European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

COST Action TD1105

INTERNATIONAL WG1-WG4 MEETING on

New Sensing Technologies and Modelling for Air-Pollution Monitoring

Institute for Environment and Development - IDAD

Aveiro, Portugal, 14 - 15 October 2014

Action Start date: 01/07/2012 - Action End date: 30/06/2016 - Year 3: 2014-15 (*Ongoing Action*)

VOLATILE ORGANIC COMPOUND (VOC) DETECTION BY POLYMER-NANOSTRUCTURED CARBON COMPOSITE

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Function in the Action: WG Member

Affiliation /Country: Institute of Technical Physics, Latvia

COST is supported by the EU Framework Programme

European Science Foundation — ESF provides the COST Office through a European Commission contract

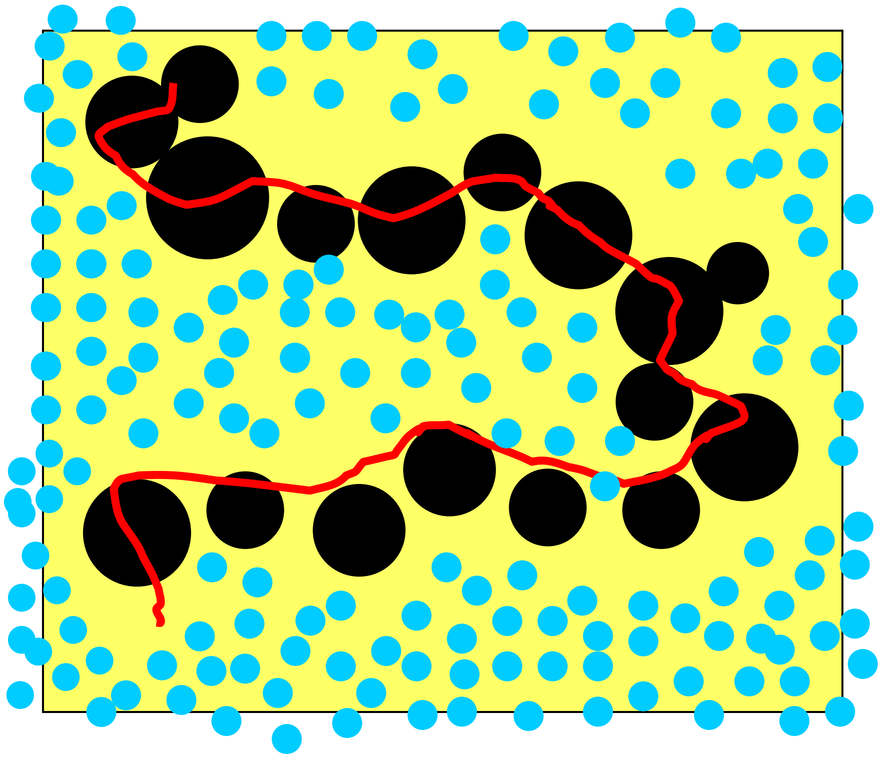
Scientific context and objectives (1/2)

- VOC detection. Why?
  - One of air pollutants → forms ozone at air-ground interface;
  - Increased health risks at work environment;
  - Explosive and highly flammable.
- Legislation
  - EU regulation on ambient air quality and cleaner air for Europe;
  - US Occupational Safety and Health Administration (TWA, PEL, IDLH, STEL).
- Available VOC detection methods → time consuming, expensive, time delay sampling-test result, sampling frequency etc..

VOC	TWA, ppm	STEL, ppm	IDLH, ppm
Toluene	100	150	500
Acetone	250	-	2500
Ethyl acetate	400	-	2000
Benzene	0.1	1	500
Formaldehyde	0.016	0.1	20

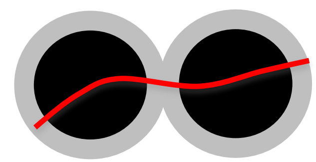
Scientific context and objectives (2/2)

- Polymer-nanostructured carbon composite (PNCC) as VOC sensor..



