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# Gas Sensor Arrays in Lab and Process Control Applications

Potential Advances in Biological and Medical Applications

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**AIRSENSE**  
A N A L Y T I C S

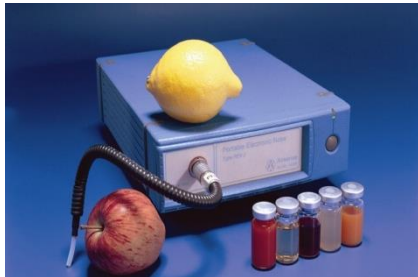
 **Ingeniería Analítica**  
Chromatography & Spectrometry

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# Technology Line

I

Sensor Arrays  
Electronic Nose  
PEN3



iPEN



II

Trap & Thermal  
Desorption  
EDU3,...



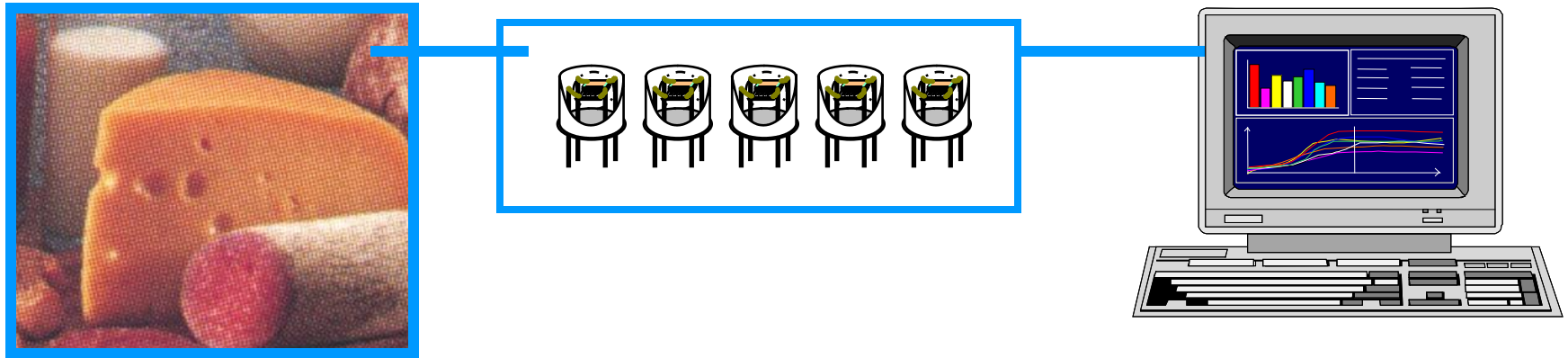
Micro-TD,  
EDU-GC, EDU-GD

III

Gas Detector Array  
GDA  
Hybrid Array

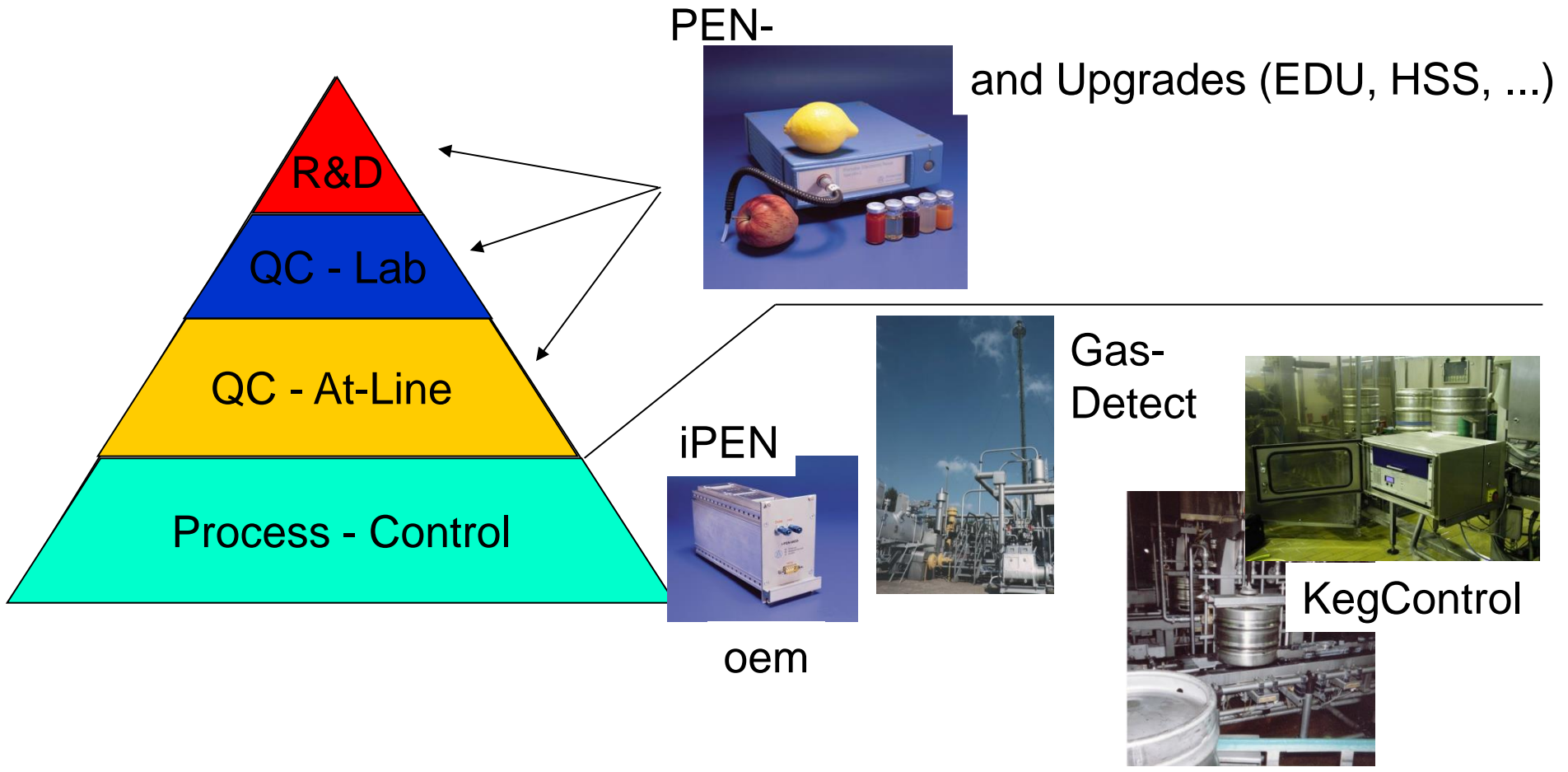


# The Electronic Nose Concept



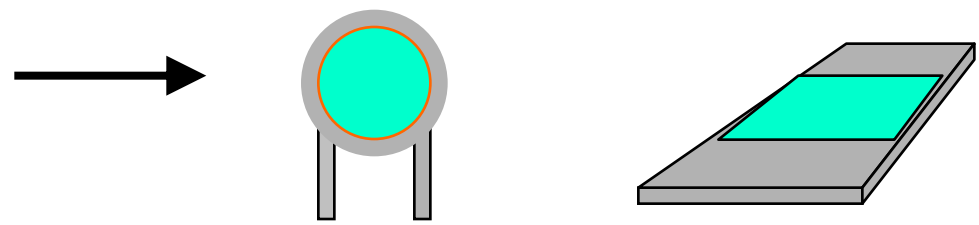
The electronic nose is an instrument, which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern-recognition system, capable of recognizing simple or complex odors (Gardner & Bartlett)

# Applications and Market

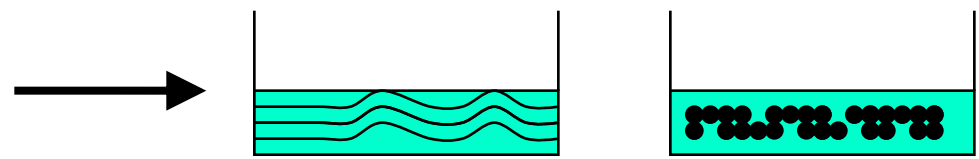


## Cold sensors:

change of mass  
 $S = \Delta f \sim \Delta m$



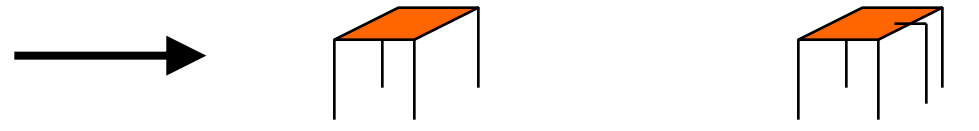
change of electrical conductivity  
 $S = \Delta R$



Polymers

## Hot sensors:

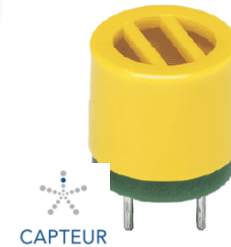
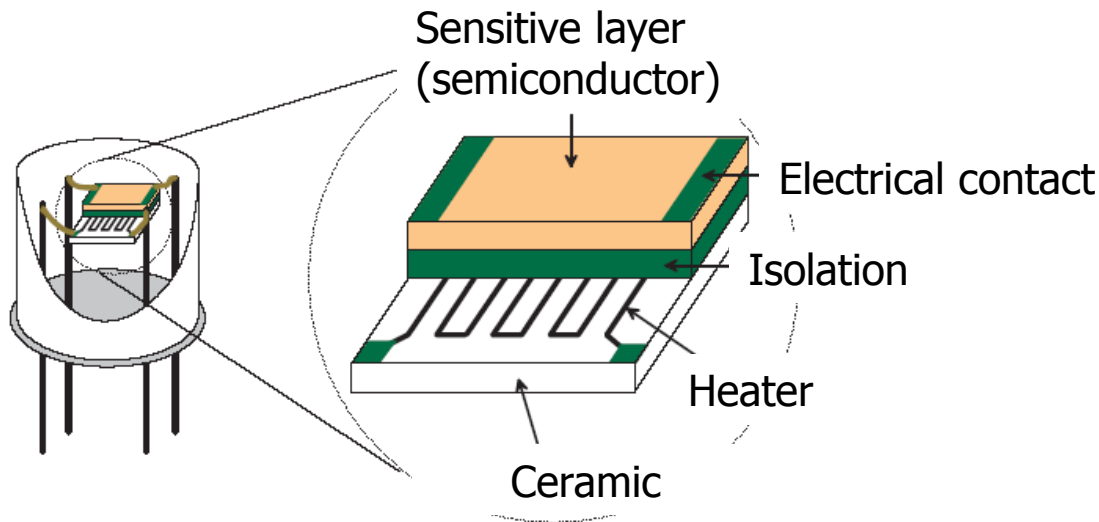
change of electrical conductivity  
 $S = \Delta R$



