SOLID-PHASE EXTRACTION WITH PAPER SPRAY MASS SPECTROMETRY FOR IMPROVING DETECTION LIMITS OF WARFARE AGENT HYDROLYSIS PRODUCTS IN WATER SAMPLES

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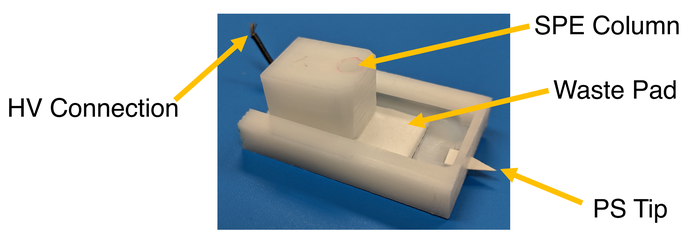
Overview

- Create an “all-in-one” SPE cartridge for sample pre-concentration and analyte retention to lower matrix effects and improve detection limits
- 10.0 mg SPE material (porous graphitic carbon, weak anion exchange, and strong anion exchange) is added to the SPE cartridge and held in place with Whatman 31ET paper disks
- Millipore water and three different fresh water samples are spiked with CWA hydrolysis products and their internal standards
- Samples are wicked through the SPE cartridge to retain CWA hydrolysis products while water matrices are collected on a waste pad
- Extraction solvents are added to the column to elute retained analytes on a paper tip for negative ion mode MS analysis

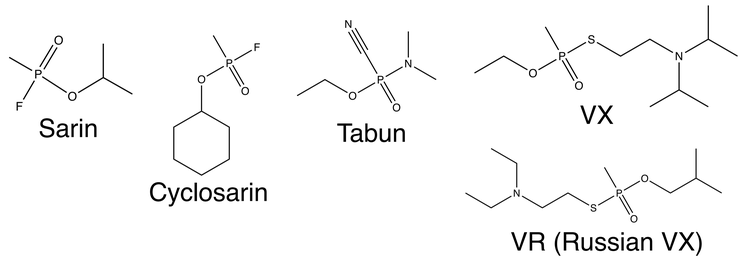
Introduction

With discoveries of G and V-series chemical warfare agents (CWAs)/nerve agents, beginning in 1936, these chemicals have been used against human populations, as recent as April 2018 in Syria (Sarin and Cl_2), despite advances made at the 1997 Chemical Weapons Convention to limit production and stockpiling of CWAs. These nerve agents readily degrade and hydrolyze under ambient conditions, due to a relatively short half-life on the order of minutes to hours, making the detection of these products imperative. Advances towards completely portable mass spectrometers and ambient ionization techniques makes on-site testing for CWAs and their degradation/hydrolysis products possible. Here, solid-phase extraction (SPE) coupled with paper-spray mass spectrometry (PSMS) is used to concentrate and improve detection limits of CWA hydrolysis products in water samples.

SPE Cartridge

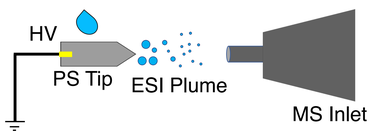


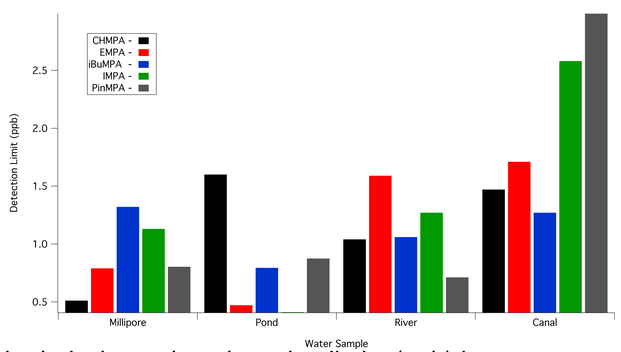
G and V-series Nerve Agents



- G-series named after Germany where they were first synthesized (1936-1949)
  - Clear, colorless, sweet smelling, heavier than air
- V-series named for venomous and first synthesized in the UK (1952-1955)
  - Clear to amber-colored, odorless, low volatility
- Inhibit acetylcholinesterase
  - Tightness in chest, convulsions, spasms, seizures, coma, and death
- Produce excessive mucus, tears, sweat
- Can cause nausea, pain, vomiting, pupil miosis (constriction)

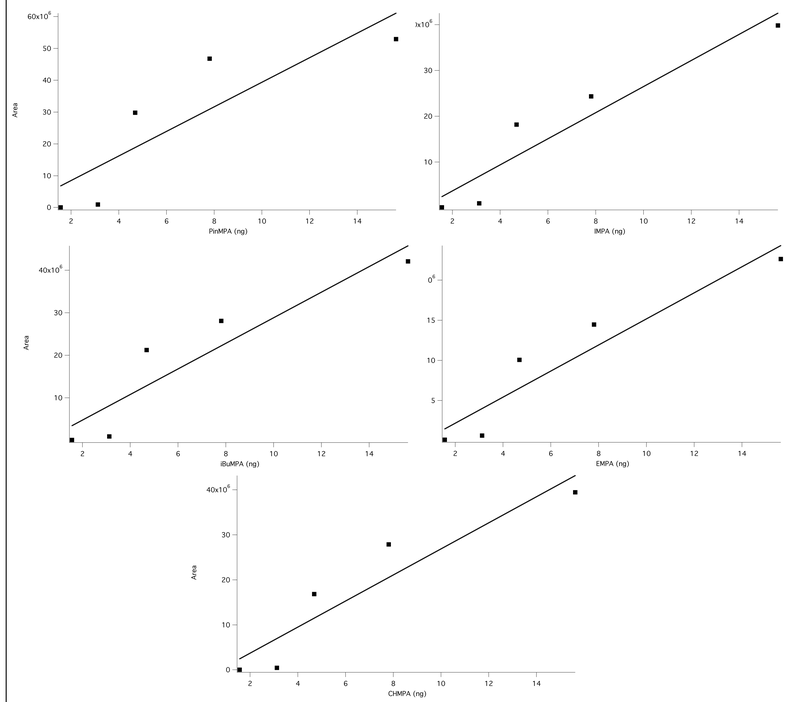
Results





CWA hydrolysis product detection limits (ppb) in water samples without SPE

Results Continued



Weak anion exchange SPE retention test

- 10.0 mg BondElut WAX SPE
- 100 μL 90:10:0.01 MeOH:CCl_4:NH_4OH extraction solvent and spray solvent

Current Directions

- From current results, determine maximum loading amounts of hydrolysis products per amount SPE
- Explore different SPE materials to optimize retention of CWA hydrolysis products and simulants (C-18, multiwalled carbon nanotubes, etc.)
- Explore different solvents to increase analyte recovery from SPE material
- Fully utilize water samples (flowing vs. stagnant) to characterize SPE efficiency

Acknowledgements

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