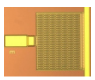
SYNTHESIS AND QSPR OF POLYMERS IN SENSOR APPLICATIONS

Stephen T. Hobson, Sabina Cemalovic, Omer Katzenelson, Sondra Steele, Amy L. Thibadeaux
Seacoast Science, Inc. 2151 Las Palmas Drive, Suite C. Carlsbad, CA 92011

ABSTRACT

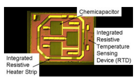
Toxic industrial chemicals (TICs) and chemical warfare agents (CWAs) present a threat to homeland security and to deployed Department of Defense personnel. Seacoast Science, Inc. has addressed this challenge by the research and development of a rapid and accurate sensor using polymer-based chemical sensors. Quantitative Structure Property Relationship (QSPR) would enable the *a priori* selection of a polymer based on the physical and chemical characteristic 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 software 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 M5 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 without lengthy testing and repeated optimization steps. This will allow these sensors to be rapidly adapted to new chemical threat lists.

SENSOR TECHNOLOGY

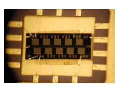


Micrograph of a Seacoast Science interdigitated electrode sensor element (~500 μm x 350 μm).

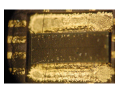
Picture of chemicapacitive sensor array on a dime. (IDT and fixed plate) are displayed. Chip size is ~2 x 5 mm



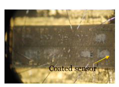
Micrograph of a Seacoast Science sensor chip with three chemicapacitors



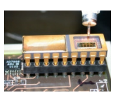
Four probe chemiresistor sensor array wire bonded for 4 probe measurement.



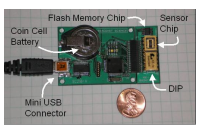
Chemiresistor array air brushed with 1.0 wt% carbon, ($PhCH_3$, Polyscience, Inc., graphitized, 0.027-0.03 mm). Final resistance ~ 1.2 kW.



Chemiresistor array after ink-jet deposition of polymers (100 drops, 0.01 wt % polymer in $CHCl_3$).



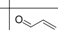
Ink jet deposition of materials on the sensor array. (30 or 80 μm diameter nozzle, drop volume 10 - 20 pL, drop diameter 30 – 100 μm)



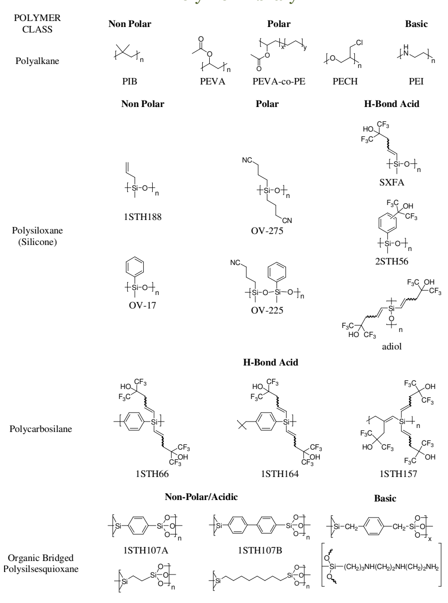
Seacoast Science's SC210 (Chemicapacitor) Prototype (6.5 x 4 x 1.5 cm), USB for fast real-time data collection directly to PC or remotely located and powered by the coin cell battery for weeks of unattended data logging (stored on flash memory).

RESULTS AND DISCUSSION

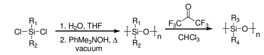
Low Vapor Pressure Analytes

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

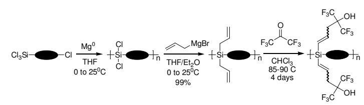
Polymer Library



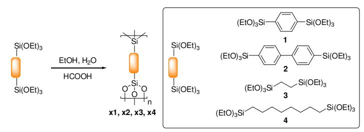
Polymer Syntheses



Silicone synthesis by polycondensation-functionalization of dichlorosilanes

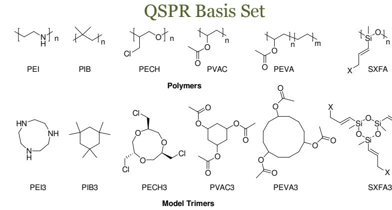


Grignard initiated polymerization of organic bridged α-chloro-ω-trichlorosilyl monomers