MOS

MOSFET

# Metal Oxide Sensor (MOS)



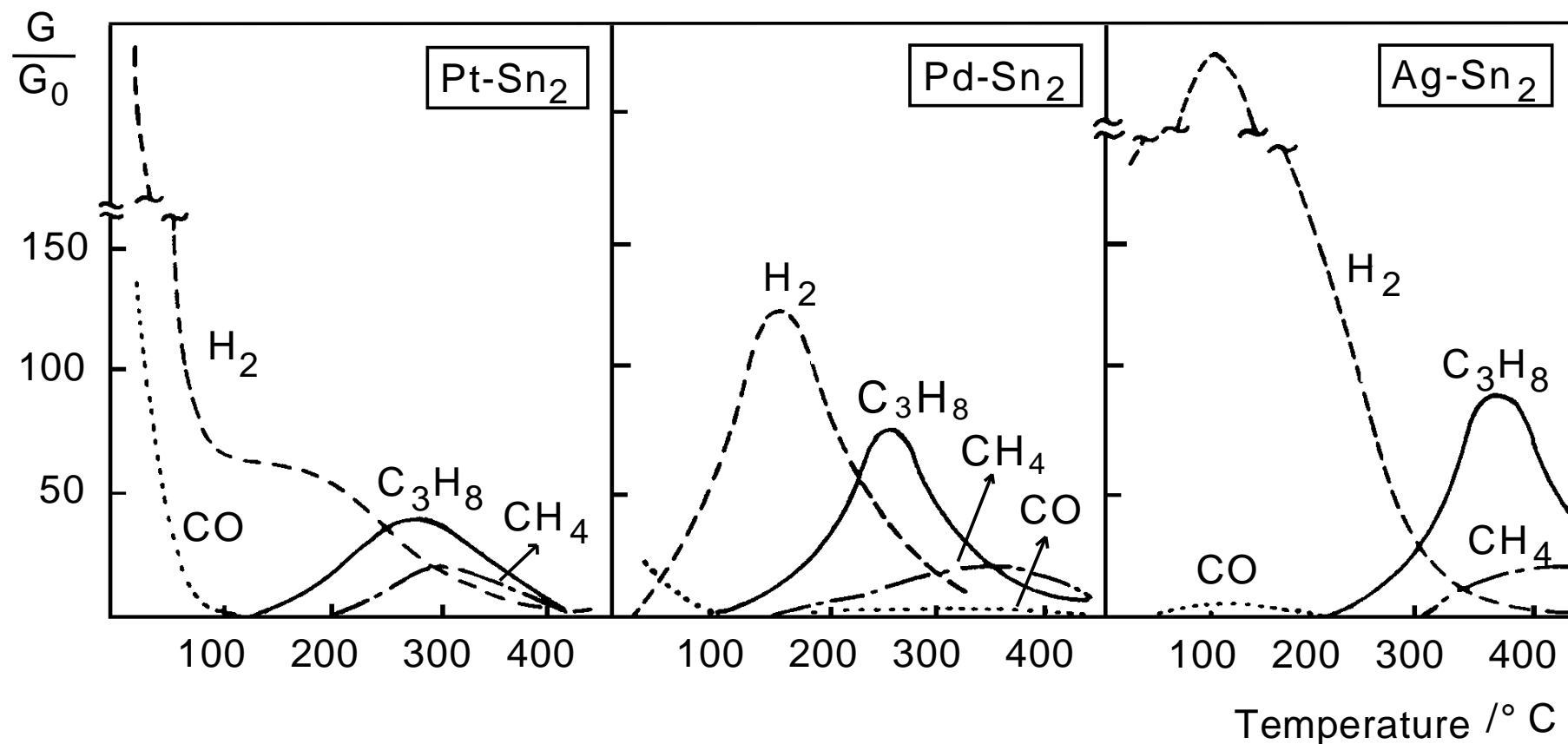
Change of electrical conductivity  
due to oxidation/reduction  
reactions

Broad range sensitivity  
(VOC, CO, NH<sub>3</sub>, H<sub>2</sub>, H<sub>2</sub>S)

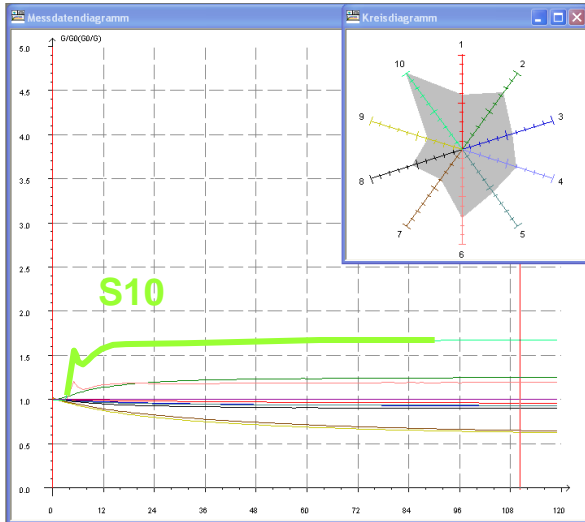
Sensitive layers of commercial  
systems:

SnO<sub>2</sub>, WO<sub>3</sub>, Cr<sub>x</sub>Ti<sub>y</sub>O<sub>z</sub> & mixtures

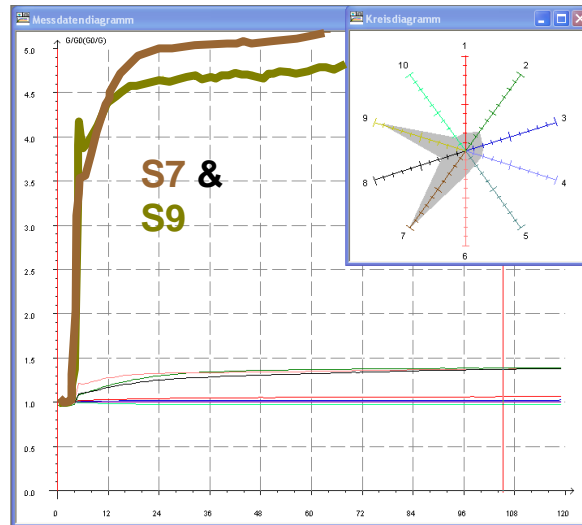
# Effect of Temperature and Dopands on the Selectivity



# Sensitivity and Selectivity of the Sensors

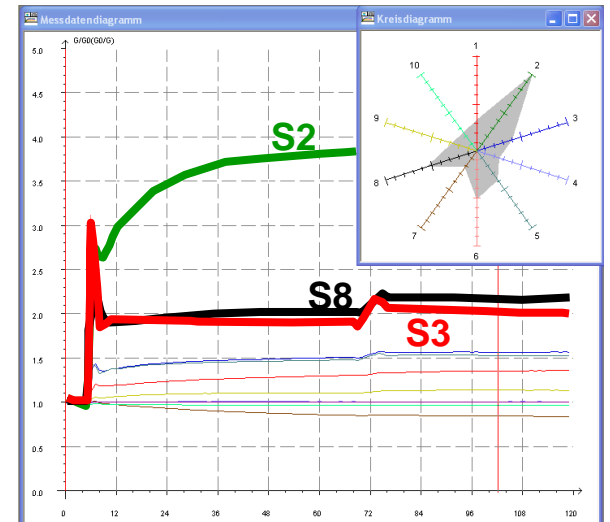


10ppm CH<sub>4</sub>



1ppm H<sub>2</sub>S

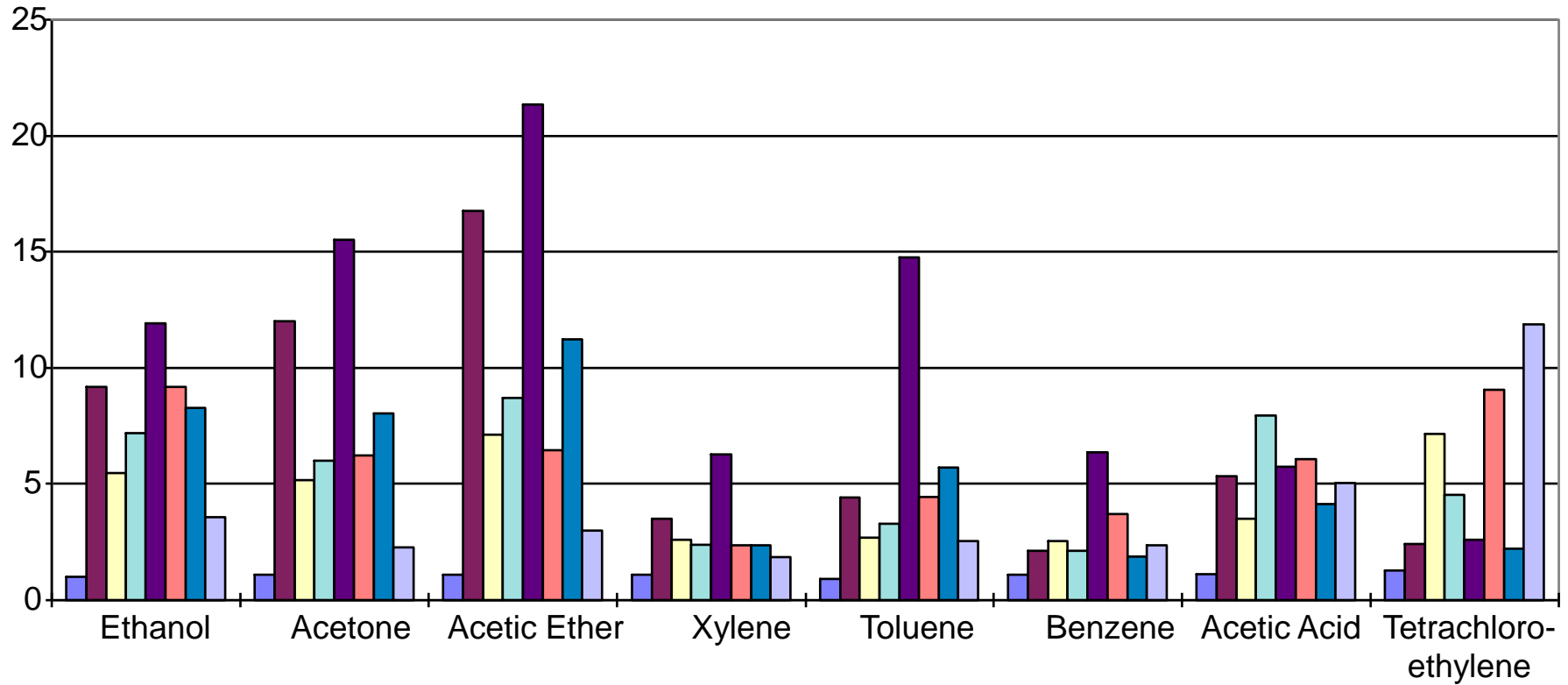
10ppm C<sub>6</sub>H<sub>6</sub>





# Different Pattern of an Array of Eight MOS Sensors

Relative Conductivity G/G0




Legend: GGS 1000 (blue), GGS 2000 (maroon), TGS 816 (yellow), TGS 880 (cyan), TGS 823 (purple), TGS 831 (red), TGS 881 (teal), TGS 830 (light blue)

## 1. Phase: Training & Verification

"Learning" through measuring known compounds  
Saving of the reference vectors and testing of  
the pattern

## 2. Phase: **Recognition**

Measurement of the actual unknown compound

Identification by comparing the reference vector  
with the actual unknown vector 

Quantification of the identified compound  
with the stored calibration file

Euklidic Distance  
Mahalanobis Distance  
Coefficient of Correlation

PCA  
LDA  
DFA  
PLS

Neural Networks: ???

