# Preconcentration and Detection of Chlorinated Alkanes and Alkenes

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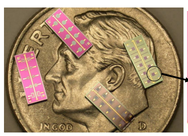
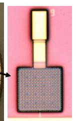
## Abstract

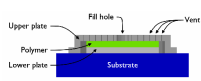
Remote and automated detection of chlorinated compounds in subsurface aquifers is crucial to superfund monitoring and environmental remediation. Current monitoring techniques involve the use of expensive laboratory instruments and trained personnel. The use of a filled tubular preconcentrator combined with a chemicapacitive detector array presents an attractive option for the unattended monitoring of these compounds. Five preconcentrator materials were exposed to common target compounds of subsurface remediation projects (trichloroethane, trichloroethylene, dichloroethene, benzene, and perchloroethylene). Rapid heating of the tube caused the collected, concentrated effluent to pass over the surface of a chemicapacitive detector array coated with four different sorbent polymers.

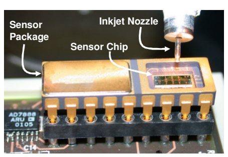
A system containing a porous ladder polymer and the sensor array was subsequently used to sample the analytes injected onto sand in a laboratory test, simulating a subsurface environment. With extended collection times, effective detection limits of 5 ± 3 ppbV were achieved for trichloroethane in the vapor phase. The effects of the preconcentrator material structure, the collection time, and sensor material on the system performance were observed. The resultant system presents a solution for remote, near-real-time monitoring of chlorinated organic compounds and other volatile organic compounds in a soil matrix.

## Experimental: Detectors

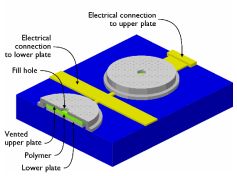



Chemicapacitor arrays

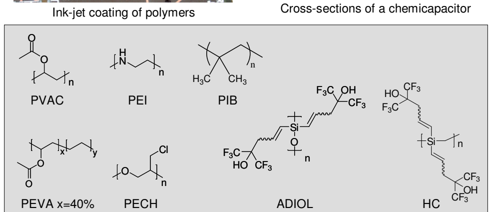



Ink-jet coating of polymers




Cross-sections of a chemicapacitor



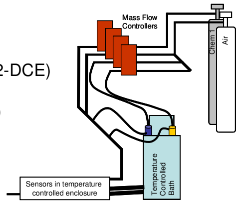

**Detector coatings:**

- PVAC: poly(vinylacetate)
- PEI: poly(ethylene imine)
- PEVA40%: poly(ethylene-*co*-vinylaceate)
- PECH: poly(epichlorohydrin)
- ADIOL: difluoroalcohol siloxane
- HC: hyperbranched difluoroalcohol carbosilane
- PIB: Polyisobutylene

## Experimental: Test System

**Analytes Tested:**

- benzene
- *t*-1,2-dichloroethylene (*t*-1,2-DCE)
- trichloroethylene (TCE)
- 1,1,2-trichloroethane (TCA)
- perchloroethylene (PCE)
- All tests in dry air

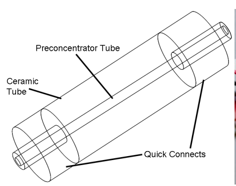


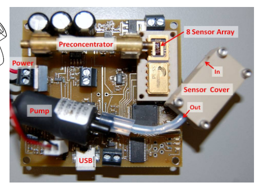

Detection limits (ppmV)* without preconcentration

| Analyte | Sensor Materials: Adiol | PECH | PEVA |
|---|---|---|---|
| t-1,2-DCE | 28 ± 13 | 162 ± 63 | 257 ± 80 |
| Benzene | 77 ± 8 | 331 ± 91 | 382 ± 128 |
| TCE | 24 ± 18 | 264 ± 73 | 359 ± 78 |
| TCA | 47 ± 1 | 65 ± 2 | 64 ± 4 |
| PCE | 0.3 ± 0.2 | 58 ± 8 | 36 ± 3 |

*all LOD's at 20°C except benzene obtained at 25°C

## Experimental: Preconcentrator

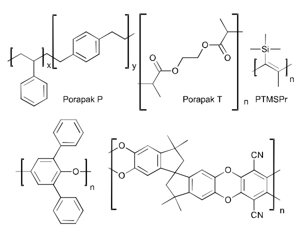


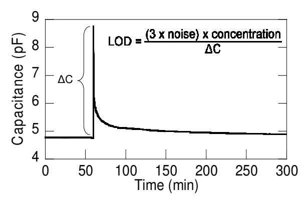




Sorbent materials used in Preconcentrators

| Preconcentrator Materials | Chemical | Recommended Chemicals | Maximum operating temperature (°C) |
|---|---|---|---|
| Porapak P | Styrene divinylbenzene | For analyte group carbonyl compounds | 250 |
| Porapak T | Ethyleneglycol dimethacrylate | $CH_2O$ & other polar compounds | 190 |
| Tenax TA | 2,6-diphenyl-p-phenylene oxide | General use, high boiling compounds | 350 |
| PTMSPr* | Polytrimethyl silylpropyne; Low polarity polymer | TBD | 200 |
| PIM-1*‡ | Polymer of intrinsic microporosity Nitrile functionalized polymer | TBD | 300 - 350 |

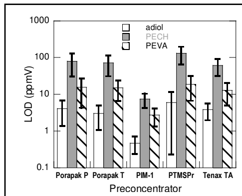
* Synthesized by Seacoast Science, Inc.
‡N. B. McKeown and P. M. Budd. *Macromolecules*, 2010, **43**, 5163-5176.