Sensitivity
Response time
Repeatability
Selectivity

I. Balberg propose percolation-tunneling model
Carbon 40 (2002) 139–143

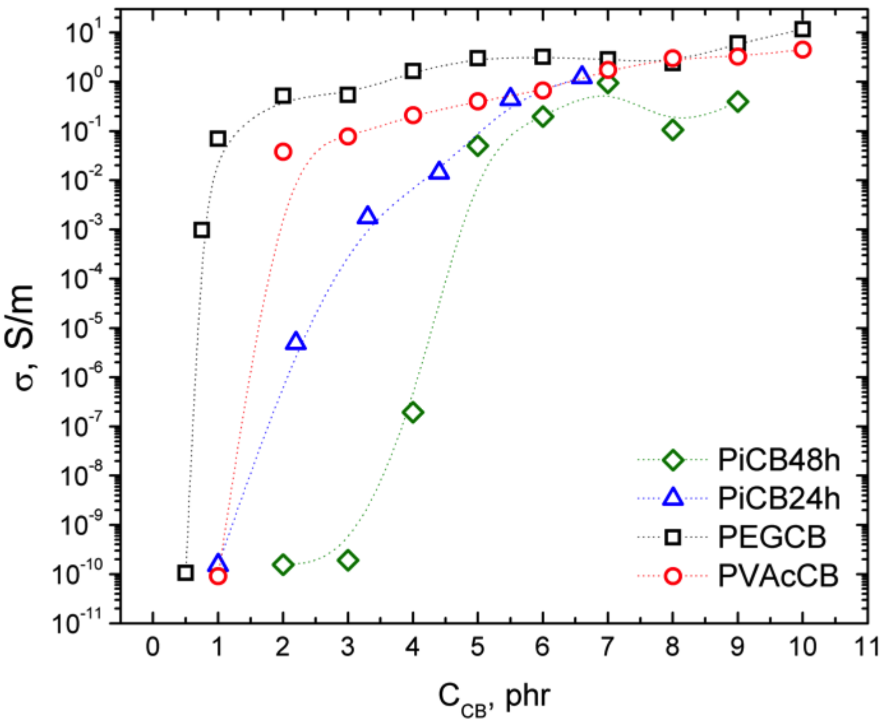


$$I_{tun} = \frac{3\sqrt{2m_e\varphi_{pot}}}{2s}\left(\frac{e}{h}\right)^2 U \exp\left(-\frac{4\pi s}{h}\sqrt{2m\varphi}\right)$$

J.G. Simmons
J. Appl. Phys. 34 (1963)

Current activities (1/2)

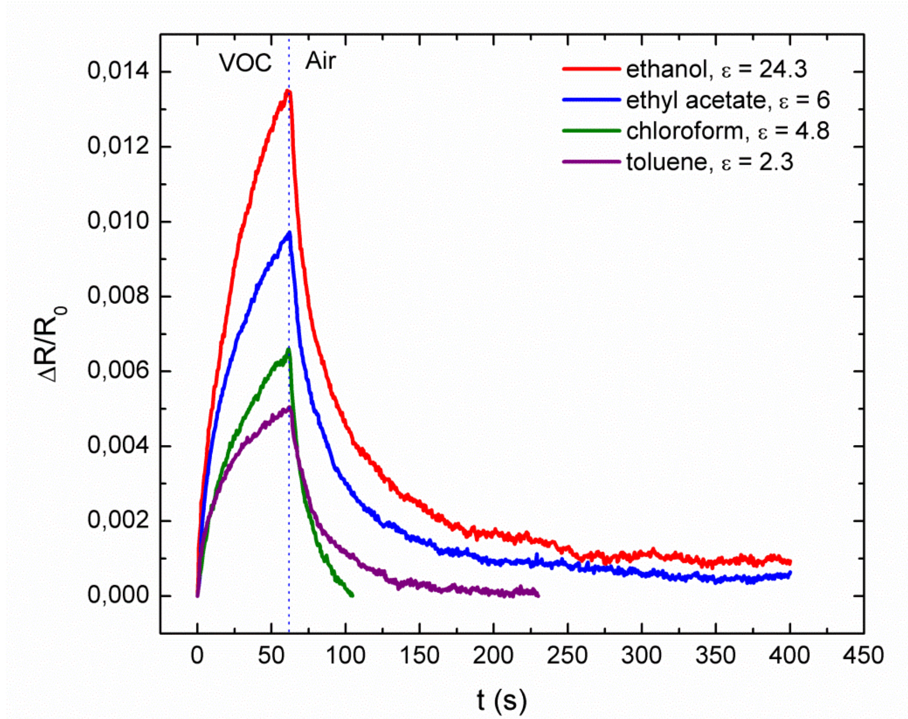
Characterization of conductive structure



Conductivity of composites versus filler concentration.

Analyze sensitivity

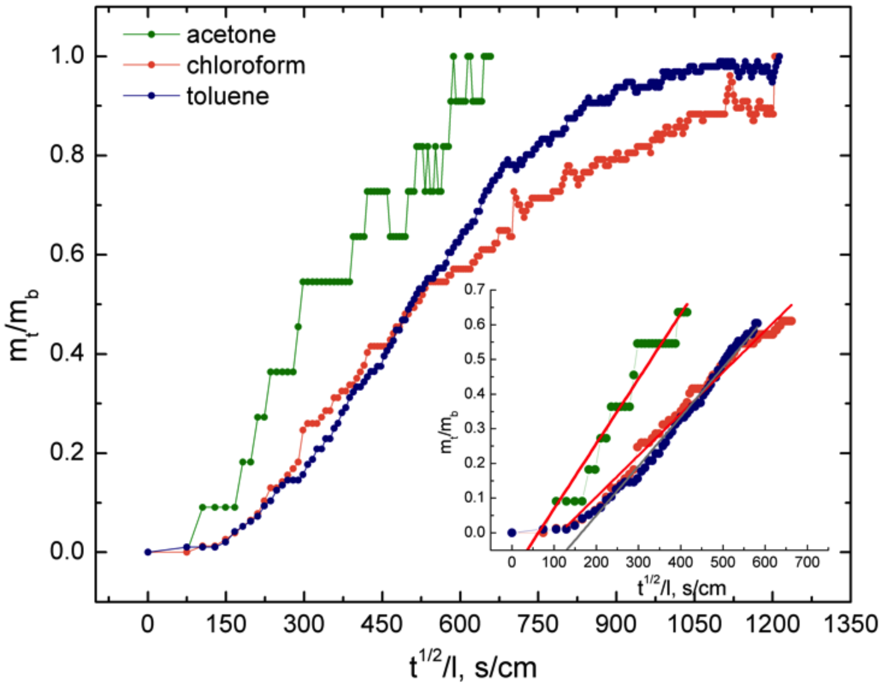
- polymers,
- fillers,
- VOC (polarity and size of molecules)



PVAcCB4 composite response to VOC at 500ppm.

