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COST Action TD1105

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Innovations and Challenges for Air Quality Control Sensors

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Monitoring of hydrocarbon contamination and emission from water using pervaporation membrane unit and MOX sensors

Speaker

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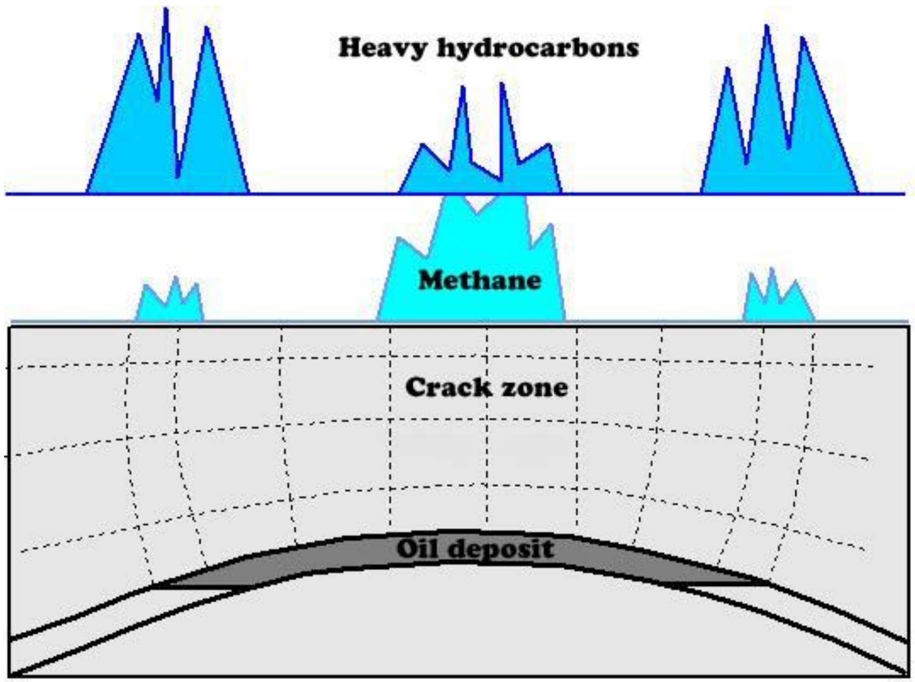
COST is supported by the EU Framework Programme

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

Participants of the Project

- *Alexey Vasiliev, NRC Kurchatov Institute, Moscow, Russia*
- *Andrey Sokolov, LLC “Delta-S”, Moscow, Russia*
- *Mikhail Yablokov, Institute of synthetic polymer materials, RAS, Moscow, Russia*

Motivation



Discovery of oil and gas fields under water

Monitoring of leakage from underwater pipelines

Motivation

Determination of gas and hydrocarbon content in drilling mud

Motivation

Control of methane (hydrocarbon) emission from natural sources

Detection of H_2 dissolved in water of nuclear reactor

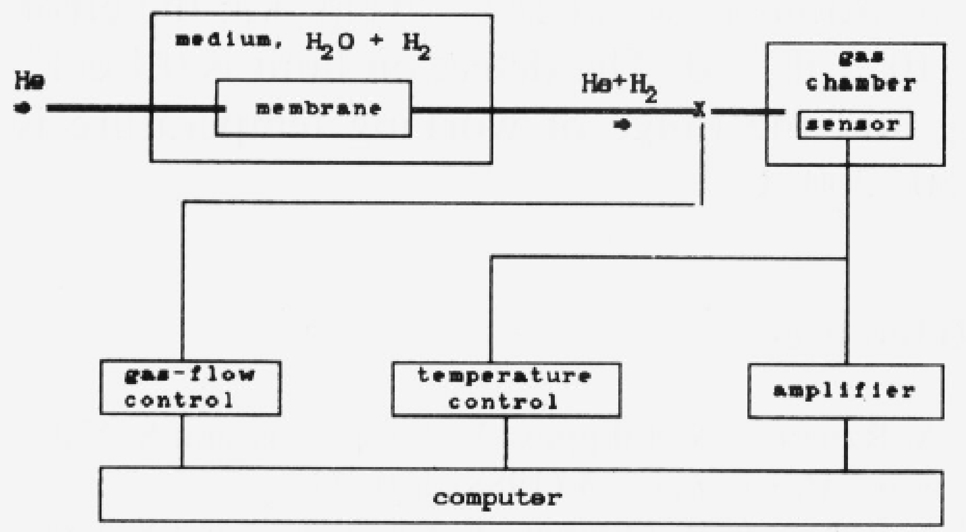


Fig. 1. System configuration.

V.I.Filippov, A.A.Terentjev et al. RRC Kurchatov Institute, Moscow, Russia.

