Comparison of SPME Sampling Conditions for GC-MS Analysis

SPME Varian C-18

Dynamic Headspace SPME

Dynamic Headspace SPME

- Major pathway: Phototransformation in water
  - Half-life under ordinary lab light: 7 days
  - Seven degradation products have been identified.
- Minor pathway: Hydrolysis
  - Half-life is 3-11 days under the conditions of 25-30 °C and environmental pH 5-9.
  - Forms polybromoxy-by-products

Preparation Methods for Pesticide Samples

- Purge-and-trap technique
- Liquid-Liquid extraction (LLE)
- Solid phase extraction (SPE)
- LLE and SPE are time consuming, difficult to automate, and use toxic, expensive, high purity solvents.

Research Goals

- Development of a sensitive method to measure HEX and other chlorinated compounds in water and urine.
- Increase the sensitivity and reduce the analysis time.
- Compare the detection limits of GC-MS analysis with solid phase microextraction (SPME) in scan mode and selected ion monitoring (SIM) mode of mass spectrometry.

Dependence of Signals on Sample Temperature

Dependence of GC-MS Signals on SPME Extraction Time

Improvement of Sensitivity by Adding Ammonium Hydroxide

Dependence of GC-MS Signals on SPME Extraction Time

Conclusion

- Dynamic Headspace mode of SPME extraction was capable of achieving better sensitivity than the SPE method by yielding detection limits at the 10⁴ and 10⁵ picogram levels for water and urine samples, respectively, using the SIM mode of GC-MS.
- SPME extraction time of 10 minutes at 95 °C is optimal for the analysis of all chlorinated pesticides except HEX, which is best extracted at 80 °C.
- Addition of NH₄OH improves the sensitivity of analysis of the pesticides by 18 % - 98 %.
- SPME can reduce the sample preparation time and the cost of analysis due to the solventless procedure.

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