Current activities (2/2)

VOC diffusion



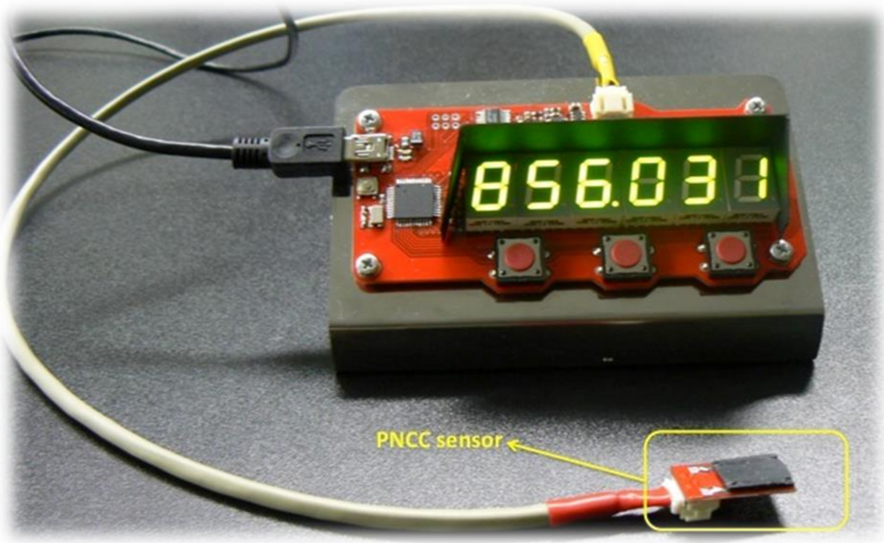
Mass change versus time, when PiCB4.4 exposed to different VOC.

Sensing mechanism

$$\frac{R}{R_0} = \frac{s}{s_0}\exp[\gamma(s - s_0)]$$

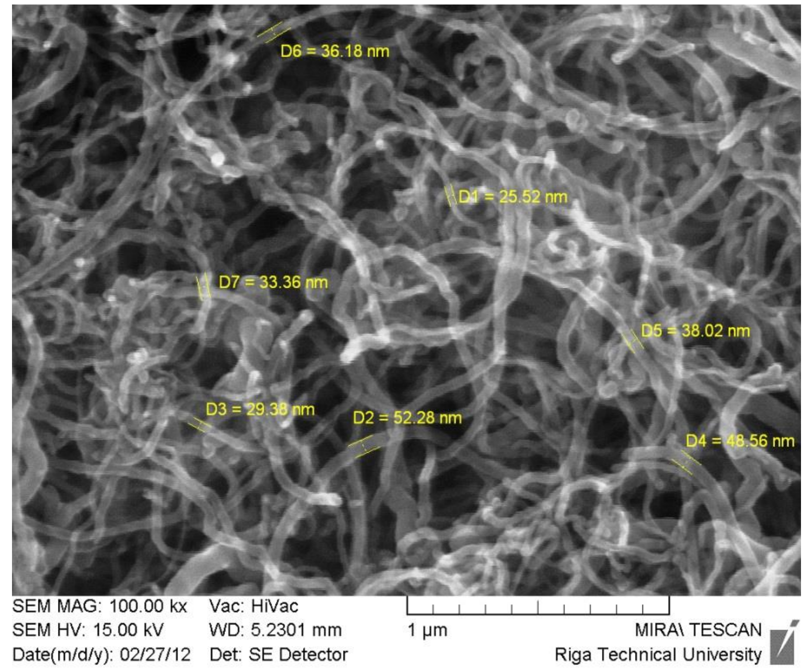
G. Sakale, D. Jakovlevs, I. Aulika, M. Knite
J. Nano Res. 21 (2013)

Prototype device

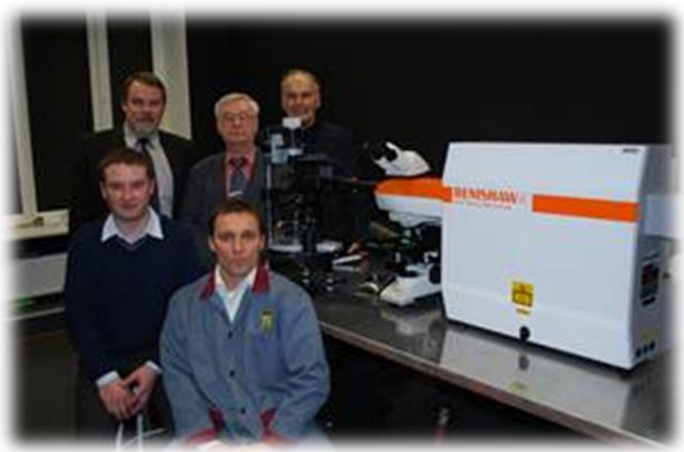


Facilities available (1/2)