# Portable Electronic Nose PEN-3



- small
- portable
- low cost
- Auto-Ranging
- Stand-Alone Operation

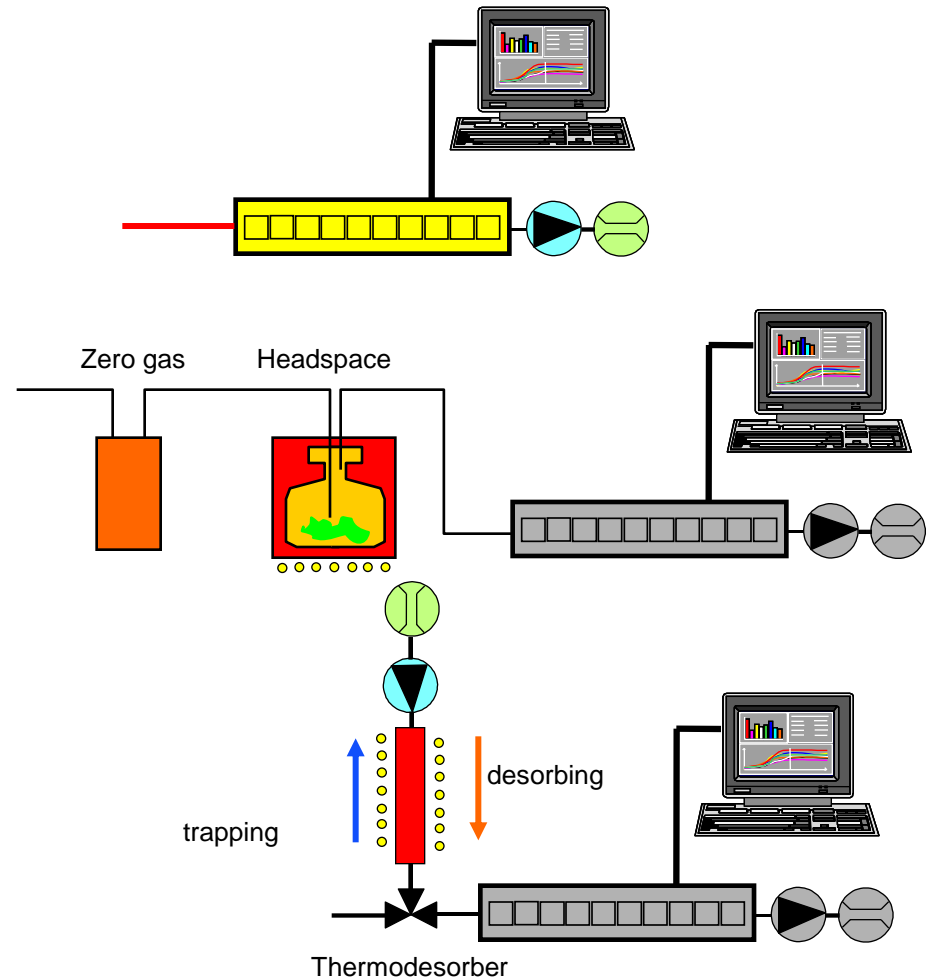
# Industrial Sensor Array: the i-PEN Series



- Same MOS Array Technology
- designed for industry
- remote operation
- stand alone unit
- optional trap available

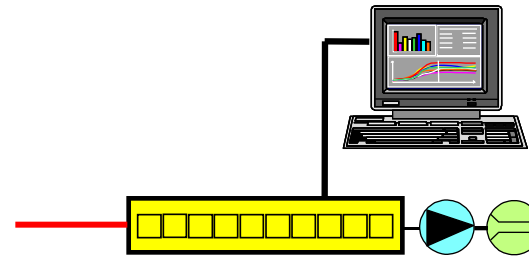
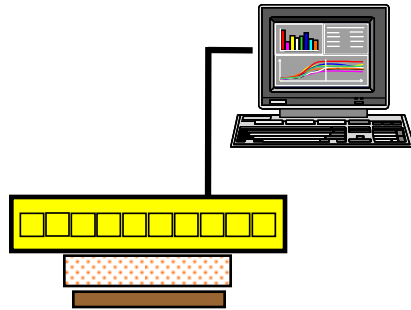
# Sampling Methods with an Electronic Nose

Sampling must be well defined and repeatable

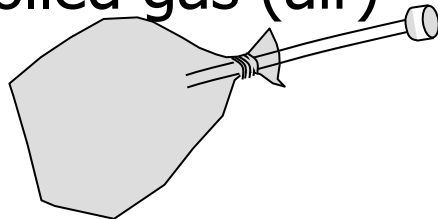


# Sampling -Direct

- Direct (passive & active): simple, most common, dependency on ambient parameters



- Sampling Bags: transport of sample to the instrument, controlled gas (air)

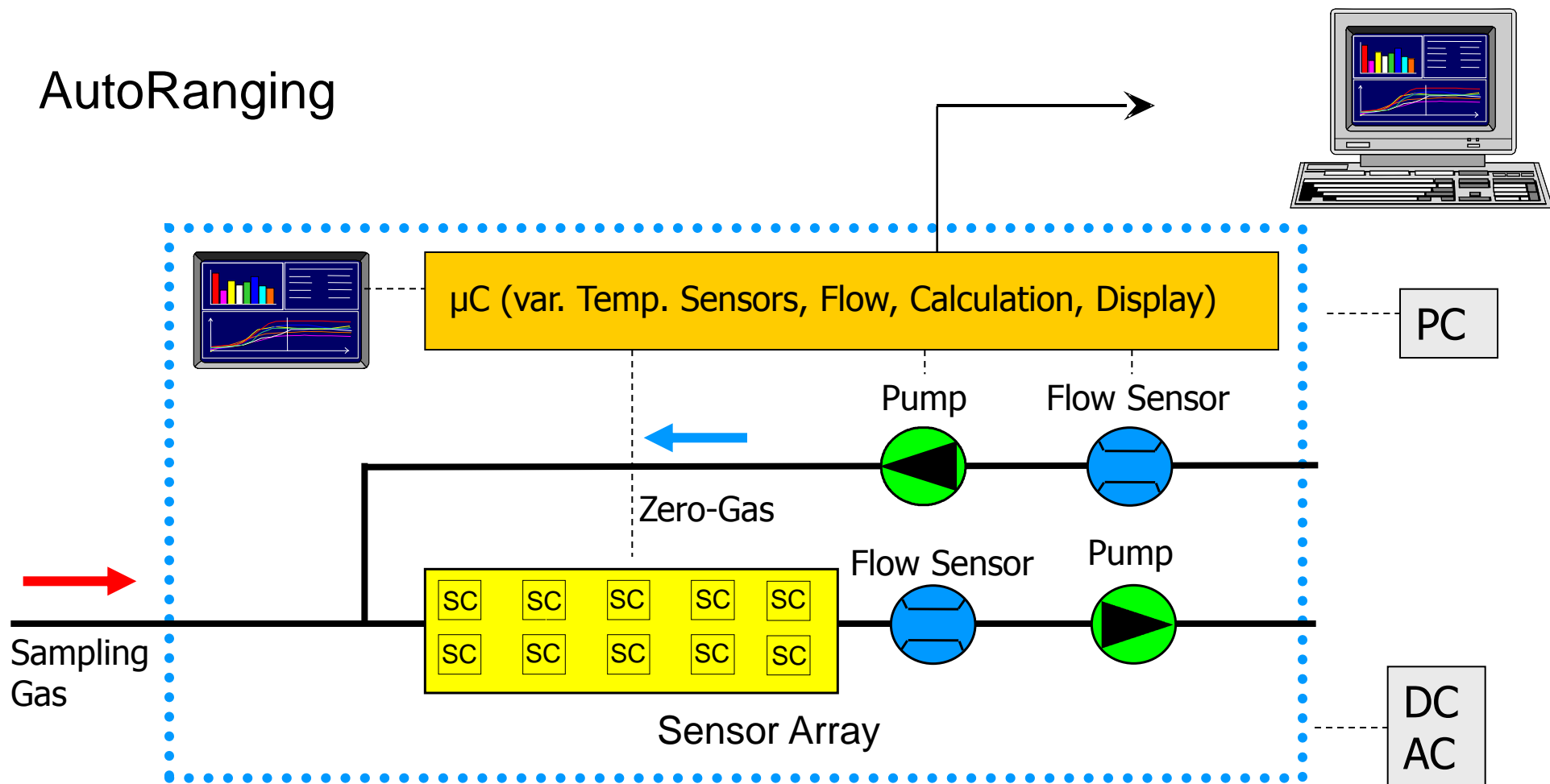


$T_{\max} = 200^{\circ}\text{C}$ , roasting bags

PET-Polyethylenterephthalate (Nalophan)