Sensors and Actuators B, 5 (1991) 185–186

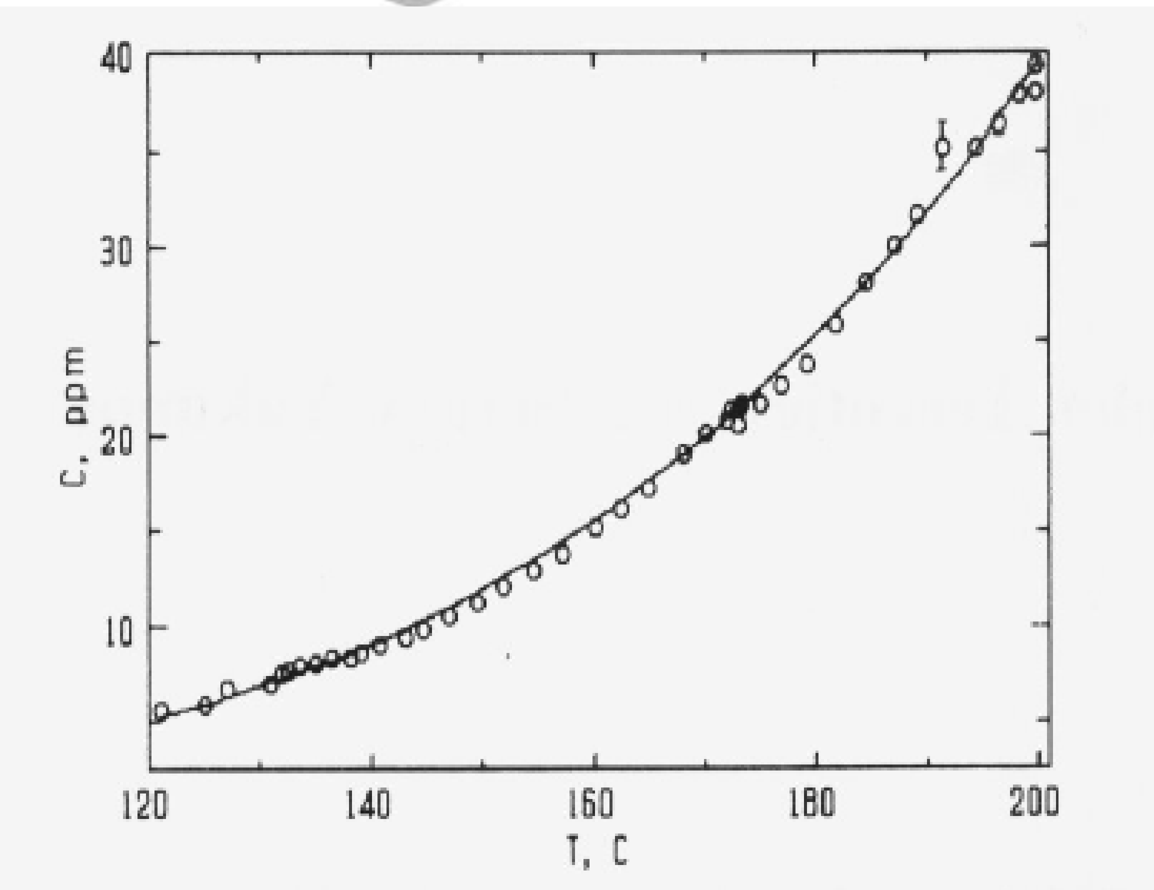
<u>Membrane material:</u>
Pd/Ru capillary
diameter 3 mm,
wall thickness 0.1 mm

<u>Sensor:</u>
MIS structure with Pd gate electrode

<u>Medium under study:</u>
Water of nuclear reactor
H_2 content 10 sccm/liter

<u>Carrier gas:</u>
Helium

H_2 concentration in carrier gas (helium) as a function of water temperature



H_2 concentration:

$C \sim exp(-E_{act}/kT)$

$E_{act} = 0.36 \pm 0.04$ eV

V.I.Filippov, A.A.Terentjev et al.
RRC Kurchatov Institute,
Moscow, Russia.