Bruker Vertex 70 FTIR spectrometer with ATR module

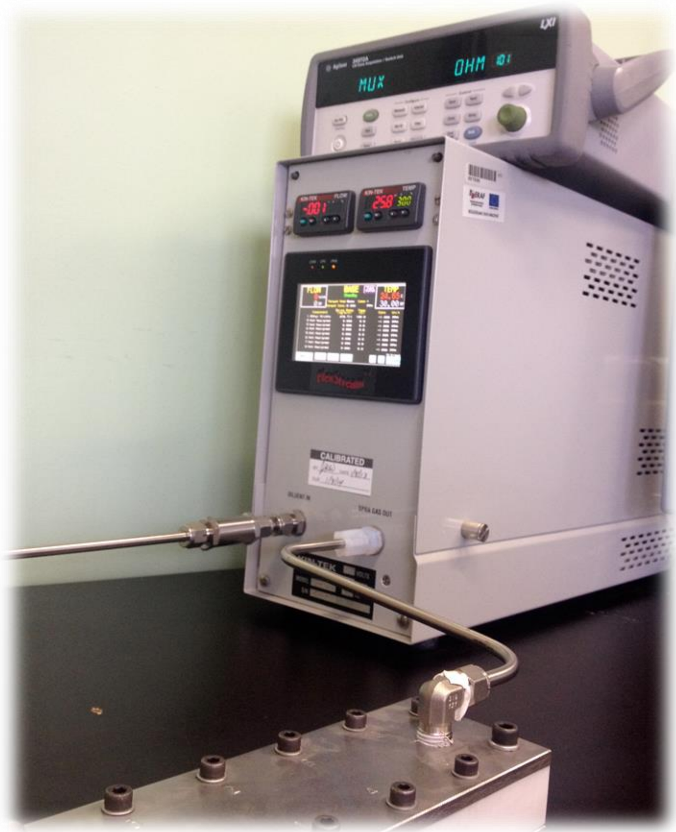


SEM Tescan Mira/LMU with EDS by RTU Deparment of General Chemical Engineering

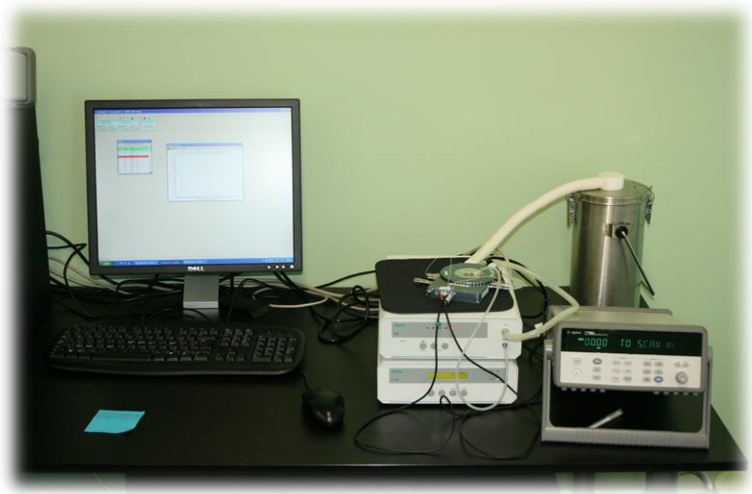


RENISHAW inVia Raman Microscope

Facilities available (2/2)



Agilent 34970A (~100MΩ) and Keithley 6487 picoampermeter (~10^{-16}Ω)

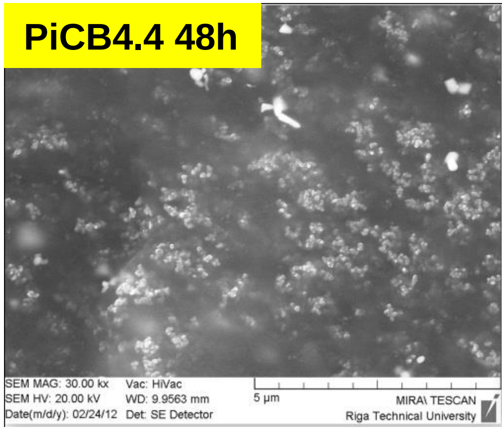


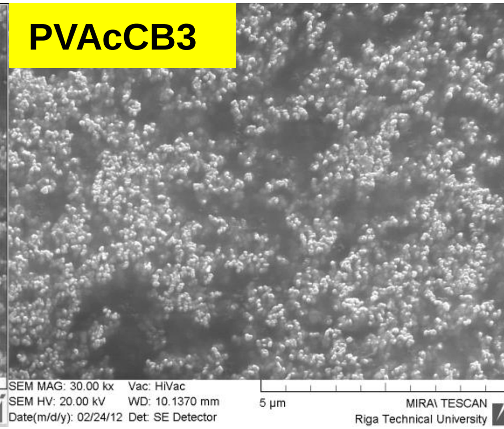
FlexStream™ Automated Permeation Tube System

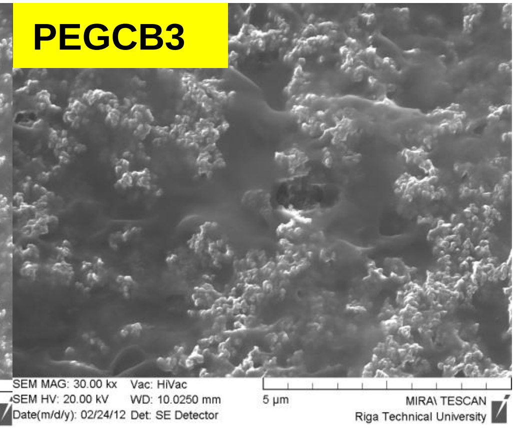
Linkam THMSE 600 low and high temperature conductivity measurement system (-190^{o}C to 600^{o}C)