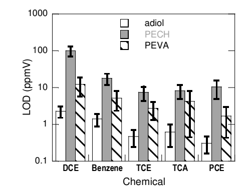




## Results: Preconcentration

Short collection times

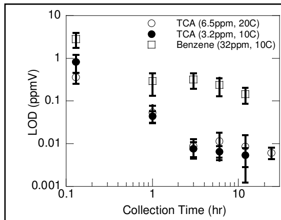



Comparison of preconcentrator materials TCE (127 ppmV) collected for 8 min.




Comparison of 5 analytes using PIM-1. Ambient concentrations: DCE = 563 ppmV; benzene = 160 ppmV; TCE = 127 ppmV, TCA = 32 ppmV; PCE = 28 ppmV.

Extended collection times



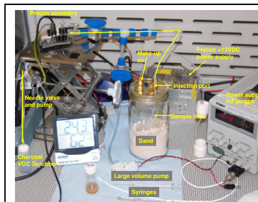

Limits of detection from the adiol chemicapacitor using extended collections on PIM-1 precon. and detector at 20° and 10°C. Collection flow rate ~5 cc/min

Comparing EPA MCL to LODs determined from 12-hour collections
(HC chemicapacitor, at 40°C, Precon. collecting 5cc/min at 23°C)

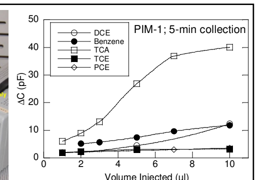
| Chemical (concentration exposed) | EPA MCL* ($\mu g_{chemical}$ / $L_{water}$) | Henry's law constant $H_{yx}$ (dimensionless mole fraction basis)** 20°C | 10°C | Headspace equivalent concentration of MCL 20°C | 10°C | LOD from 12hr Collection |
|---|---|---|---|---|---|---|
| trans 1,2 DCE (141 ppmV) | 100 | 425 | 273 | 7.9 ppmV | 5 ppmV | 2.1 ± 1 ppmV |
| Benzene (40 ppmV) | 5 | 244 | 148 | 281 ppbV | 171 ppbV | 0.5 ± .2 ppmV |
| TCE (30ppmV) | 5 | 448 | 263 | 307 ppbV | 180 ppbV | 160 ± 44 ppbV |
| 1,1,2-TCA (8.1 ppmV) | 5 | 38 | 21 | 26 ppbV | 14 ppbV | 25 ± 10 ppbV |
| PCE (7ppmV) | 5 | 772 | 427 | 419 ppbV | 232 ppbV | 50 ± 30 ppbV |

*MCL values from: http://water.epa.gov/drink/contaminants/basicinformation/index.cfm
**Henry's law constants from: http://www.epa.gov/athens/learn2model/part-two/onsite/esthenry.html

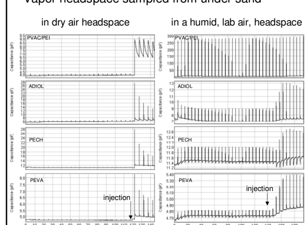
Simulated environment



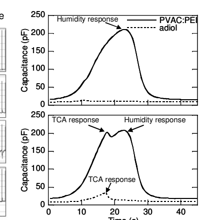
Vapor headspace sampled from under sand




Adiol responses to vapor diffusing through sand from injected liquids

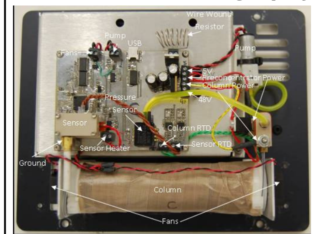
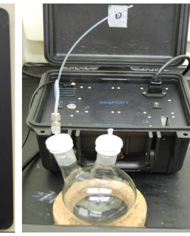



Simulated environment: 5μL (7.3 mg) liquid TCA injected onto clean sand (500 g) in a 900ml bottle. Each spike is a preconcentrator firing event. In both tests, the preconcentrator collection cycle is 5 min.

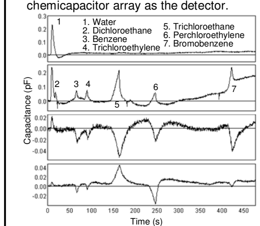



Overlap of the adiol & PVAC/PEI shows that signal from the TCA occurs prior to the signal from the ambient water peak.

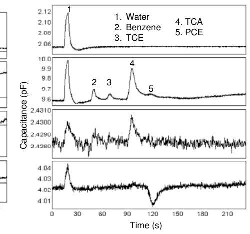
## Results: Chromatography

Prototype Mini-GC: uses air as the carrier gas, directly heated column, and chemicapacitor array as the detector.




- 5-min collection on Tenax
- Collected from liquid headspace in vial
- Detectors: PVAC-PEI (top), adiol, PECH, PEVA




- 18-hour collection on Tenax
- Collected from vapor in 190L glove box
- Detectors: PVAC (top), HC, PIB, PEVA

Seacoast's Mini GC separates several compounds, and water from a premixed vapor. The water peak indicated comes from humidity in the laboratory air.

## Summary

This work represents the initial efforts towards an unattended sensor to track subsurface contamination of chlorinated organic compounds in near real-time while logging and transmitting contaminant concentrations. Such a system would be used in tandem with geophysical and other methods, to provide comprehensive contamination management.

Use of preconcentrator and chemicapacitive sensor array with an improved preconcentrator packing material and sensor materials resulted in the detection the target analytes at levels below regulated levels. The modular nature of the system will allow future systems to be tailored to other analytes by changing the structure of the preconcentrator material and the sensor array coatings.

In addition, the preconcentrator may be integrated with more complex devices for solving other environmental monitoring problems, such as vapor intrusion monitoring or fence-line monitoring.

## Acknowledgement

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