Electronic Noses: Potential for Mine Detection?

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Outline

• Introduction
• Chemical Sensing
  – Sensitivity
  – Stability
  – Selectivity
• Application Examples
  – Good Case
  – Bad Case
  – Why?
• Situation for Mine Detection
• “Offer” of the Sensor Community
• Summary
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Motivation
Sensor system

Species to be detected

gas sensing: NO\textsubscript{x}, NH\textsubscript{3}, CO, CO\textsubscript{2}, H\textsubscript{2}O, O\textsubscript{3}, SO\textsubscript{2}, CH\textsubscript{x}, HCs, PER, VOC\textsubscript{s}, ...

odors: olive oils, coffee, perfume, packaging materials, plastics, ...

Analytical values

C(NO\textsubscript{2})
C(CO)
TOC
ok, not ok, A/ B/ C

Interaction Mechanisms

Heat electrons ions masses light

O\textsubscript{2}, CO\textsubscript{2}

Analytical values
Issues / Problems / Goals

• Sensitivity
  ➢ to detect also very low concentrations

• Stability
  ➢ To get the same result over time (one day, one week, one year)

• Selectivity
  ➢ To get the right information even if other compounds are around

(3S Problem of Chemical Sensing)

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Actual Sensor Structures
Overview "sensor"

Actual sensor structures
Powder based (450°C, undoped)
Planare Sensor Struktur

25.4mm x 4.2mm

High Sensitivity
DC Results

CO (ppm)

CO concentration (ppm)

Electrochemical Cell (TSI)

resistance (Ω)

home-made SnO₂ (Pd doped)

0.00 0.01 0.02 0.03 0.04 0.05 0.06

0.00 0.01 0.02 0.03 0.04 0.05 0.06

0 5 10 15 20 25 30 35 40

time (hours)

10¹ 10² 10³ 10⁴ 10⁵ 10⁶ 10⁷

10¹ 10² 10³ 10⁴ 10⁵ 10⁶ 10⁷

standard dev EC vs SnO₂ (Pd)
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High Stability
Long Term Results

![Graph showing sensor signals for SnO2 sensors and an Electrochemical sensor over time.]

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Pattern Generation

Polydimethylsiloxane (PDMS)

Poly(isopropylcarboxylic acid) methylsiloxane (PiPCAMS)

Polyaminopropyl)methylsiloxane (PAPMS, 10% amino-groups)

Polyoctylmethylsiloxane (POMS)

Poly(cyanopropyl)methylsiloxane (PCPMS)

Poly[2-carboxy(D-valin-t-butylamide)propyl]methylsiloxane (Chirasil-Val, 10% valin-groups)
synthesized Bayer/Koppenhöfer, Organic Chemistry, Tübingen

Polarplots

POLAR PLOTS

n-octane

propan-1-ol
mixture of n-octane/propan-1-ol

PLS - n-octane
### Polarplots

**POLAR PLOTS**

- **Acidity**
- **Basicity**
- **Dispersion**
- **Polarizability**
- **H-Bonding**

**Chemicals**

- **Trichloromethane** (chloroform)
- **n-Octane**
- **Propan-1-ol**

**Tensors**

- PDMS (1)
- PPMS (4)
- PCPMS (3)
- CSVAL (5)
- PiPCAMS (2)
- PAPMS (6)
- PPCAMS (2)
- PDMS (1)
Polarplots

POLAR PLOTS

Dispersion
Polarity
Acidity
H-Bonding
Polarizability
Basicity

propan-1-ol
propan-2-ol

PLS - propan-1-ol

Predicted concentration [ppm]
True concentration [ppm]

propan-1-ol
**PLS - propan-2-ol**

![PLS graph with data points and concentration values](image)

**Polarplots**

![Polarplot diagram with molecules and descriptors](image)

- **molecules**: propan-1-ol, propan-2-ol, toluene, tetracloroethene, trichloromethane, n-octane
- **descriptors**: Basicity, Polarity, Dispersion, H-Bonding, Polarizability, Acidity, Basicity

**POLAR PLOTS**

- Scale 1:5

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Quality control of packaging material

State of the Art:
Human Odour Panel

Automated investigation
with “Electronic Nose”
Better called application specific
sensor system (a triple s)
Application: Quality control of packaging material

Odour prediction by MOSES

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0

Training data

RMSE = 0.26

Test data with re-calibration of the array

RMSE = 0.57

Odour prediction by human sensory panel

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Wine Differentiation

PC1: 66.0%
PC2: 20.8%
PC1 : PC2 = 0.925

Wine A
Wine B
Wine C
Wine D
Silvaner
Riesling
Kerner

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GC/MS of Packaging Material “Good Case”

more than 70% cyclohexane in the headspace

GC/MS of instant coffee “Bad Case”
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Situation for Demining:

• Sensitivity
  ➢ Considerable improvement during the last decade!
  ➢ We are at the medium ppb level and have to go to the ppt level
    (4 to 5 orders of magnitude improvement required!) \( \rightarrow 10.000.000\% \)

• Selectivity
  ➢ Even more a challenge!
  ➢ Concepts are developed (during the last two to three years) for other
    purposes, but have to be tested after/while solving the sensitivity issue

• Stability
  ➢ Nobody has experience in this concentration domain!