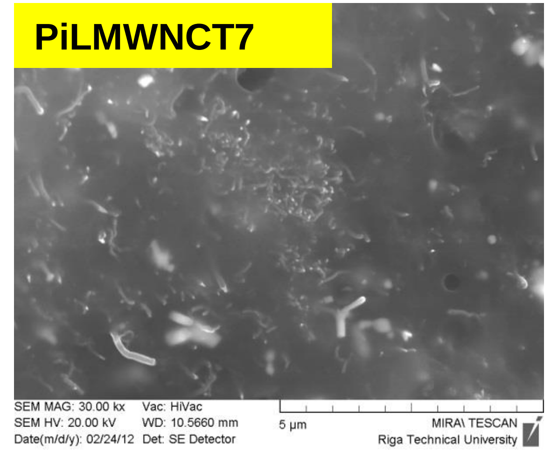
Achieved RESULTS (1/4)

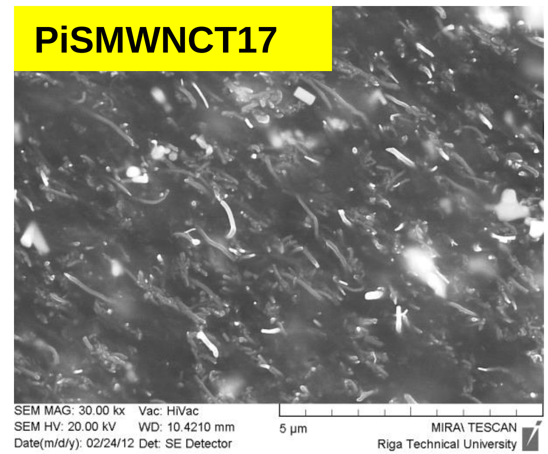
Characterization of conductive structure