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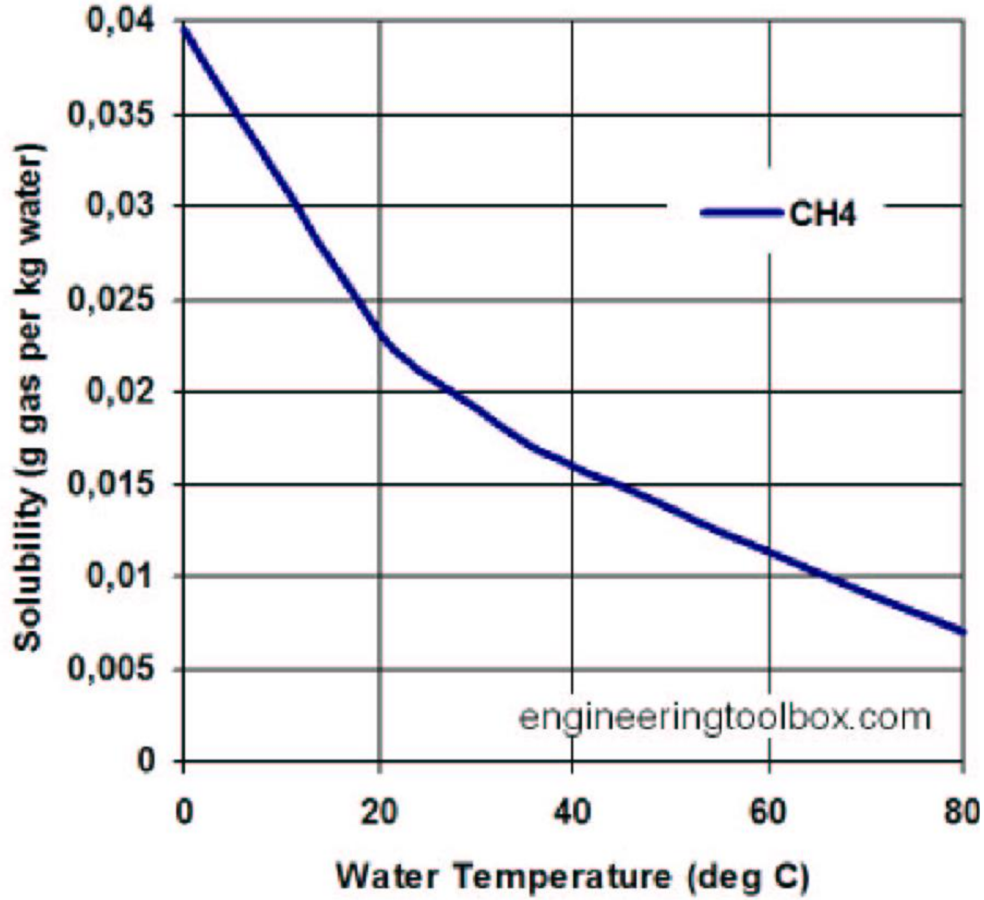
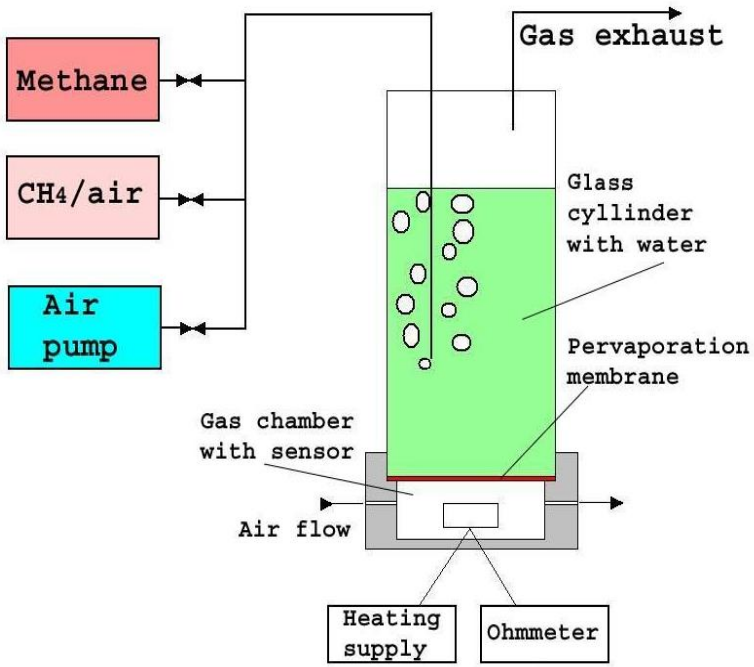
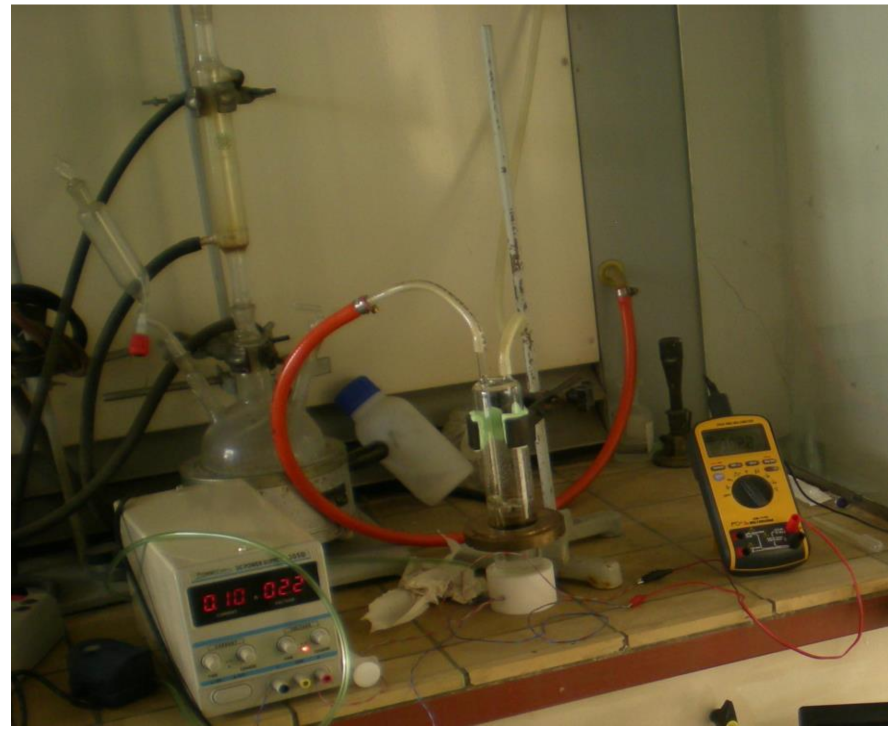
Solubility of methane in water



Preliminary experiments:
Installation used for the measurement of methane concentration in water





(A) Scheme of the setup used for the measurement of the concentration of methane dissolved in water. (B) Photo of the setup used for the measurement of the concentration of methane dissolved in water.