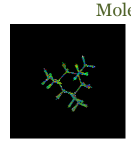


Sol-gel polymerization of α,ω-bis-trialkoxysilyl monomers

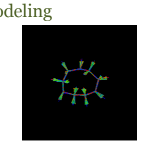
QSPR Basis Set



Molecular Modeling

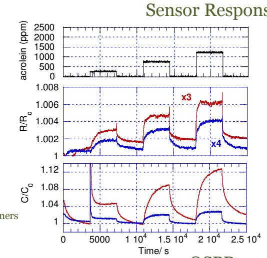


Minimized structure: cyclic trimer of PIB, 36 atoms x3 degrees of freedom=108 normal modes (including one for translation and two for rotation) 108x20 = 2160 superimposed structures



Minimized structure: cyclic trimer of PEI. 24 (atoms) x 3=72 normal modes (including one for translation and two for rotation) 72x20 = 1440 superimposed structures

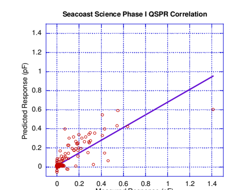
Sensor Response



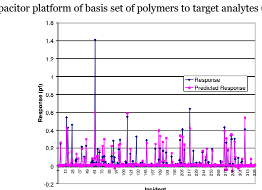
Response of **x3** and **x4** to acrolein (25°C, 30% RH) on a capacitive (LOD: **x3**= 11 ppm; **x4** = 113 ppm) and resistive (LOD: **x3** = 37 ppm; **x4** = 120 ppm) platform

QSPR

S= [c]f(ANALYTE)+[c]f(COATINGS)+f(ANALYTE, COATINGS) S = Activity = D(resistance) or D(capacitance) [c] = concentration of analyte; f() is a descriptor or a function of the analyte or coating	
Descriptors	
Molar_Refractivity [cm³/mol]	Polaraizability
Hydrophobicity: cLog P	# Hydrogen bond donors
Total Charge	# Hydrogen bond acceptors

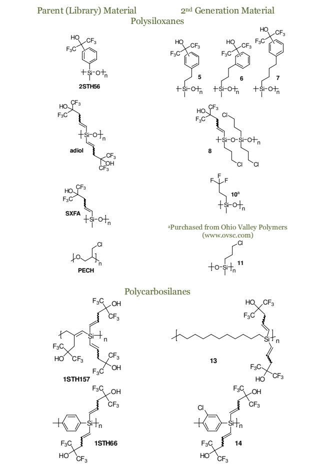


QSPR Correlation between calculated and measured response on chemicapacitor platform of basis set of polymers to target analytes (R^2 = 0.83)



Calculated vs. Measured response for QSPR Equation.

New Materials



Material Response

Material Class	Analyte	Library Material	LOD (ppm)	New Material	LOD (ppm)	Increase
Polycarbo-silane	EO	**1STH66**	15	**14**	6.1	2.5
	Acrolein	**1STH66**	26	**14**	3.3	7.9
		1STH157	41	**13**	12	3.4
Poly-siloxane	Acrolein	**adiol**	31	**8**	1.1	28.2
		SXFA	67	**10**	7.2	9.3
		1STH56	39	**5**	1.3	30
	HCN	**1STH56**	NR	**5**	5.8	--
Organic Polymer	Acrolein	**PECH**	580	**11**	1.7	341.2

References

Kendall, R.A.; Aprà, E.; Bernholdt, D.E.; Bylaska, E.J.; Dupuis, M.; Fann, G.I.; Harrison, R.J.; Ju, J.; Nichols, J.A.; Nieplocha, J.; Straatsma, 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*, 260-283.

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Acknowledgements

Work was funded by internal Seacoast Science R&D funding, by SBIR contract #NBCHC080014 topic # H-SB07.1-007 (DHS), and SBIR contract #W911NF-04-C-0026 topic #03-053 (ARO).