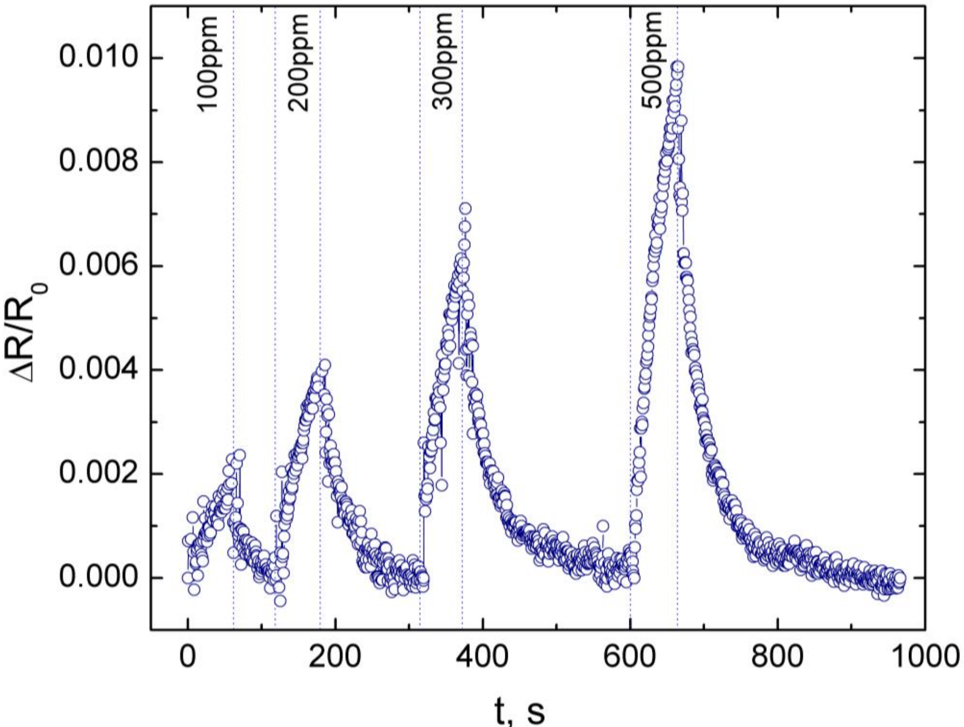




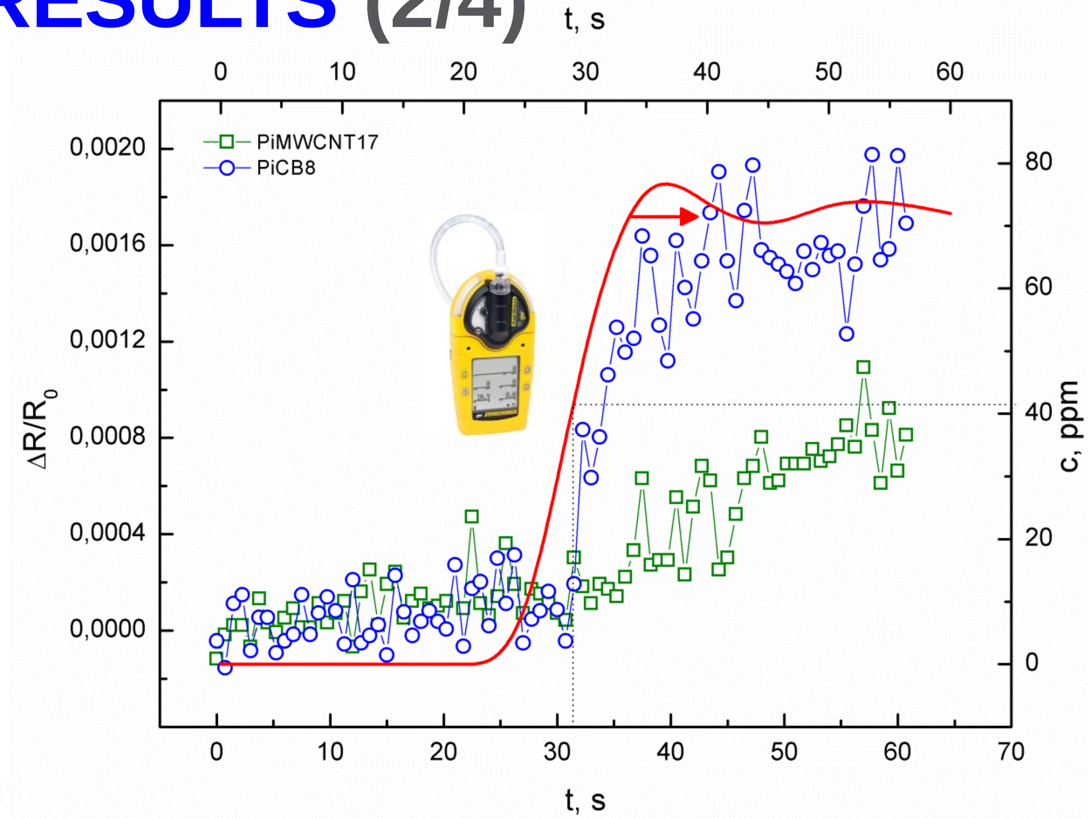
Composite	f_c, phr	t	Notes
PiCB24h	1,2	7,4	Production technology impact
PiCB48h	2,6	1,08	
PiCBRoll	8,1	6,6	
PiCB48h	2,6	1,08	Polymer matrix impact
PVAcCB	2	2,05	
PEGCB	0,75	1,28	
PiCB48h	2,6	1,08	Filler impact
PiLMWCNT	3.15 w.% = 3,4 phr	4,95	
PiSMWCNT	5.8 w.% = 6,13 phr	4,54	

Achieved RESULTS (2/4)

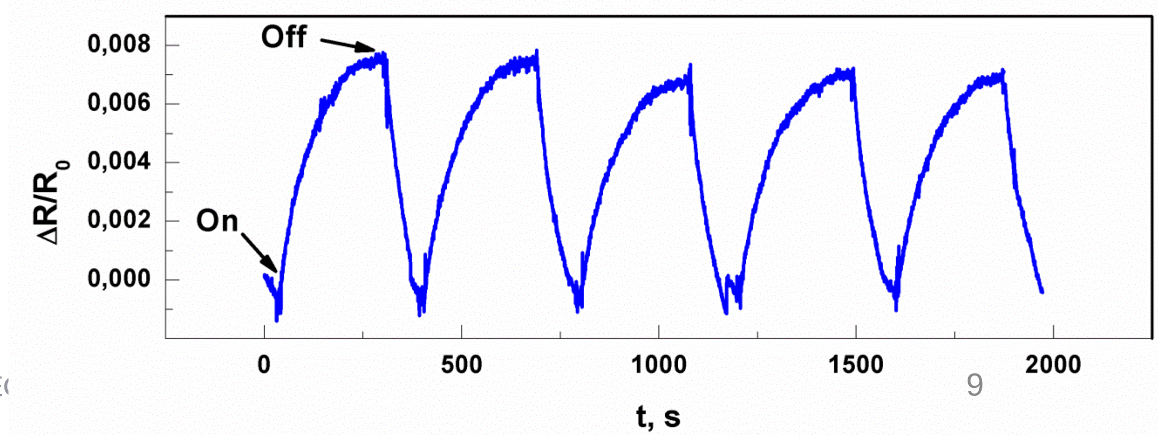
Sensitivity



PiCB8 48h relative electrical resistance change vs. time, when exposed to toluene.



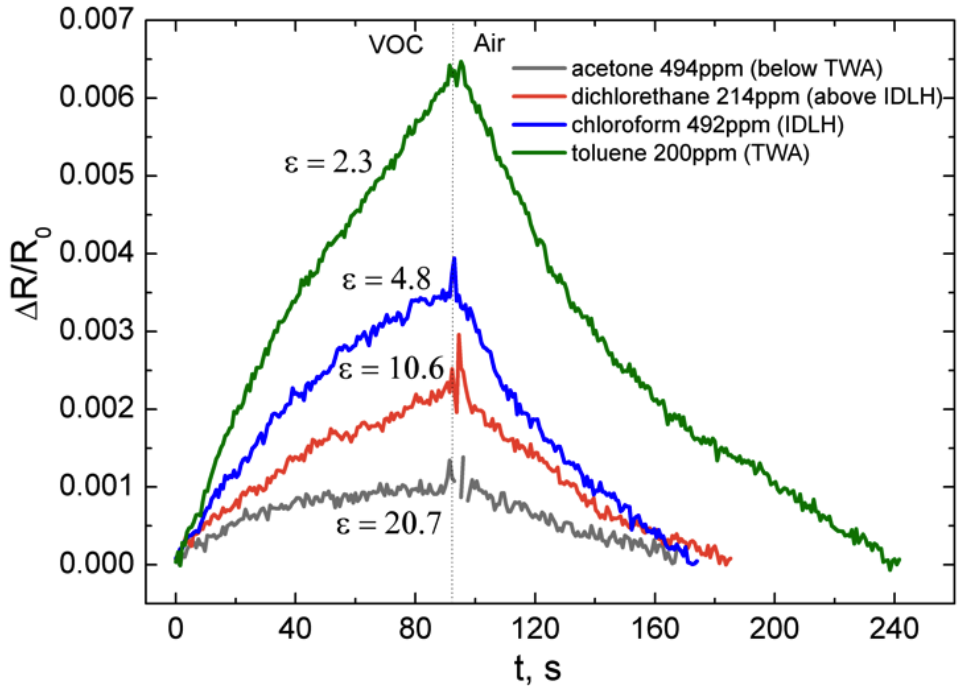
PiCB8 and PiMWCNT17 relative electrical resistance change vs. time, when exposed to toluene.