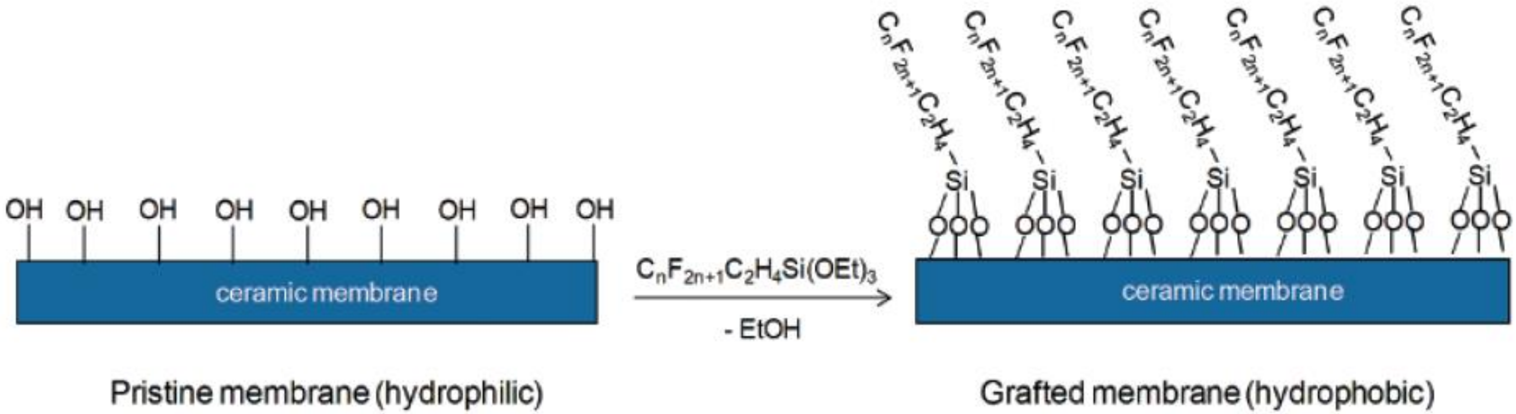
A.A. Vasiliev, A.V. Sokolov, W. Kujawski, A. Rozicka, V. Guarnieri, L. Lorenzelli. Gas Sensor System for the Determination of Methane in Water. Procedia Engineering, v. 87, 2014, Pages 1445-1448

Preliminary experiments: membranes in use

- *Polydimethylsiloxane (PDMS) membranes (contact angle 104^0)*
- *Ceramic TiO_2 membranes modified by grafting of perfluorinated ethoxysilane compound $C_nF_{2n+1}C_2H_4Si(OEt)_3$ (n = 6 and n = 12). Contact angle is 127^0 and 148^0, for n = 6 and n = 12, respectively.*

A.Rozicka, W. Kujawski, V. Guarnieri, et al., Hydrophobic membranes for system monitoring underwater gas pipelines. Architecture, Civil Engineering, and Environment 5 (2012) 99-106.

Hydrophobized ceramic membrane

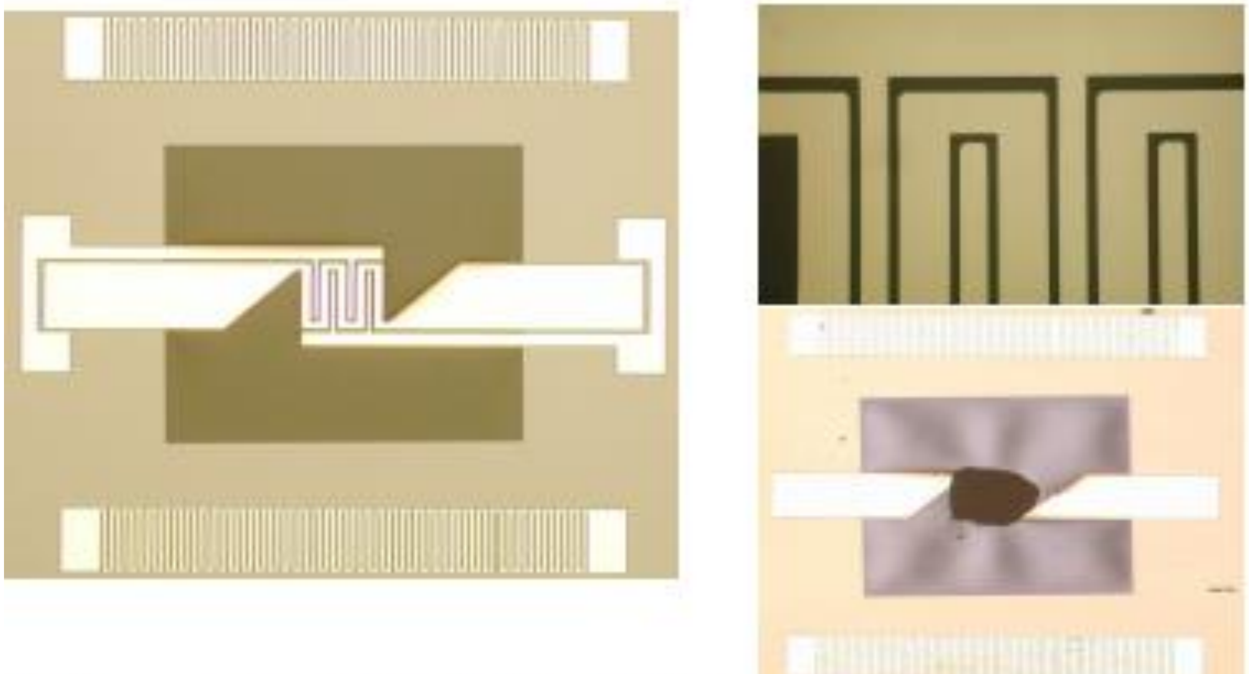


Water drop on PDMS membrane surface

and on ceramic membrane surface

A.Rozicka, W. Kujawski, et al., Hydrophobic membranes for system monitoring underwater gas pipelines. Architecture, Civil Engineering, and Environment 5 (2012) 99-106.

