



Homeland Security

SYNTHESIS AND QSPR OF POLYMERS IN SENSOR APPLICATIONS

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ABSTRACT

Toxic industrial chemicals (TICs) and chemical warfare agents (CWAs) present a threat to homeland security and to deployed Department of Defense personnel. Seacoast Science, Inc. has addressed this challenge by the research and development of a rapid and accurate sensor using polymer-based chemical sensors. Quantitative Structure Property Relationship (QSPR) would enable the *a priori* selection of a polymer based on the physical and chemical characteristics of the target analyte. A library of polymers and materials was exposed to three high-vapor pressure TICs and their response on a chemiresistor and chemicapacitor platform was measured. Molecular modeling was used to minimize representative polymers and analytes and to generate molecular descriptors. From the response of the materials and the descriptors, a QSPR equation was generated using a 10-fold cross-validation to build the model with M_2 pruned model rules (using smoothed linear models) that showed acceptable correlation ($R = 0.8$). The optimized QSPR will allow for the rapid and accurate selection of a material for polymer-based sensor with lengthy testing and repeated optimization steps. This will allow these sensors to be rapidly adapted to new chemical threat lists.

SENSOR TECHNOLOGY



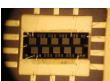
Micrograph of a Seacoast Science interdigitated electrode sensor element (-500 μm x 350 μm).



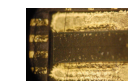
Picture of chemicapacitive sensor array on a dime. (IDT and fixed plate) are displayed. Chip size is ~2 x 5 mm



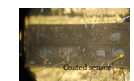
Micrograph of a Seacoast Science sensor chip with three chemicapacitors



Four probe chemiresistor sensor array wire bonded for 4 probe measurement.



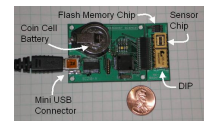
Chemiresistor array air brushed with 1.0 wt% carbon, (PhCH₃ Polysciences, Inc., graphitized, 0.027-0.03 mm). Final resistance ~1.2 kW.



Chemiresistor array after ink-jet deposition of polymers (100 drops, 0.01 wt % polymer in CHCl₃).



Ink jet deposition of materials on the sensor array. (30 or 80 μm diameter nozzle, drop volume 10 - 20 pL, drop diameter 30 - 100 μm)



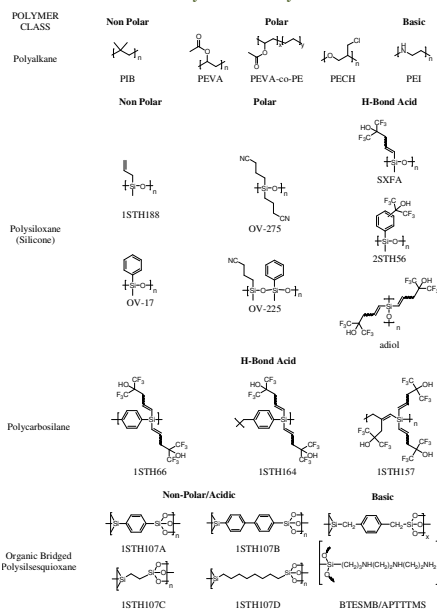
Seacoast Science's SC210 (Chemicapacitor) Prototype (6.5 x 4 x 1.5 cm), USB for fast real-time data collection directly to PC or remotely located and powered by the coin cell battery for weeks of unattended data logging (stored on flash memory).

RESULTS AND DISCUSSION

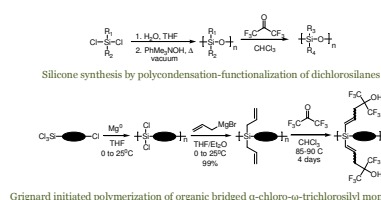
Low Vapor Pressure Analytes

Analyte	Structure	Proposed Interaction
HCN (AC)	NEC-H	Proton transfer/addition, dipole-dipole
Acrolein		p-p interaction, H-bond base, dipole
Ethylene Oxide (EO)		Electrophile/Nucleophile, H-Bond base

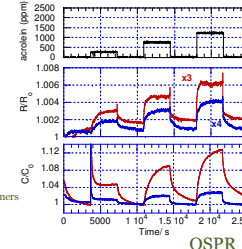
Polymer Library



Polymer Syntheses



Sensor Response



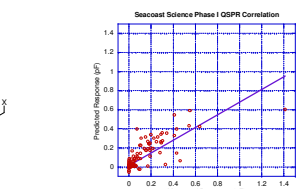
Response of x3 and x4 to acrolein (25°C, 30% RH) on a capacitive (LOD: x3 = 11 ppm; x4 = 113 ppm) and resistive (LOD: x3 = 37 ppm; x4 = 120 ppm) platform

QSPR

$$S = [c]([ANALYTE]) - [c](COATINGS) + [ANALYTE, COATINGS]$$

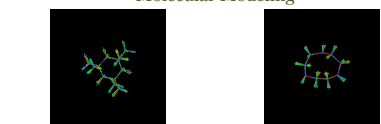
S = Activity = D(resistance) or D(capacitance)
[c] = concentration of analyte; [c] is a descriptor or a function of the analyte or coating

Descriptors	
Molar Refractivity [cm ³ /mol]	Polarizability
Hydrophobicity: -cLog P	# Hydrogen bond donors
Total Charge	# Hydrogen bond acceptors

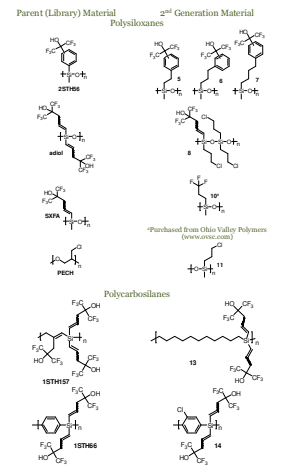


QSPR Correlation between calculated and measured response on chemicapacitor platform of basis set of polymers to target analytes ($R^2 = 0.83$)

Molecular Modeling



New Materials



Material Response

Material Class	Analyte	Library Material	LOD (ppm)	New Material	LOD (ppm)	Increase
Polycarbosilane	ED	ISTH166	16	14	0.4	2.5%
		ISTH160	26	14	3.3	12.0%
Polysiloxane	Acrolein	ISTH167	41	13	1.2	3.4%
		adial	8	8	1.1	28.2%
Organic Polymer	HCN	SXFA	67	10	7.2	8.3%
		ISTH56	39	5	1.3	30%
Organic Polymer	Acrolein	ISTH56	NR	5	5.8	...
		PECH	580	11	1.7	341.2%

References

Kendall, R.A.; Apyl, E.; Bernholt, D.E.; Bjalska, E.J.; Dupuis, M.; Fann, G.L.; Harrison, K.J.; Ju, J.; Nichols, J.A.; Njolecha, J.; Strauszma, T.P.; Windus, T.L.; Wong, A.T. High Performance Computational Chemistry: an Overview of NWChem a Distributed Parallel Application. *Computer Phys. Comm.* **2000**, 128, 269-283.

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Acknowledgements

Work was funded by internal Seacoast Science R&D funding, by SBIR contract #NCHC080014 topic # H-SB07.1-007 (DHS), and SBIR contract #W911NF-04-C-0026 topic #03-033 (ARL).