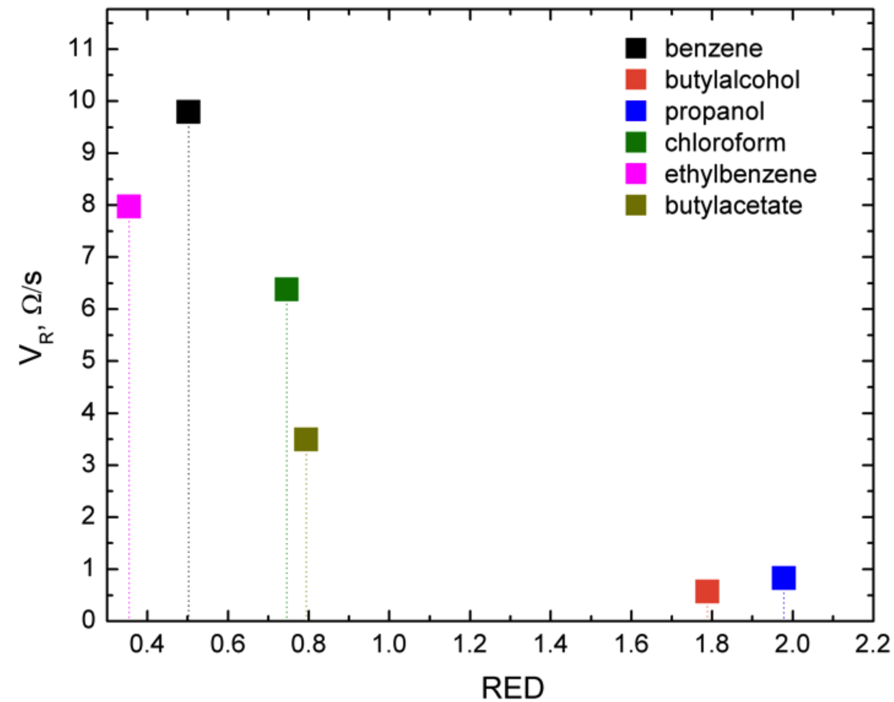
PiCNT(7)CB(5) relative electrical resistance change vs. time, when exposed to toluene 200ppm.

Achieved RESULTS (3/4)

Selectivity



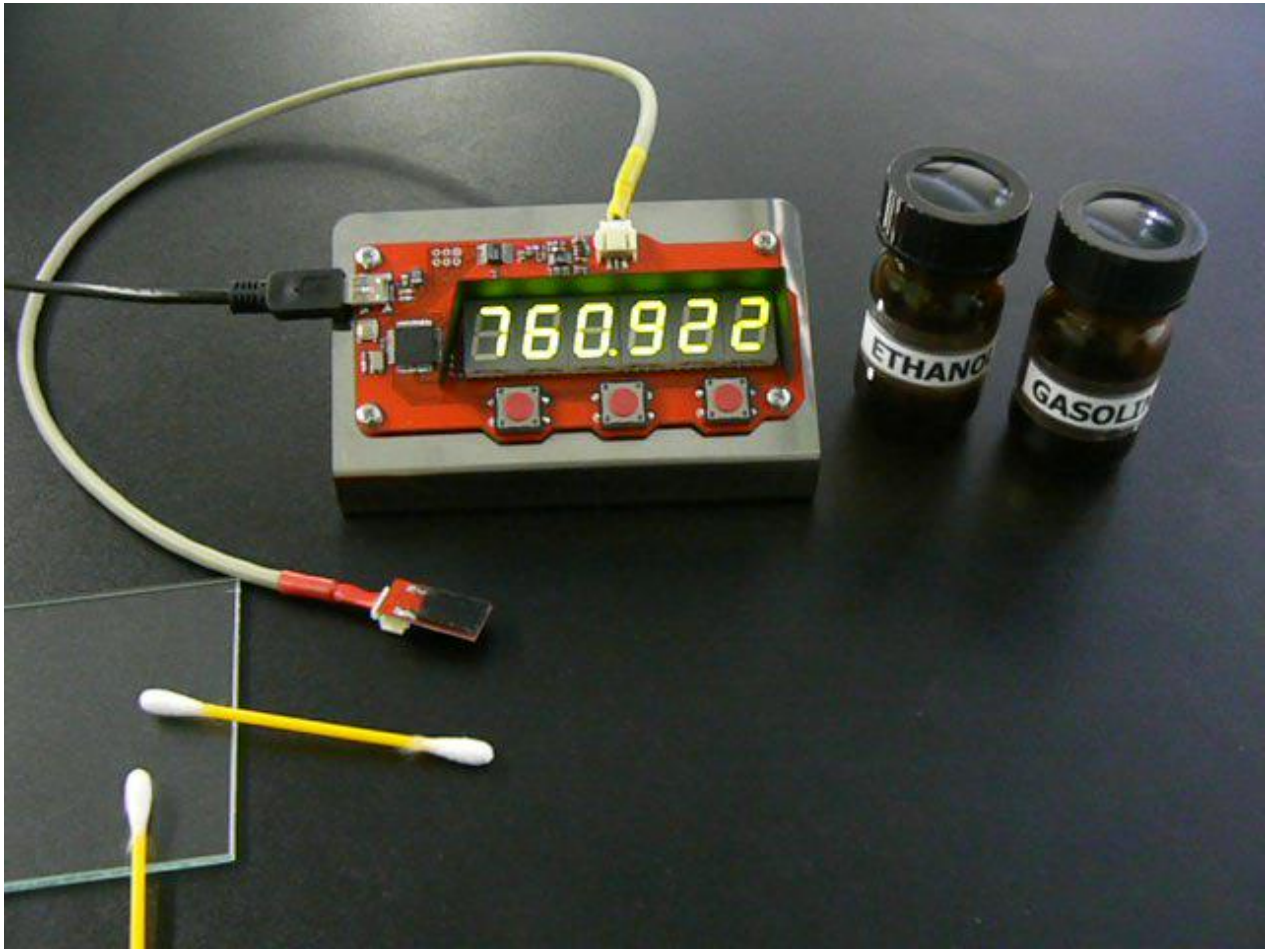
PiCB4.4 24h relative electrical resistance change vs. time.