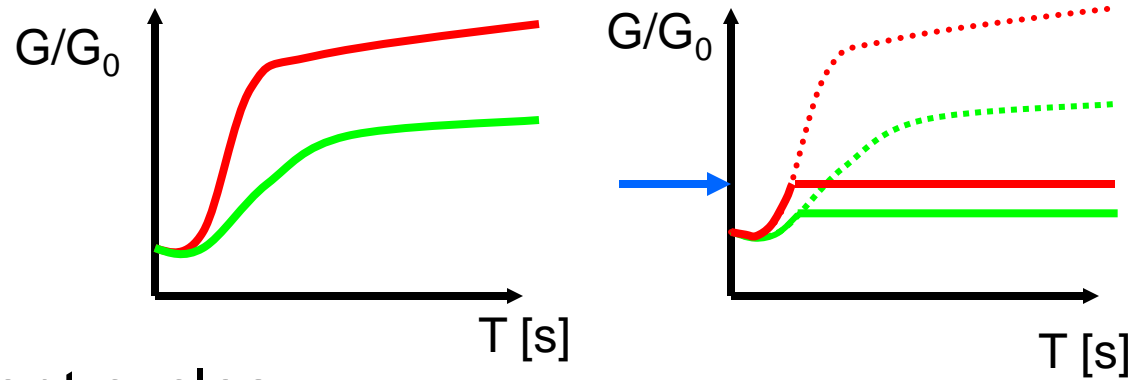
# PEN3: Sample Flow & Dilution

## AutoRanging

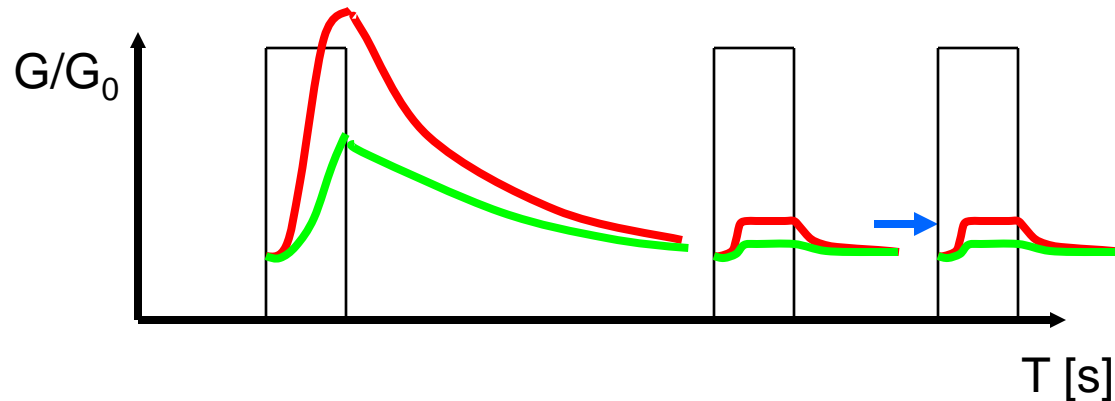


# Autoranging

- better lifetime



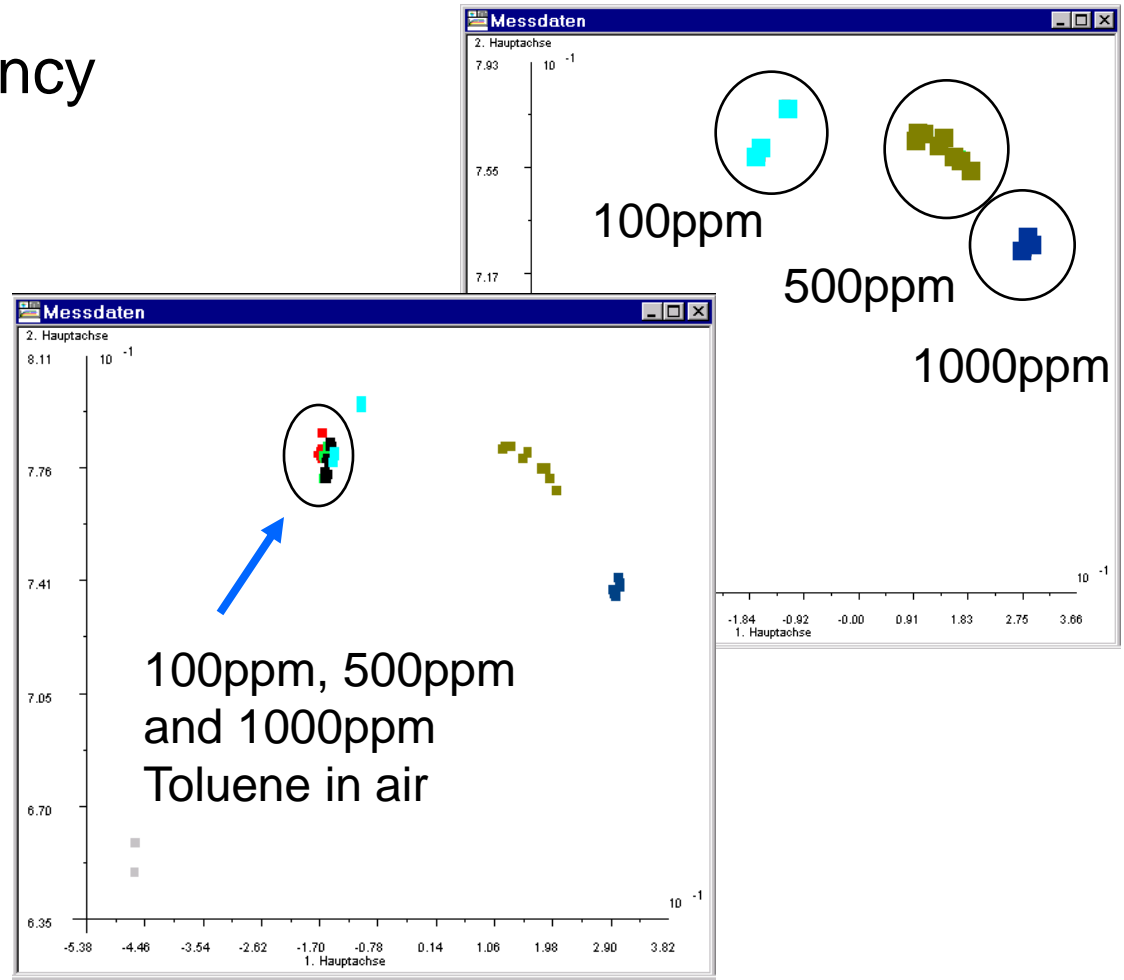
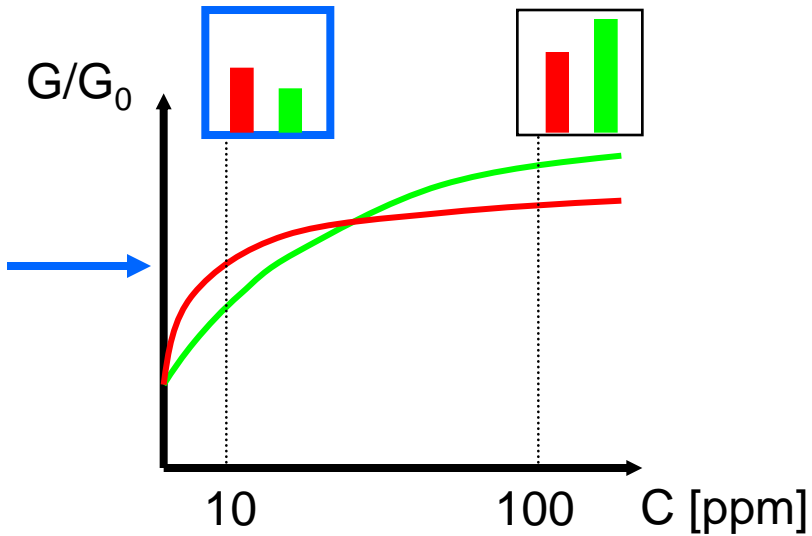
- faster measurement cycles





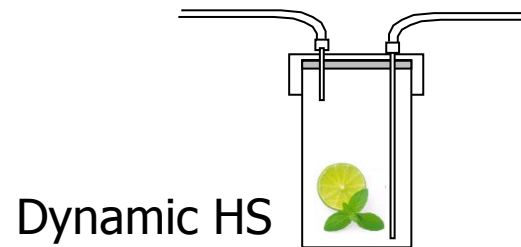
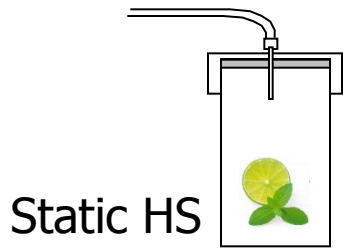
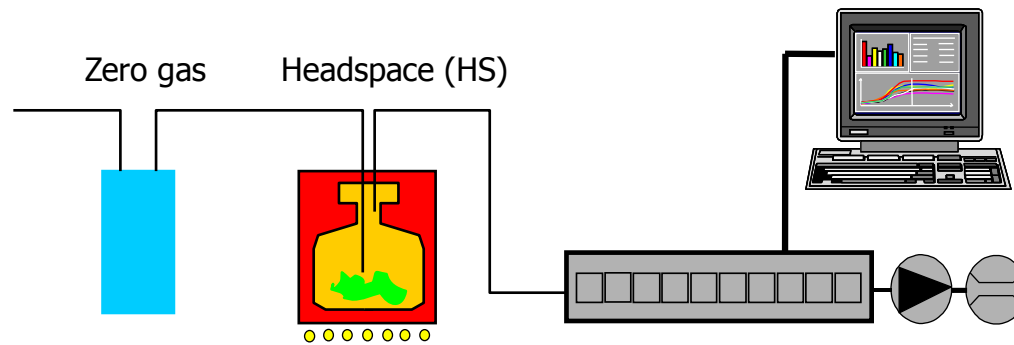
# Autoranging

- Pattern without dependency on the concentration



# Sampling : Headspace

Headspace, Autosampler: better reproducibility due to controlled temperature, time and carrier gas (air)