Further issues: (next transparency)
Further issues:

- Speed
  - How long takes an analysis (→ online)?

- Power
  - Power consumption of the overall system (battery operated)

- Costs

- Field applicability

A lot of work to be done!

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NOSE II

The **Second Network on Artificial Olfactory Sensing**

Topics: sensors, sensor systems, and electronic noses

IST Project 2001-32494

100 Members from **18** European countries
NOSE II website
www.nose-network.org

NOSE II office
University of Tübingen, ipc
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Auf der Morgenstelle 8, 72076 Tübingen, Germany

Website: http://www.nose-network.org
Email: nose@ipc.uni-tuebingen.de
General Olfaction and Sensing Projects on a European Level

IST 507610

Coordination: ipc, Tübingen
Project Officer: Thomas Sommer
2004-2007

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SME Association:
• Alpha MOS
• Gerstel
• Sensirion
• GasTec
• Microsensor Technology
• AppliedSensor

- use of existing excellence
- Durable networking /integration
- Use of synergy
- Assembling of critical mass
Æwe are a strong consortium

Applications
Æhealth (disease management)
Æbuildings (intelligent ventilation)
Æsafe transportation
Æpersonal safety
Æ...

Research emphasis
• Microsensors
• Microsensor Systems
• Nano-materials
• Signal processing
• Data analysis
• Biometrics
• Biological Olfaction

Measurement of Integration:
- Extent of mutual specialisation
and complementarity
- Common use of research
infrastructures, equipment...
- Regular execution of joint
research projects
- Complementarity of knowledge
portfolios and joint training programme
- Common management.

Jointly executed research activities
Research focus
• Microsystems
• Microsensor System
• Nano-materials
• Data analysis
• Biometrics
• Biological Olfaction

GB

Integrating activities
Scientific Council

ÄGOSPEL

Spreading excellence activities
Knowledge Transfer

Training activities
• Interdisciplinary exchange
• Research → industry
• Science → general public
• Knowledge base build-up
• Knowledge clustering at
new centers
• Internal exchange for
training, collaboration
and new projects seeding
• Individuals
• Team mobility
• Mobility from outside
network
• Attracting excellence
• Build-up of world
leader research

CoEs

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2003 2005 2010

Other funding agencies:
• National funding, e.g. VDI, DFG
• Innovative funding, EUREKA, EURIFORS

- Extent of mutual specialisation
and complementarity
- Common use of research
infrastructures, equipment...
- Regular execution of joint
research projects
- Complementarity of knowledge
portfolios and joint training programme
- Common management.

CoEs

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Summary (take home message)

• Mine detection with currently available chemical sensors not feasible
• Boundary conditions for the development (partially) understood
• Big challenges for research and development
• Need for a coordinated approach with all stake holders (very interdisciplinary!)
• Potential frame for discussion with sensor partners in Europe is NOSE and GOSPEL
Einführung

Sensor

physikalische Größe  
physikalisch leicht messbare Größe
Applications

Technology

Monitored parameters

Physical
- speed
- distance
- environmental control

Chemical
- pH-value
- CO-pressure

Basic sensors and their detection principles

Electronic conductance
- liquid electrolyte
- solid electrolyte

Quantum mechanics
- statistics
- thermodynamics

Mathematics, physics, and physicochemical theory

Mathematics
- mechanics
- electricity
- electrodynamics

Physics
- optics

Technology
- ceramics
- spin coating
- thin film
- thick film

Electrochemistry
- liquid electrolyte
- solid electrolyte

Basic sensors and their detection principles
- electronic conductance
- quantum mechanics

Einführung

Sensor

Physikalische Größe

Physikalisch leicht messbare Größe

Sensor

Analyt

Elektrisches Ausgangssignal

Sensitive Schicht

Transducer

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taken from: Göpel, Hesse Zemel, Sensor Series Volume 2
physikalisch leicht messbare Größen

• Potential (Potentialdifferenz, Spannung)
• Strom
• Masse (Massenänderung)
• Temperatur (Temperaturdifferenz)
• Kapazität (Kapazitätsänderung)
Analytabsorption

C$_2$Cl$_4$ gaseous phase

fast volume adsorption

polymer phase, polymethylsiloxane

small $E_A$ for adsorption
High mobility of the chain (low glass temperature)
Schwingquartz (QMB, QCM)
Dickenscherschwinger (TSMR)

Elektrode (Au)
Quarzkristall
Goldelektroden

Perchloroethene on Chirasil-Val
gas in gas out

Mikrosystem

Quelle: Byong Hak Kim, Arbeitsgruppe Prof. Kern, Angewandte Physik, Universität Tübingen
Cantilever array signal reading