Gas sensors used for the measurement of methane concentrations: SnO2 + 3 wt.% Pd (~ 10 nm particles)



Micromachined thin film membrane and Platinum microheater

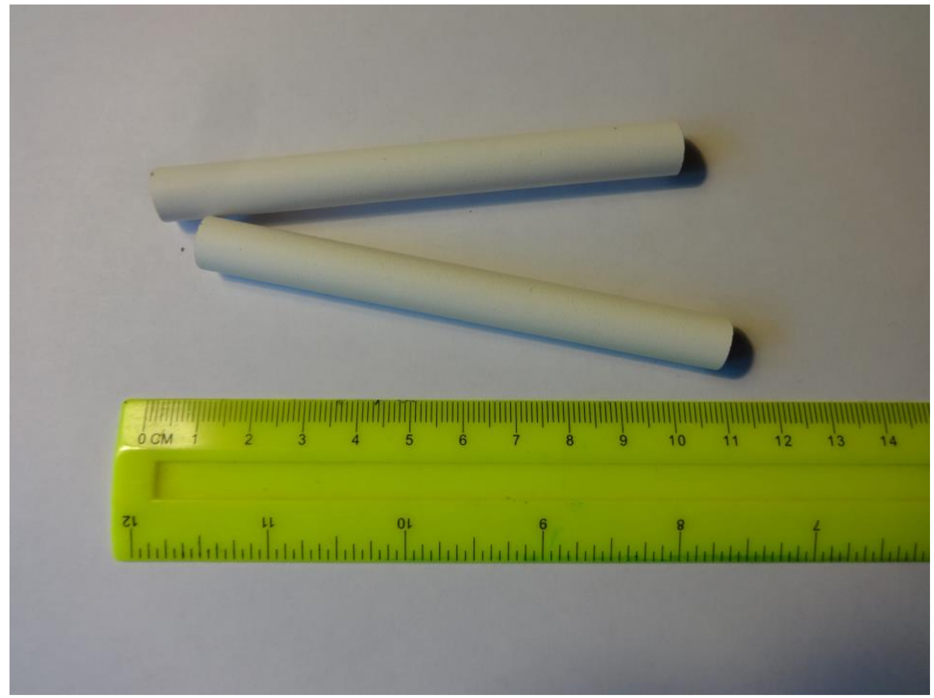
TO-8 packaged thick film sensor chip. Chip size 2.5 x 0.3 x 0.1mm

A.A. Vasiliev, A.V. Sokolov, W. Kujawski, A. Rozicka, V. Guarnieri, L. Lorenzelli. Gas Sensor System for the Determination of Methane in Water. Procedia Engineering, v. 87, 2014, Pages 1445-1448

Pervaporation tubes used in the experiments

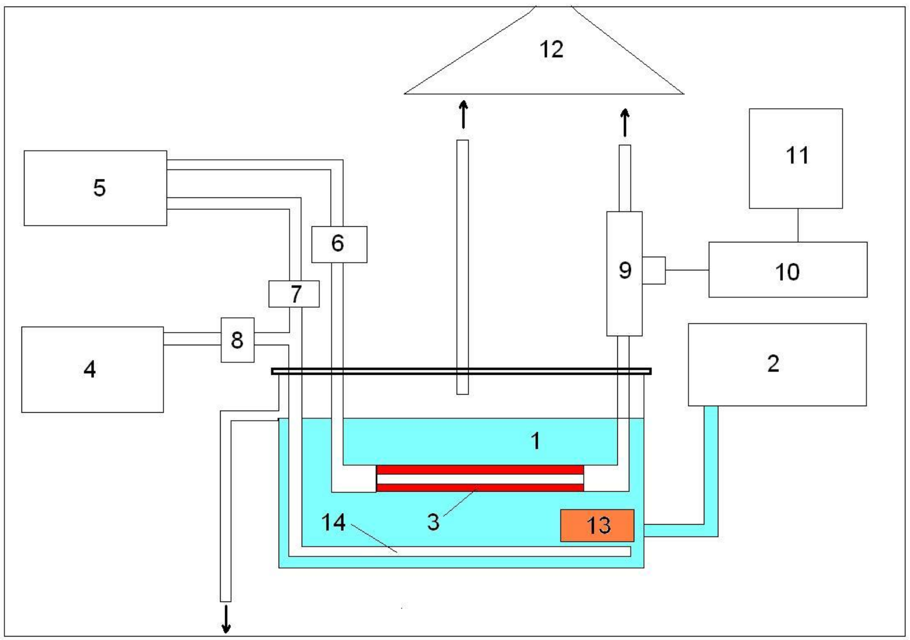
- ***Alumina ceramic tube 100 mm long, 100 mm in diameter, 6 mm inner diameter. Pore size 10 μm. Impregnated with perfluorinated ethoxysilane liquid.***
- ***Alumina tubes with TiO_2 coating. Pore size is 0.1 μm. Impregnated with perfluorinated ethoxysilane liquid.***
- ***Alumina tube with pore size of 0.1 mm. Coating with electron beam sputtered PTFE.***