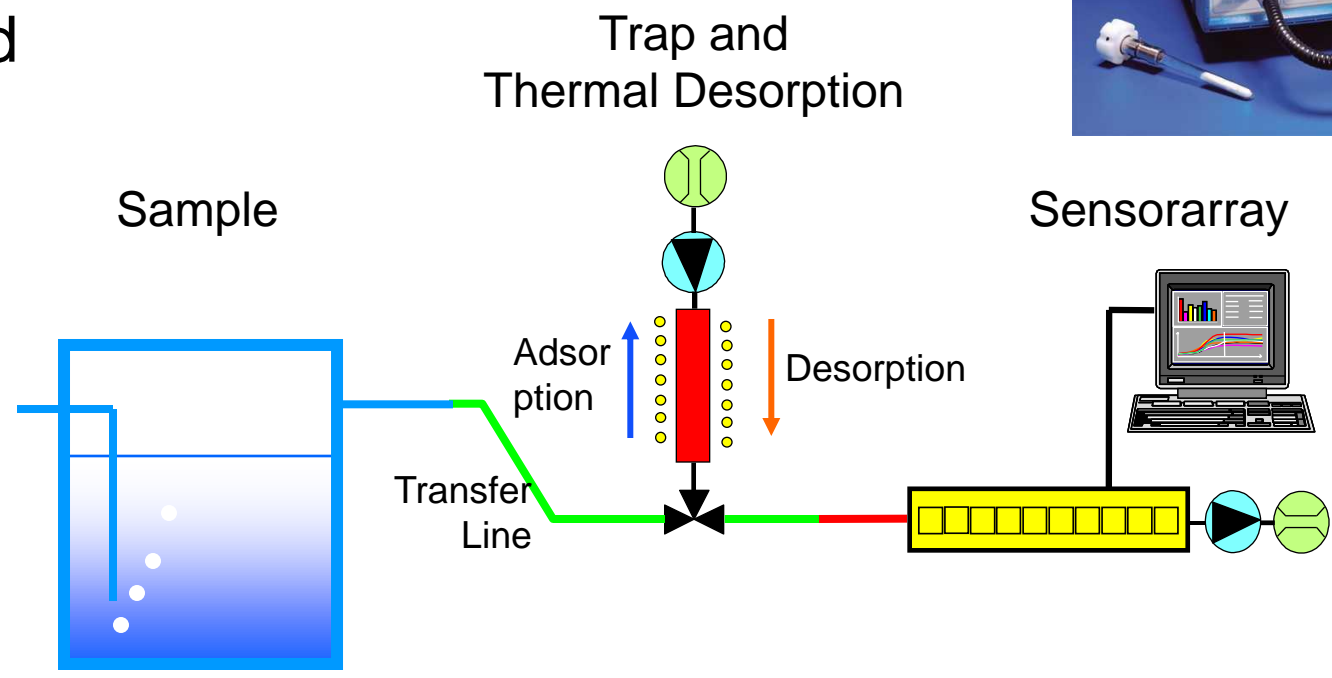
# Enrichment & Desorption Unit EDU2 with the PEN2



- new technology:  
Automatic trapping and desorption
- increase in selectivity
- lower detection limits (100 x)
- $\mu$ P-controlled

# Enrichment and Desorption

- lower detection limits (100...1000)
- Enhanced selectivity
- on-line / remote controlled



# Breakthrough Volumes

- BV [L/g]

| BV <sup>T</sup>  | 20°C  | 80°C   | 180°C   | 220°C |
|------------------|-------|--------|---------|-------|
| CH <sub>3</sub>  | 0.006 | <0.001 | <0.0001 |       |
| EtOH             | 1.80  | 0.055  | <0.001  |       |
| Toluene          | 400   | 12.5   | 0.015   | 0.003 |
| Phenol           | 1630  | 17     | 0.02    | 0.005 |
| Geosmin          | 6300  | 30     | 0.011   | <0.01 |
| H <sub>2</sub> O | 0,065 | 0,01   | 0,001   | 0     |

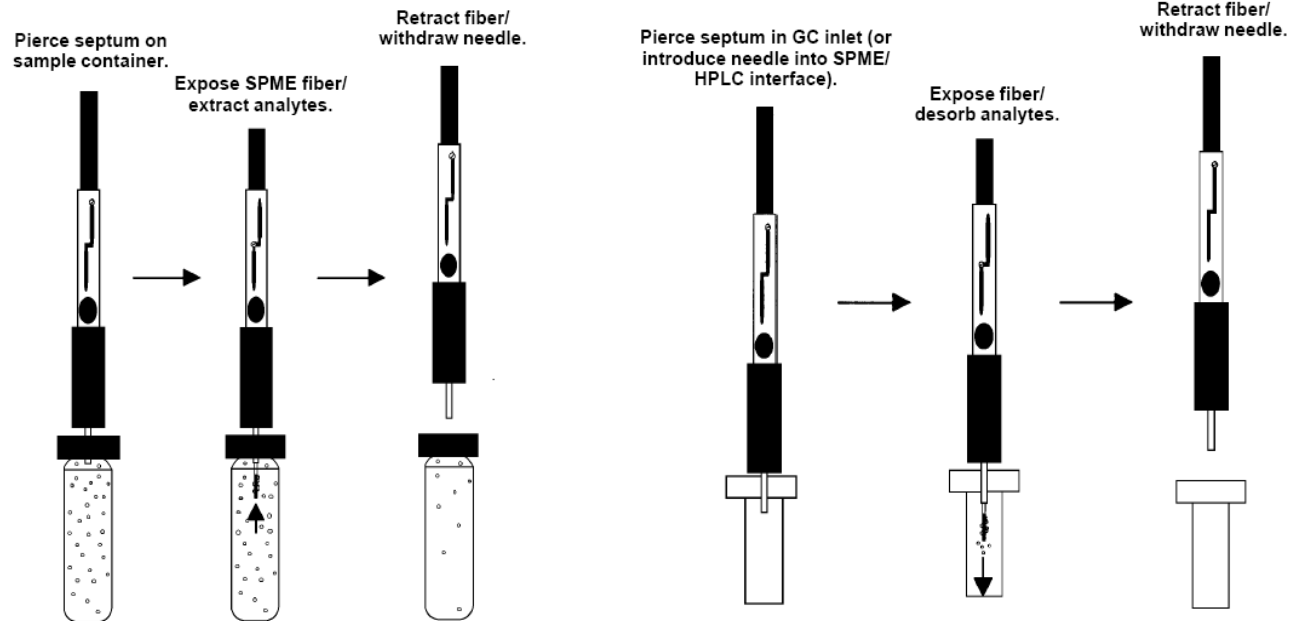
- Discrimination of highly volatile compounds / [Water](#)
- High enrichment factors achievable by increasing the sampling time

Adsorption Tubes, SPME: modification of selectivity, better detection limits, transport of sample to the instrument

## Extraction Procedure

## Desorption Procedure

SUPELCO®



## SPME materials:

PDMS (Polydimethylsiloxane),  
PDMS / DVB (Divinylbenzene),  
PDMS / Carboxen,  
CW (Carbowax)/ DVB,  
Polyacrylate

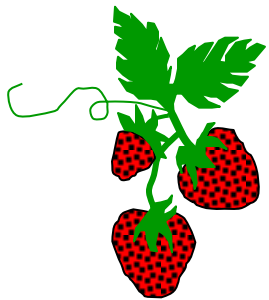


- **Quality control:**  
Food (rancidity, freshness, off flavor, contamination)
- **Safety:** work place areas,  
storage places (natural gas)
- **Environment:** dispersion of air  
pollutants, supervision of filters  
(compost plants, sewage plants)
- **Medicine** (identification of fungi, bacteria,  
flavor in diagnosis)
- **Process control:**  
polymers (packing material, automobiles)

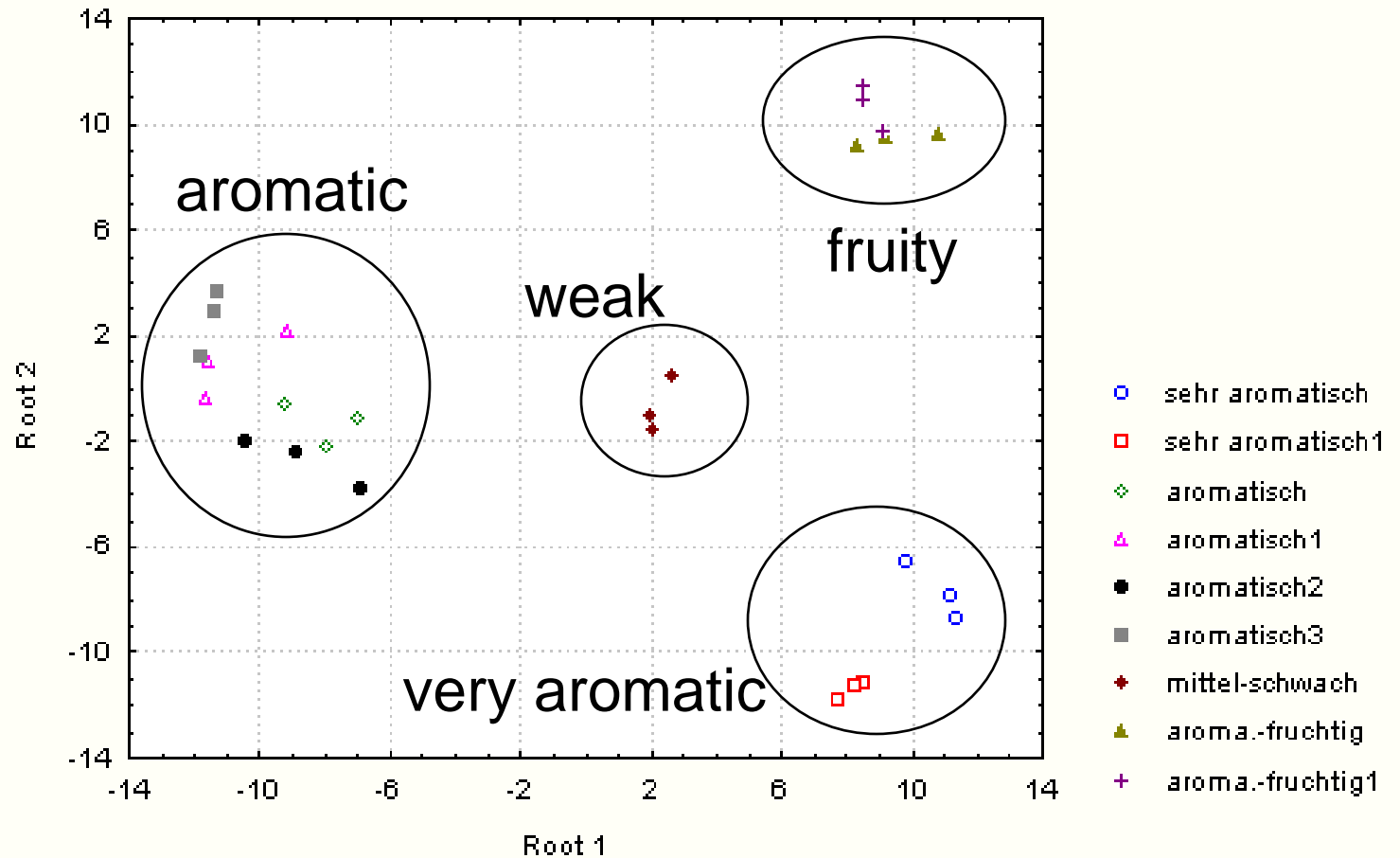


# Differentiation of Food

• Food  
(aroma of strawberries)