Electrical resistance change velocity PiCB10Roll in different VOC vs. relative energy difference (RED).

Sensitivity toluene	
< 5 ppm (polyaniline)	Sens. Actuators, B 202 (2014) 732–740
15±10 ppm (conducting polymer–carbon black nanocomposite)	Sens. Actuators, B 201 (2014) 308–320
72 ppm (MWCNT-polyethylene oxide)	Sens. Actuators, B 191 (2014) 24–30

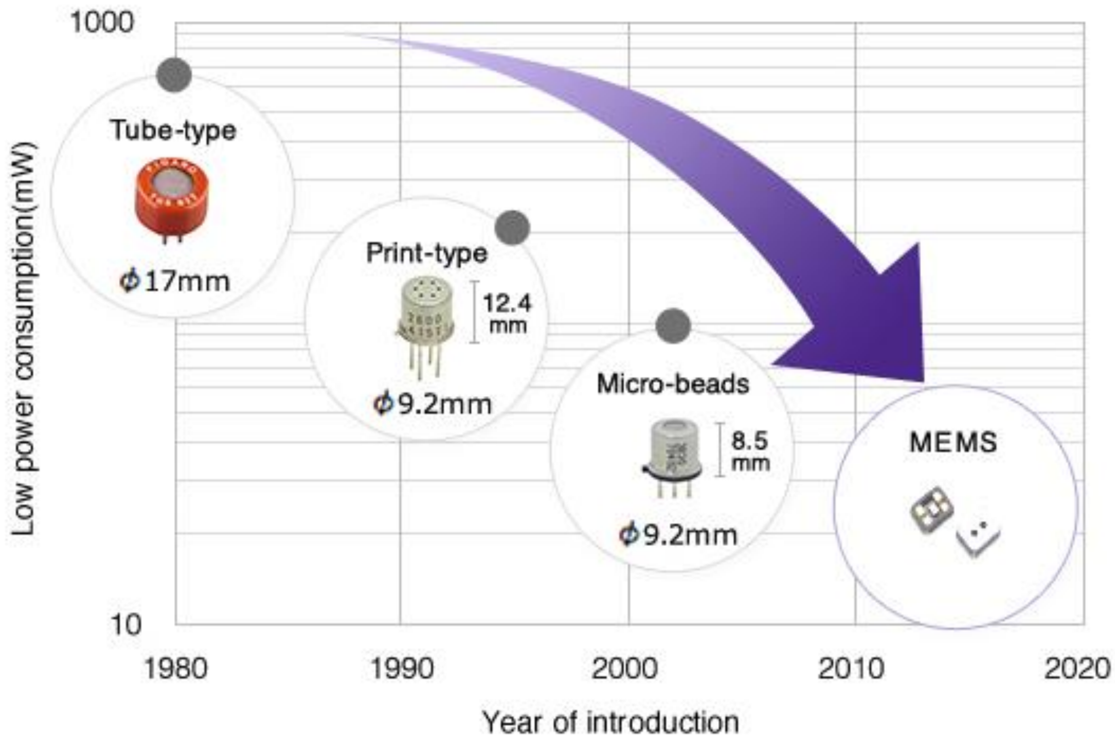
Achieved **RESULTS** (4/4)



CONCLUSIONS

- Several types of polymer-nanostructured carbon composite sensor materials have been produced, which show promising sensitivity to VOC below required permissible exposure limits.
- Composite conductive structure (network formed) is dependent of used polymer matrix (crystalline – low; elastomers – high percolation threshold values), filler type (higher aspect ratio lower percolation threshold) and production technology applied.
- More favorable for gas sensor materials are elastomer like matrix material: faster and more stable response, reduced steady state electrical resistance drift, faster recovery after exposure.
- Sensor material has higher sensitivity to VOC, which are compatible with polymer matrix material.

Future planned Activities



http://www.figaro.co.jp/en/challenge/mobile.html

- Miniaturization!
- Sensor printing.
- Improve prototype for field tests.
- Replace composite matrix material - polyisoprene with other elastomer.
- New filler materials (graphene?) - Journal of Environmental Chemical Engineering 2, 2014,1514–1526.

EIROPAS SOCIĀLAIS FONDS

IEGULDĪJUMS TAVĀ NĀKOTNĒ

EIROPAS SAVIENĪBA

EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY


Thank you for attention!