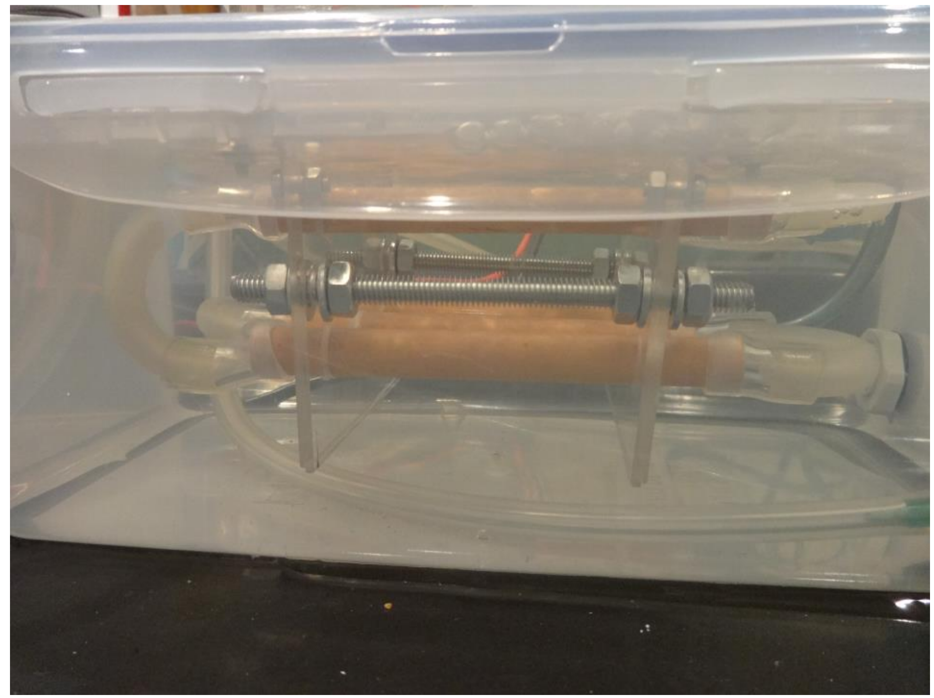
Ceramic tubes hydrophobized by perflurinated liquid



Alumina tubes with pore size of 10 μm (left) a alumina tubes with titania coating (pore size 0.1 μm).

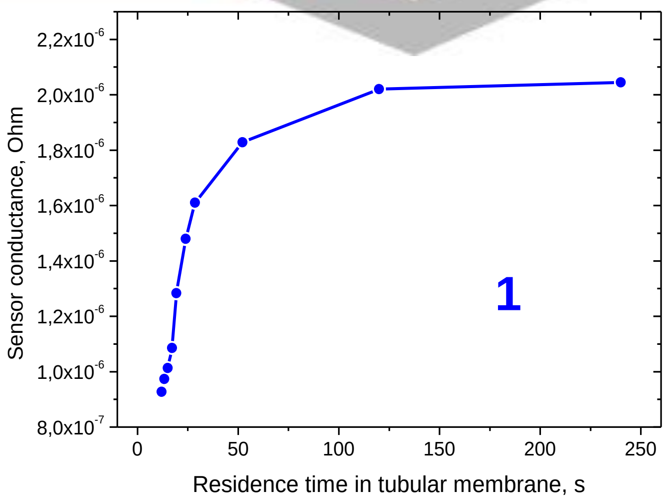
Scheme of the set-up and photo of permeation unit applied in the experiment

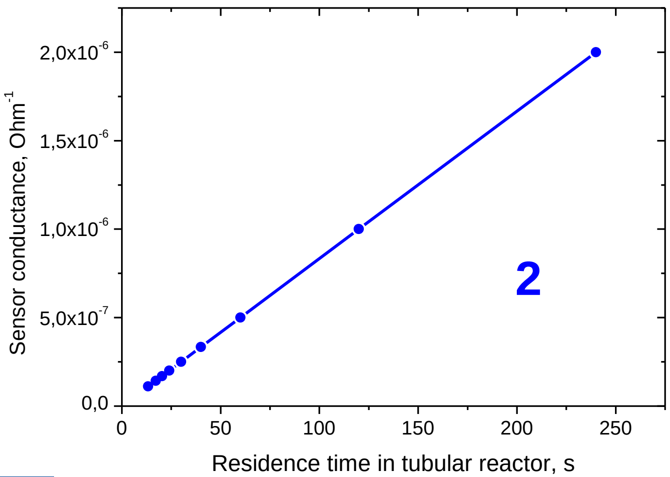




The scheme of the set-up used for the study of hydrocarbon content in water. (1) cell with water; (2) water tank; (3) porous ceramic tubes with hydrophobic coating; (4) cylinder with methane; (5) generator of purified air; (6-7) air flowmeters with valves; (8) methane flowmeter; (9) gas sensor cell; (10) voltage source and ommeter for the measurement of MOX sensor response; (11) computer; (12) fume hood; (13) pump for water stirring; perforated tube for gas mixture bubbling through water.

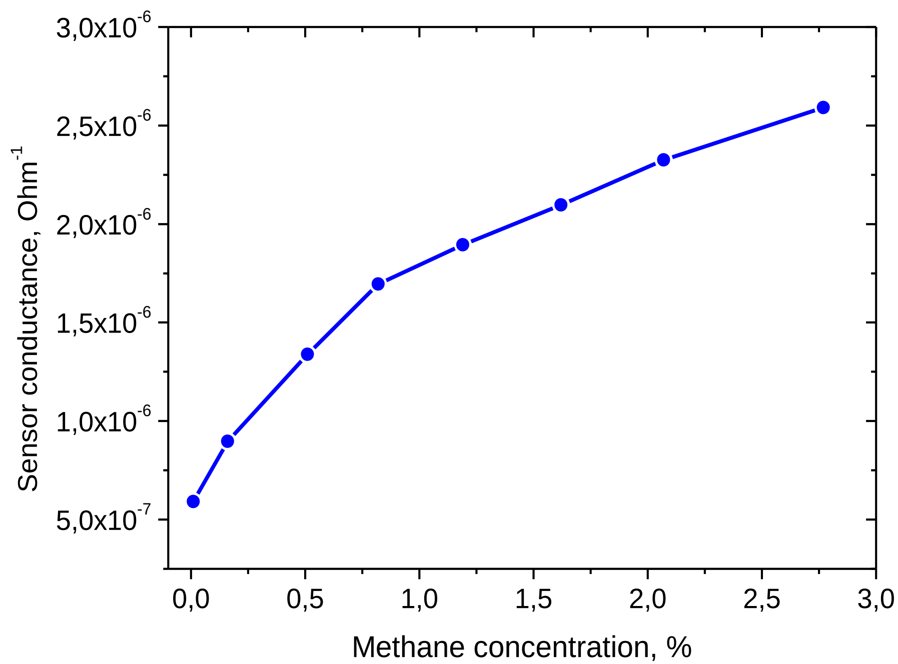
Membrane unit made of "red" ceramics (10 μm pores)