Erdbeeren, Discr. Analyse (automatische Messung, Sample nach 19s)

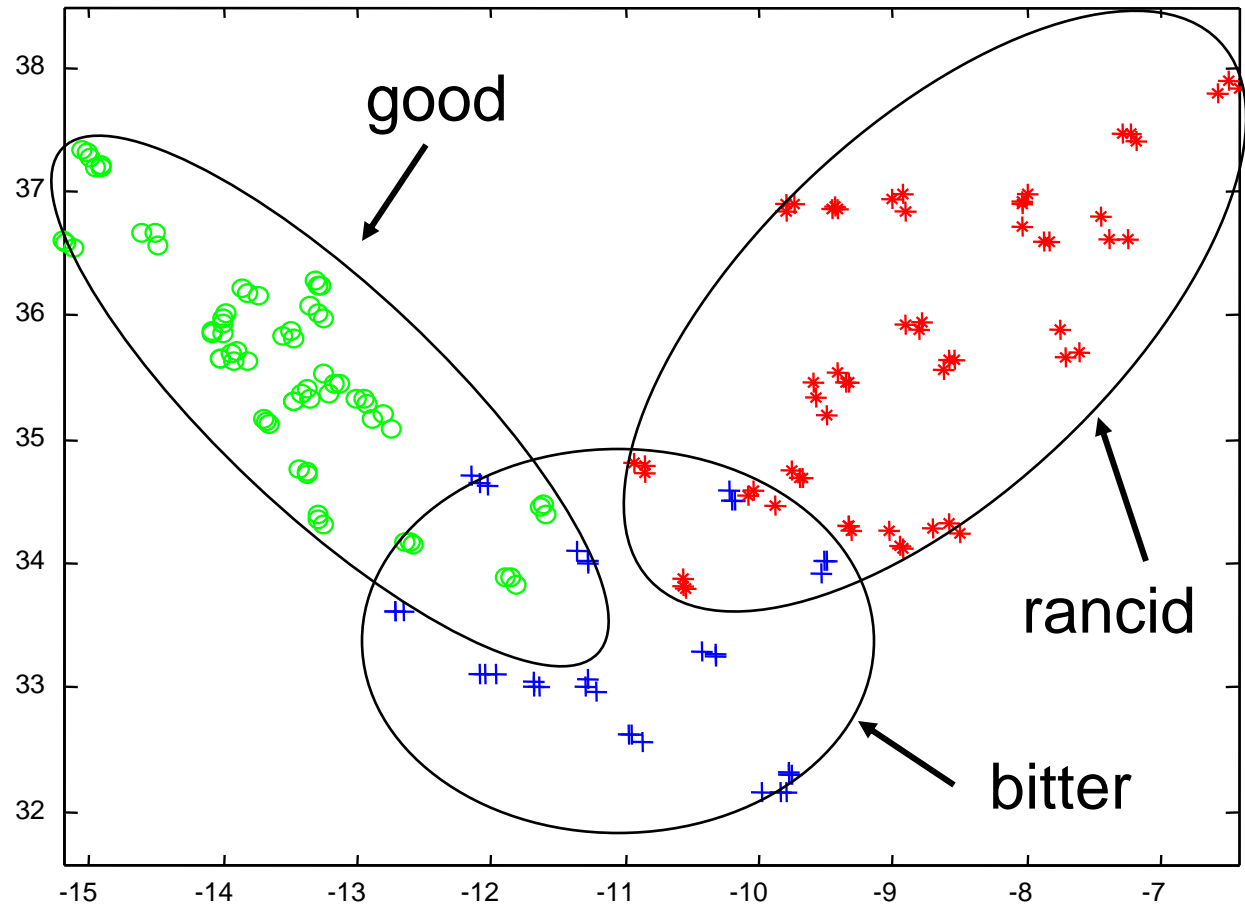




# Fast Rancidity Detector

- Walnuts:  
rancidity

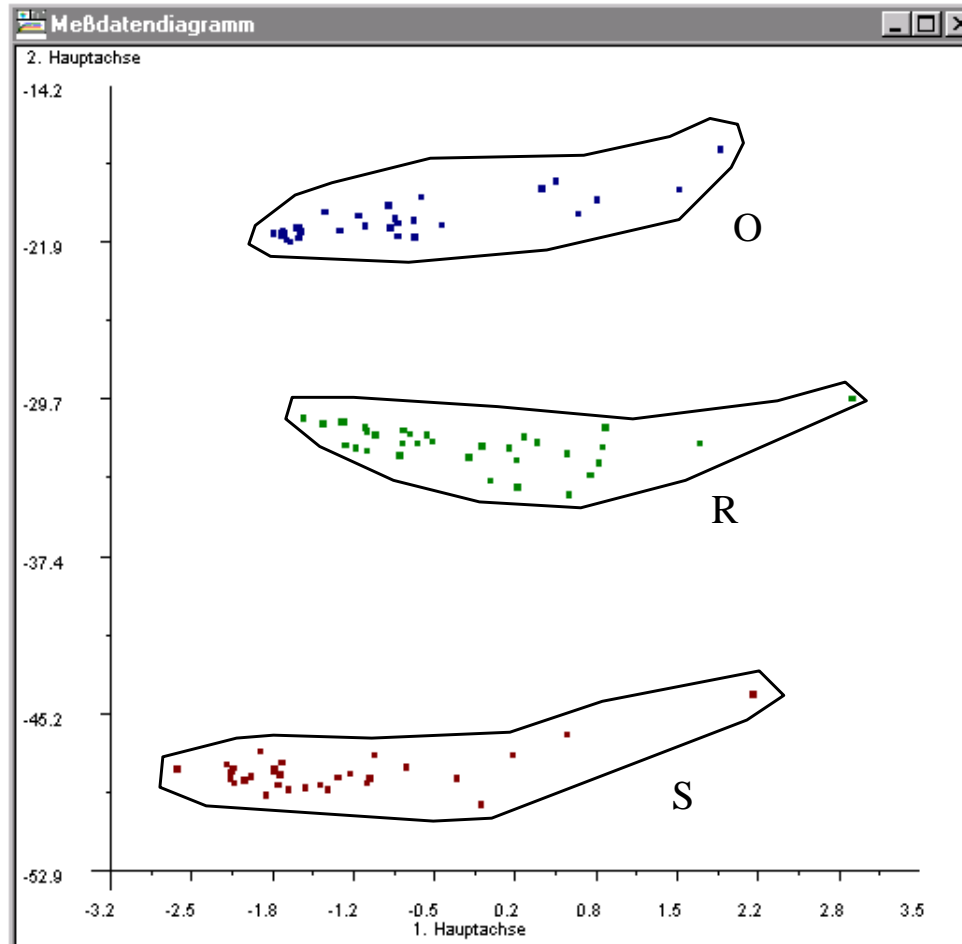
(Application tested over 6 months with the same pattern. Probability that a rancid sample will be identified as a good one is less than 0,5%)



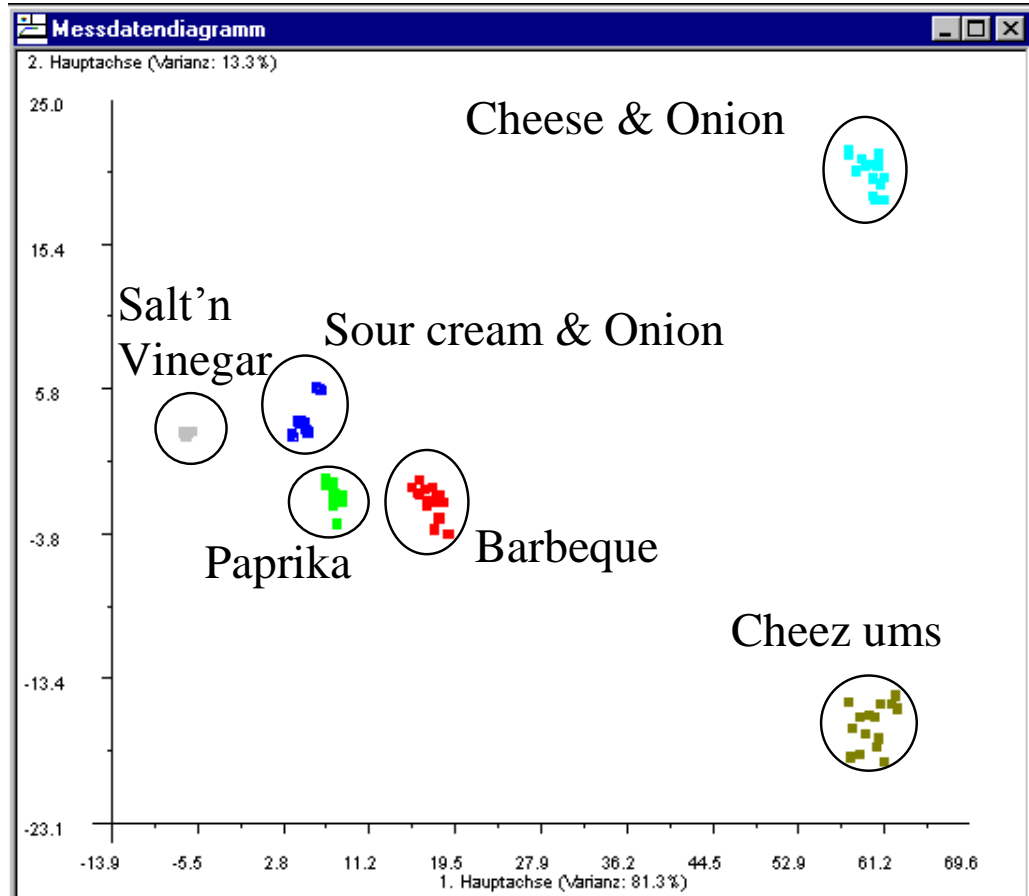
# Differentiation with Trap & Thermal Desorption

- Food:  
vinegar

(no differentiation possible  
without selective  
enrichment)