Entsprechendes µ-System: Cantilever

Quelle: PEL, Physical Electronics Lab, ETH Zürich
Realisierung: Cantilever, 100x120 µm, 380 kHz, incl. Amplifier

physikalisch leicht messbare Größen

- Potential (Potentialdifferenz, Spannung)
- Strom
- Masse (Massenänderung)
- Temperatur (Temperaturdifferenz)
- Kapazität (Kapazitätsänderung)
Analytabsorption

\[ \rightarrow \Delta T \]

Seebeck Effekt

Elektronen zuviel fehlen

\[ T \text{ niedrig} \quad T \text{ hoch} \]

Aufbau: Kalorimetrischer Sensor (Thermopile)

Heat of sorption leads to a pulse of thermovoltage between inner and outer junctions:

\[ Q \rightarrow \Delta T \rightarrow \Delta U \]

Kalorimetrischer Sensor - Messkurve

Trichloromethane on Polyetherurethane
Calorimetric Sensor

Micro calorimeter, 300 TC poly-Si/Al, incl. amplifier
physikalisch leicht messbare Größen

- Potential (Potentialdifferenz, Spannung)
- Strom
- Masse (Massenänderung)
- Temperatur (Temperaturdifferenz)
- Kapazität (Kapazitätsänderung)

Drucksensor

\[ C = \varepsilon_0 \cdot \varepsilon_r \cdot \frac{A}{d} \]

Beschleunigungssensor

\[ C = \varepsilon_0 \cdot \varepsilon_r \cdot \frac{A}{d} \]


Analytabsorption - kapazitives Signal

\[ \Delta C \]
Kapazitiver Sensor

Kapazitiver Sensor - Messkurve

\[ C = \varepsilon_0 \cdot \varepsilon_r \cdot \frac{A}{d} \]
Capacitive Multi-Sensor Chip

5 Reference capacitors
Tunable reference (6 bits)
7 Sensing capacitors

Read-out circuitry ($\Sigma \Delta$) (digital output)
$\Delta f \sim \Delta C$

Multiplexer

Fabrication:
1. Standard CMOS
2. Post processing:
   Polymer coating

A. Kummer, A. Hierlemann, H. Baltes, Tuning the Sensitivity of Capacitive Chemical Microsensors, Eurosensors 2002, Prague, Czech Republic

Capacitance sensor

Polymer coating
Thin polymer layer
E2 E2 E2 E2 E2

First metal layer
Second metal layer
Electrode E2
Electrode E1
Thin polymer layer
Thick polymer layer

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Zusammenfassung

- Chemische Parameter sind wichtige Kenngrößen
- Wandlung chemischer Information in elektronische Signale ist möglich
- Mikrosysteme helfen uns, machen manche Messungen erst möglich
Ende

Danke für Ihre Aufmerksamkeit!

Sensing Principle

\[ \Delta C \sim c \cdot K_C \cdot A \cdot \left[ G_P \cdot \chi_A + G_S \cdot Q_A \cdot \chi_P \right] \]

A. Kummer, A. Hierlemann, H. Baltes, Tuning the Sensitivity of Capacitive Chemical Microsensors, Eurosensors 2002, Prague, Czech Republic
Outline

• Einleitung und Motivation
• Messprinzipien
  – Massenänderung
  – Temperaturänderung
  – Kapazitätsänderung
  – Leitfähigkeitsänderung
• Anwendung Teil 1
• Mustererkennung
• Anwendungen Teil 2
• Möglichkeiten und Grenzen
• Ausblick

Wechselwirkungsmechanismen
Micromechanical cantilevers (active)
ETH Zurich

Actuators and piezoresistors
Analyte molecules
Polymeric coating
Vibrating cantilever beam ($f_0 \approx 350$ kHz)
Silicon frame

Capacitive sensor

Frequency shift [kHz]

-4 0 4 8 12 16

Toluene
Ethanol

0.3 µm PEUT
2.3 µm PEUT

Time [h]

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Piezoelektrischer Effekt

Quarz: SiO₂
blau: Sauerstoff
rot: Silizium

longitudinaler Effekt transversaler Effekt

Principal Component Analysis (PCA)
mixture of n-octane/propan-1-ol

Loadings

propan-1-ol

n-octane
Mixtures of n-octane, propan-1-ol and chloroform

Loadings

PC 1(77%), PC 2(21%), PC 3(2%)
PLS - chloroform

Predicted concentration [ppm]

True concentration [ppm]

mixture of propan-1-ol/propan-2-ol

propan-1-ol

propan-2-ol

PC 1(99%), PC 2(0%)
Loadings

PC1: 96.4%
PC2: 2.6%
PC1 : PC2 = 2.725

"Branches Cailler" Small, batch a and b
Medium, batch a and b
Large, batch a and b

"Frigor Noir", batch a and b
"Frigor Rouge", batch a and b

PC1 : PC2 = 2.725  PC1: 96.4%