Sensor conductivity as a function of carrier gas time of residence in membrane unit: (1) fresh membrane unit is put to water; (2) membrane unit was in water during 1 month and is imbued with water.

CH4 concentration 1.06 % in air corresponds to sensor conductance of $7.6 \cdot 10^{-6}$ Ohm^{-1}



Sensor signal as a function of the concentration of methane bubbling trough water. Carrier gas velocity in membrane unit is of 0.5 cm/s.

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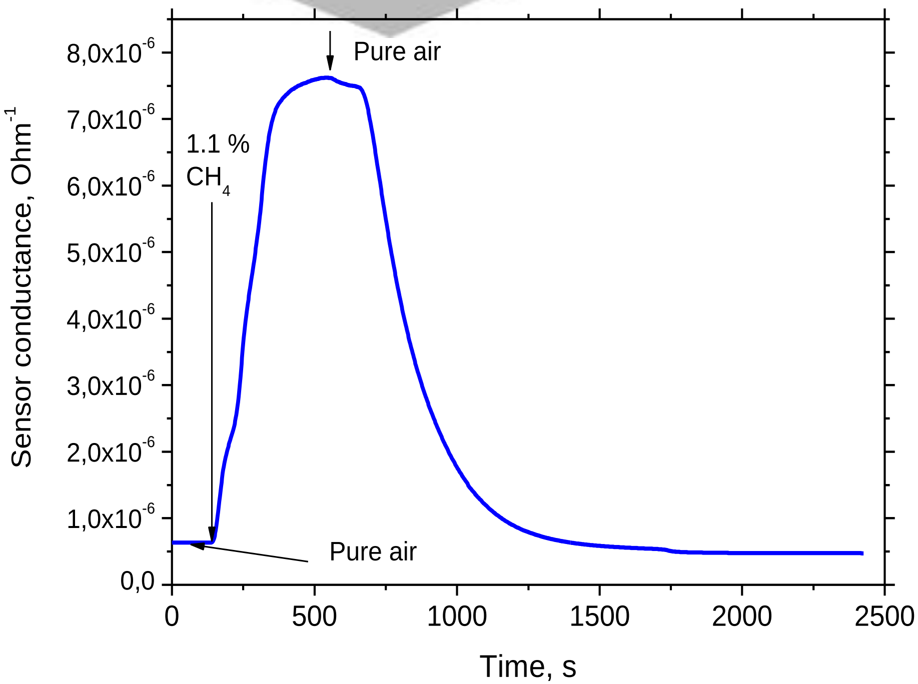
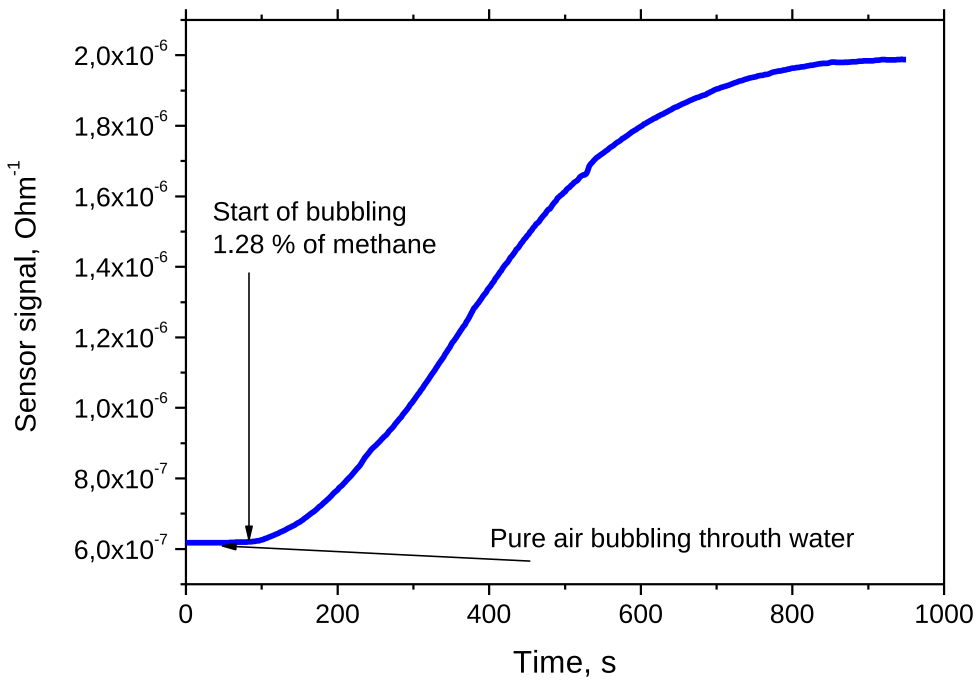
Membrane unit made of "white" ceramics (0.1 μm pores)





Response time of the sensor; the measurement was performed without water in water cavity, gas concentration is 1.1 %.