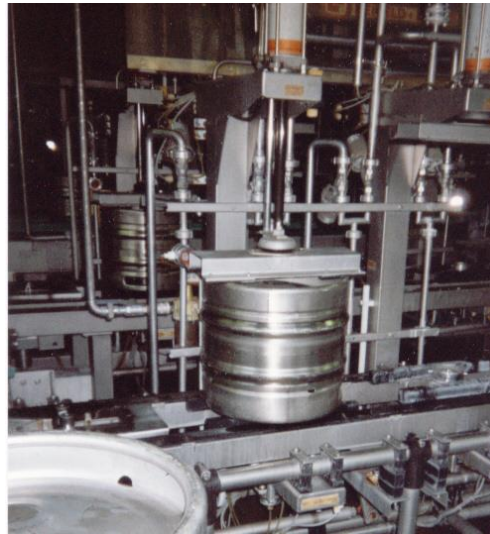


- Differentiation of spices for potato chips

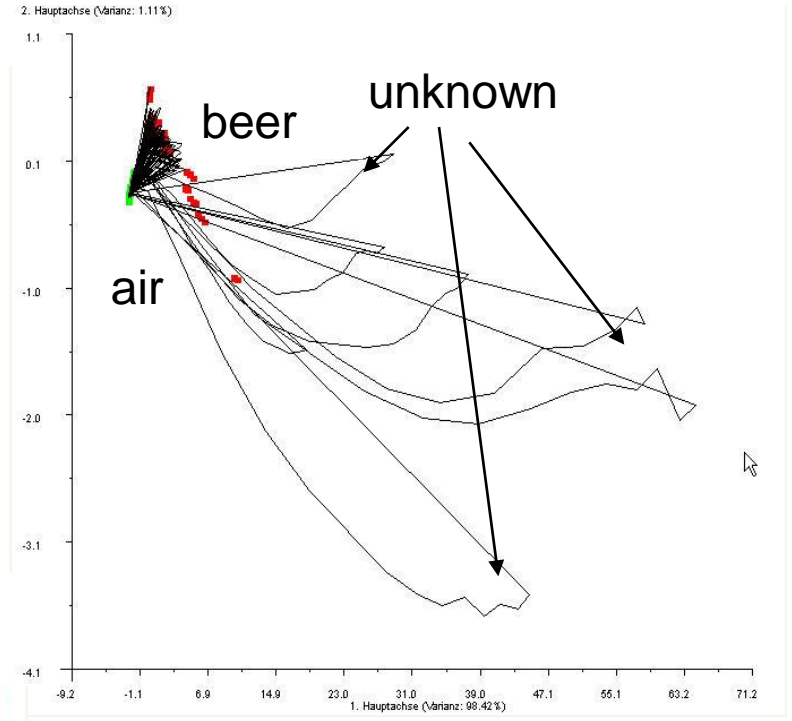
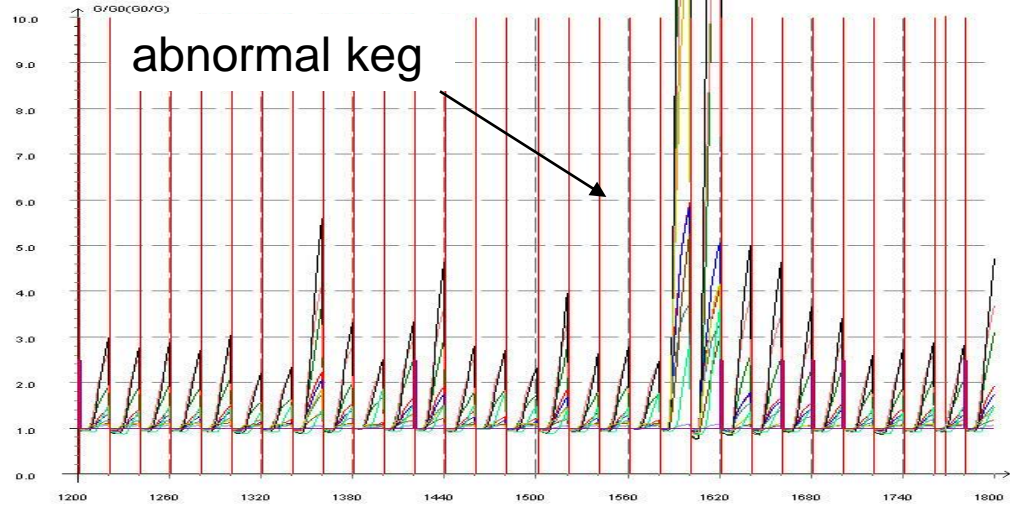


## Recycling of containers (water, beer)

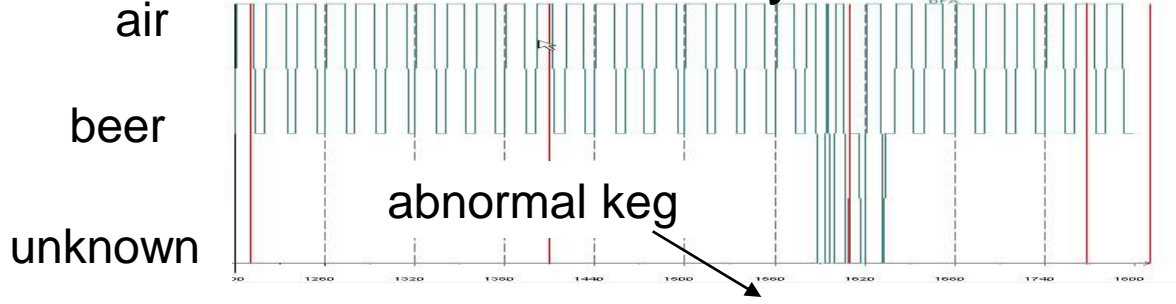
- Detection of solvents and off odors
- Low detection limits
- Fast analysis



## Raw Data



## Pattern Analysis

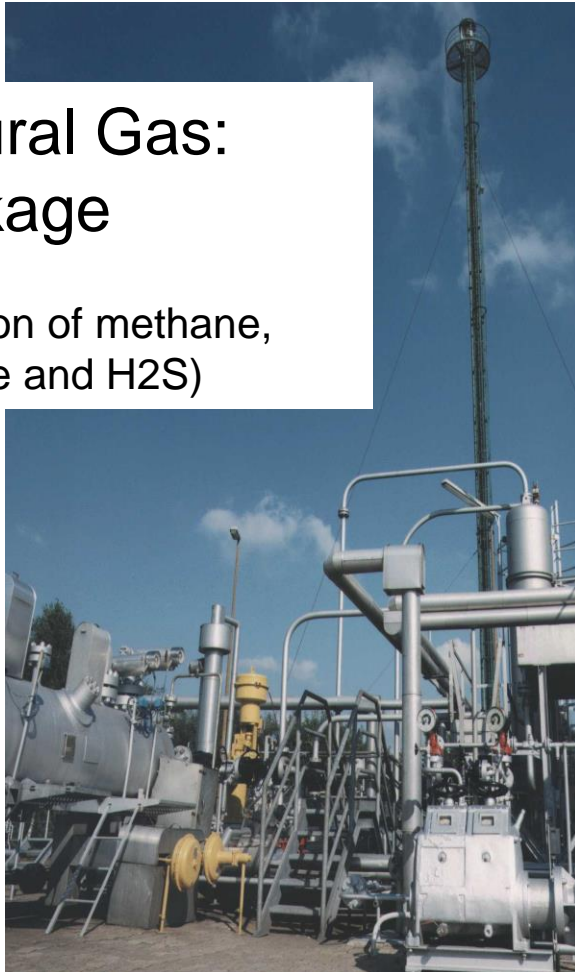


PCA of the complete series (500 meas.)

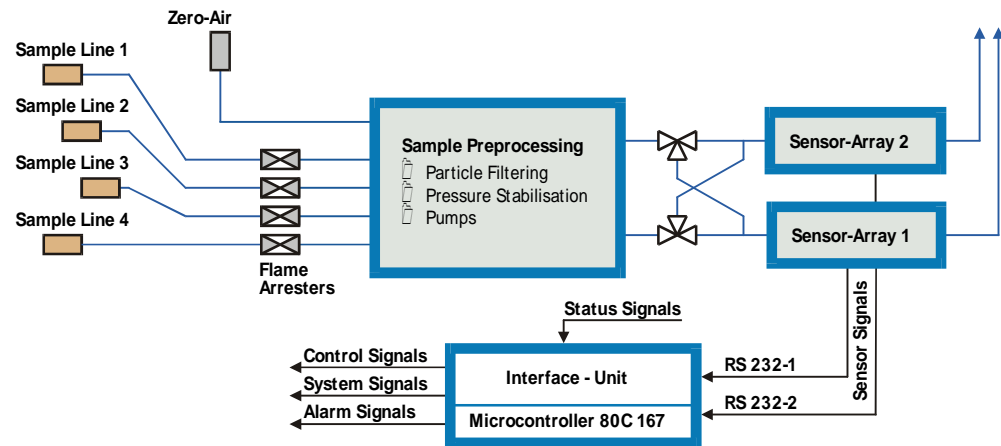
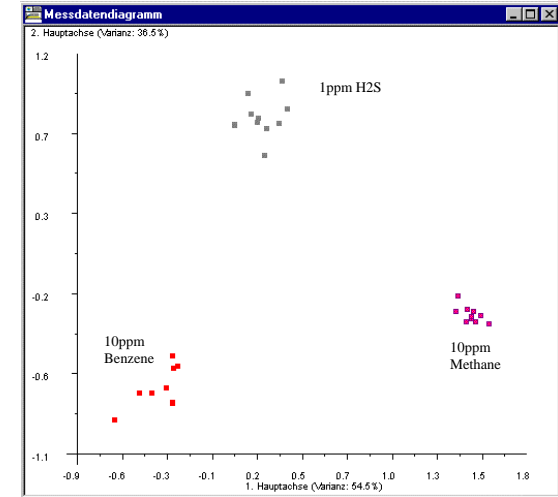
# PEN: Leakage of Sour Gas

## • Natural Gas: Leakage

(detection of methane, benzene and H<sub>2</sub>S)