Response time with water in water cavity. This response time is a superposition of time necessary for the water saturation with methane and response time of the sensor.

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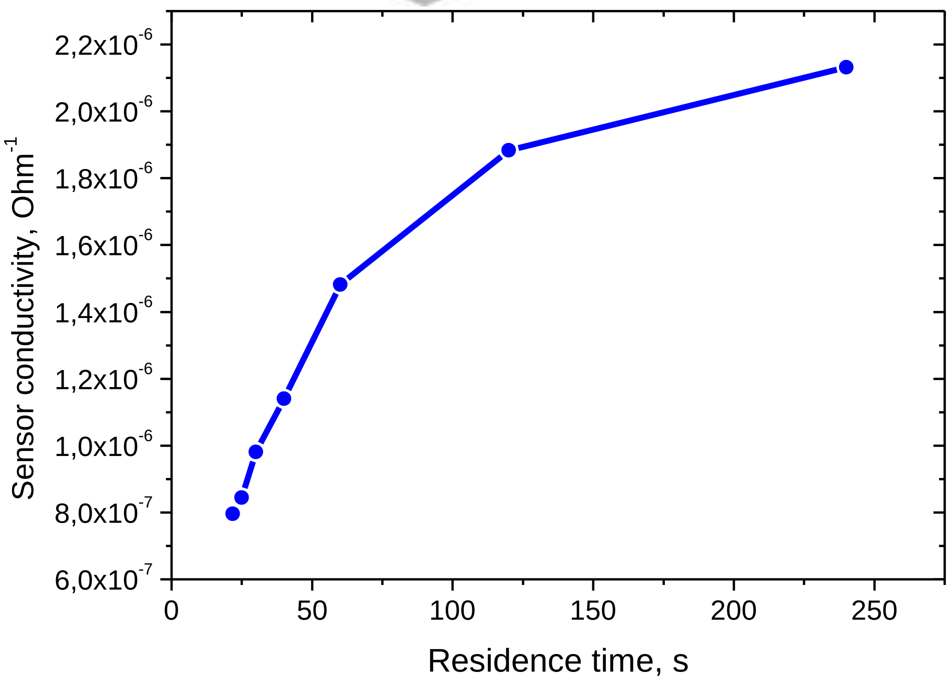
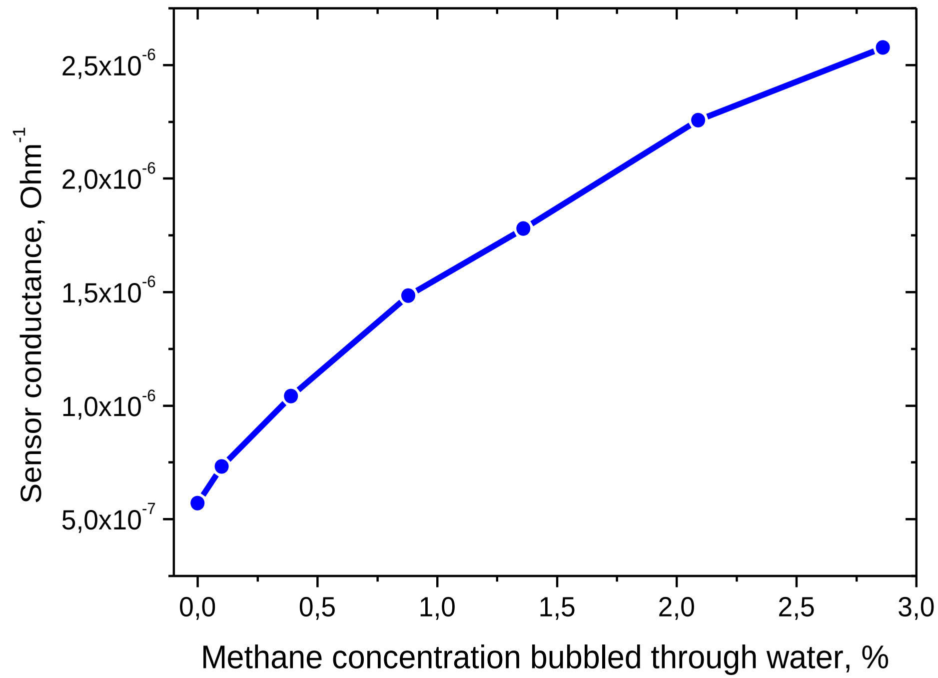
Membrane unit made of "white" ceramics (0.1 μm pores)



Sensor signal as a function of carrier gas residence time in membrane unit. Concentration of methane bubbling through water is of 1.26 %.



Sensor signal as a function of the concentration of methane bubbling trough water. Carrier gas velocity in membrane unit is of 0.5 cm/s.

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CONCLUSIONS

The analysis of the results shows that

- *the methane detection limit of the sensor system consisting of pervaporation membrane and gas sensor can be of about 10 – 20 ppb (mass);*
- *response time of the system after the optimization can be of about 10 s; to get this response time it will be necessary to decrease significantly the thickness of porous tubular membrane and to optimize hydrophobic coating;*
- *localization of the leakage or gag/oil field can be of about 10 m at towage speed of ~1 m/s.*

Acknowledgements

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Thank you for attention!