Variation (PCA) between sensor arrays

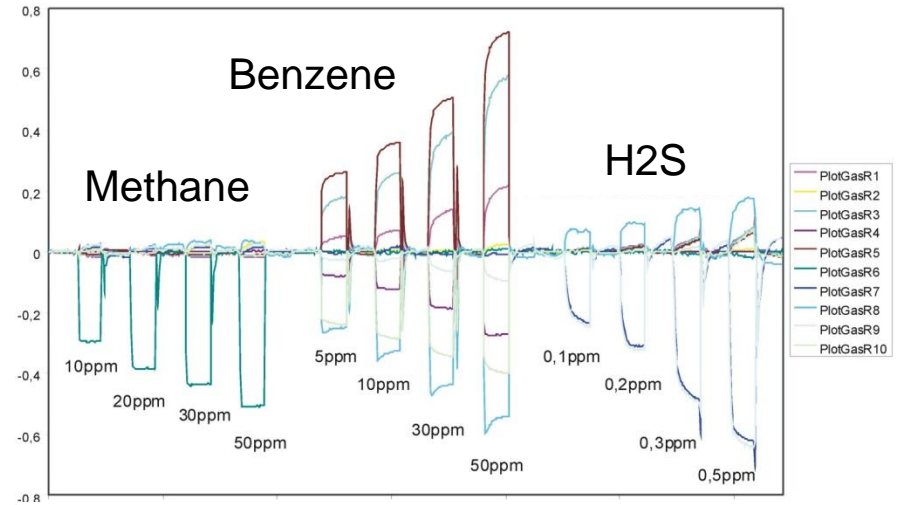




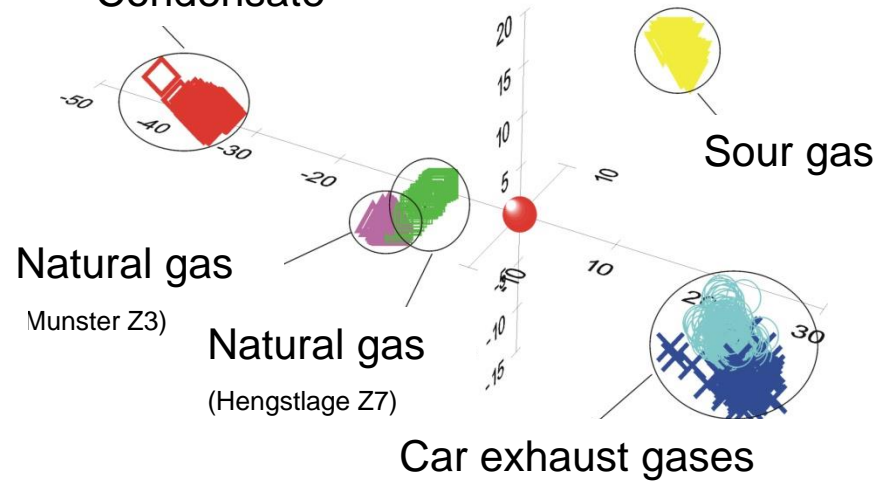
# iPEN: Leakage Control



Detection device with dual sensor array



Condensate

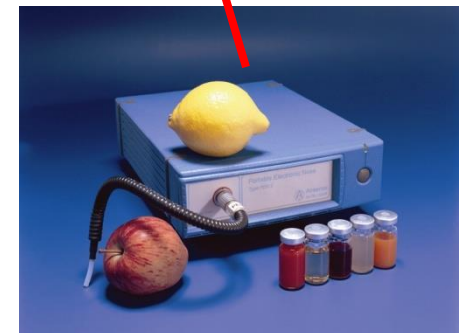
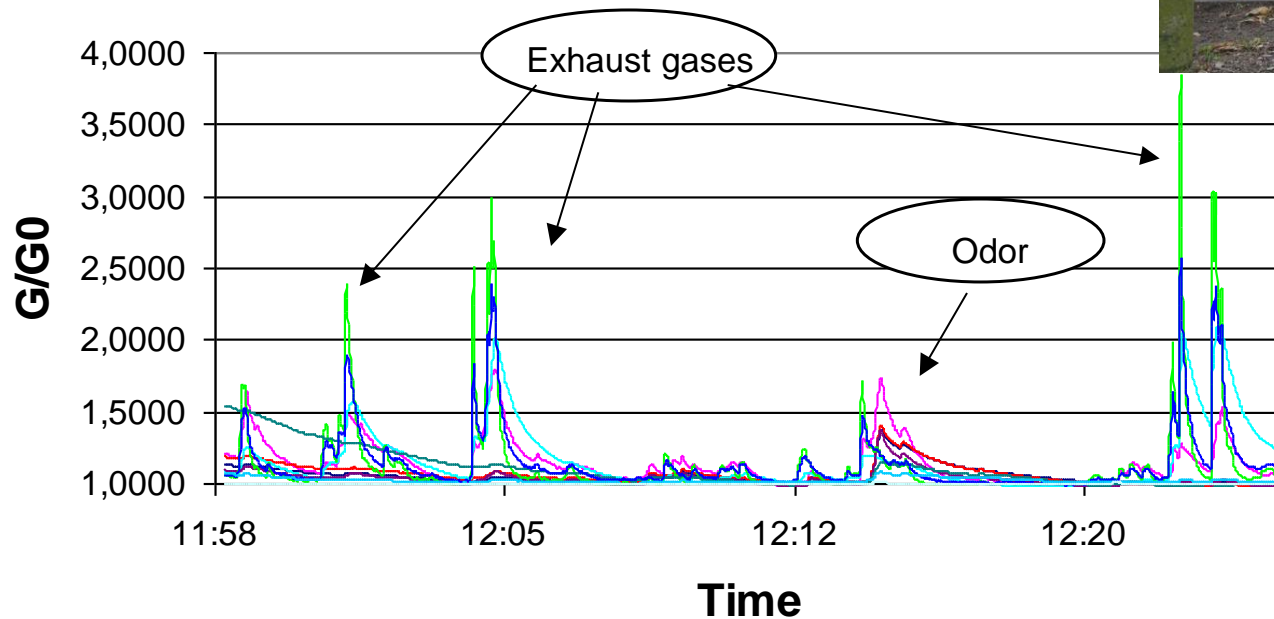


# Monitoring of Biofilters

- Odor complains at a shopping center: Monitoring of sporadic releases of odors from a subterranean biofilter of a sewage duct

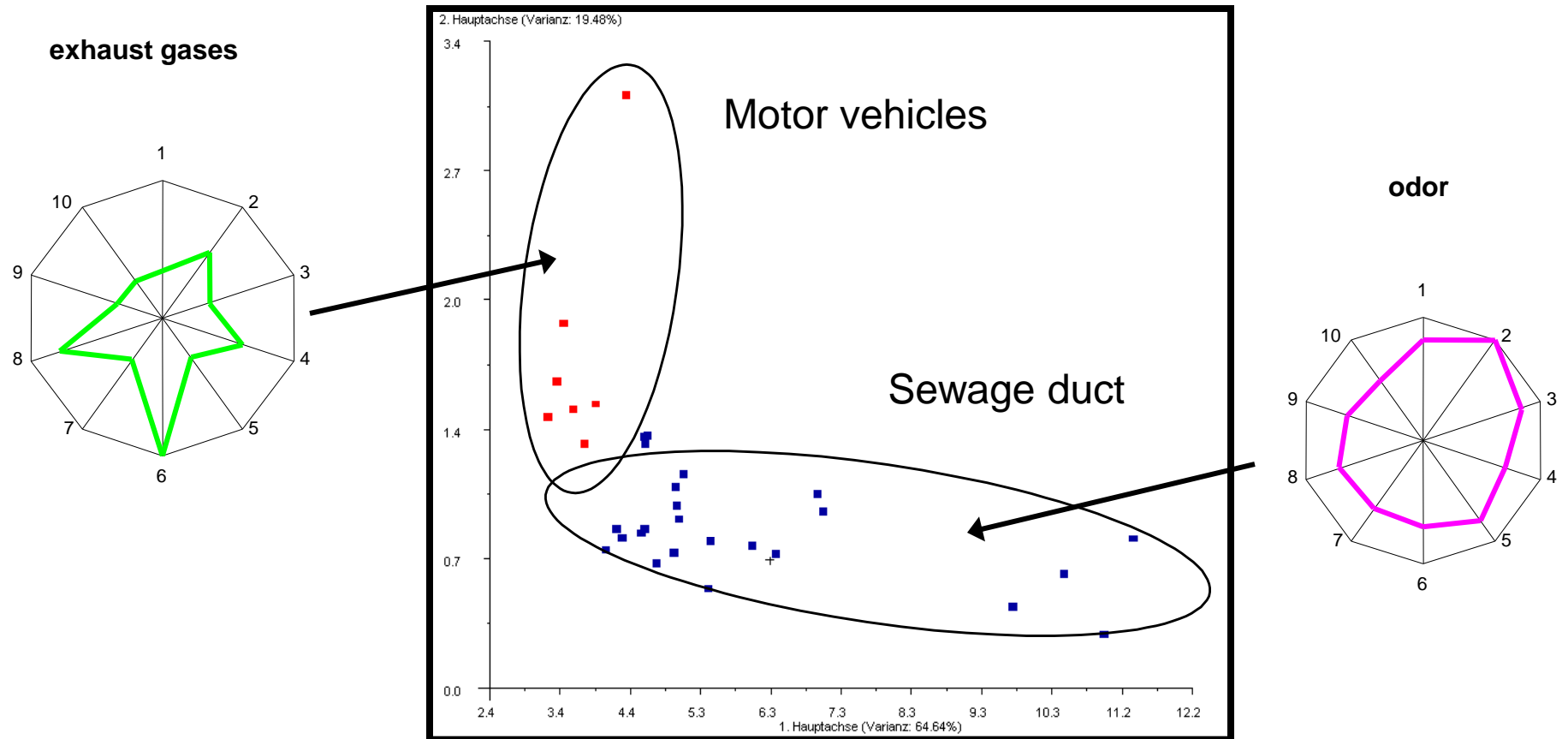


## Sensor Data



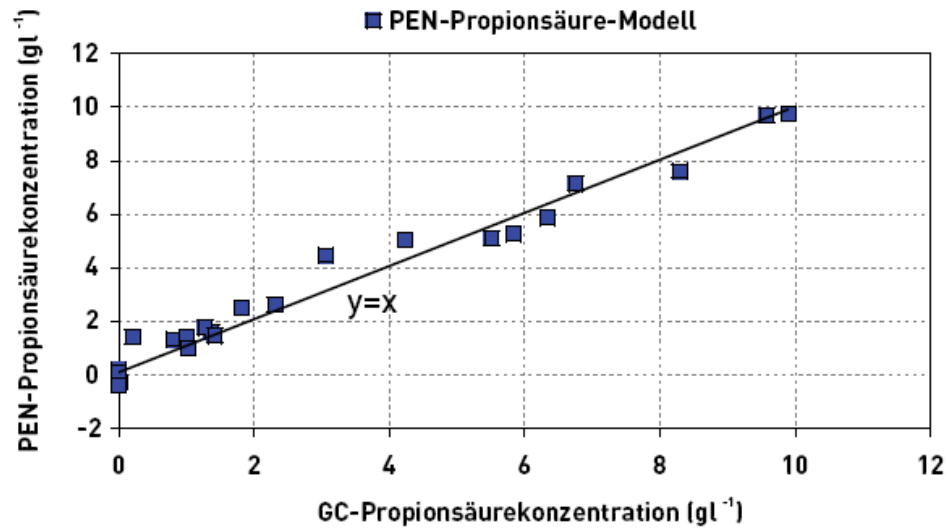


- Principal Component Analysis



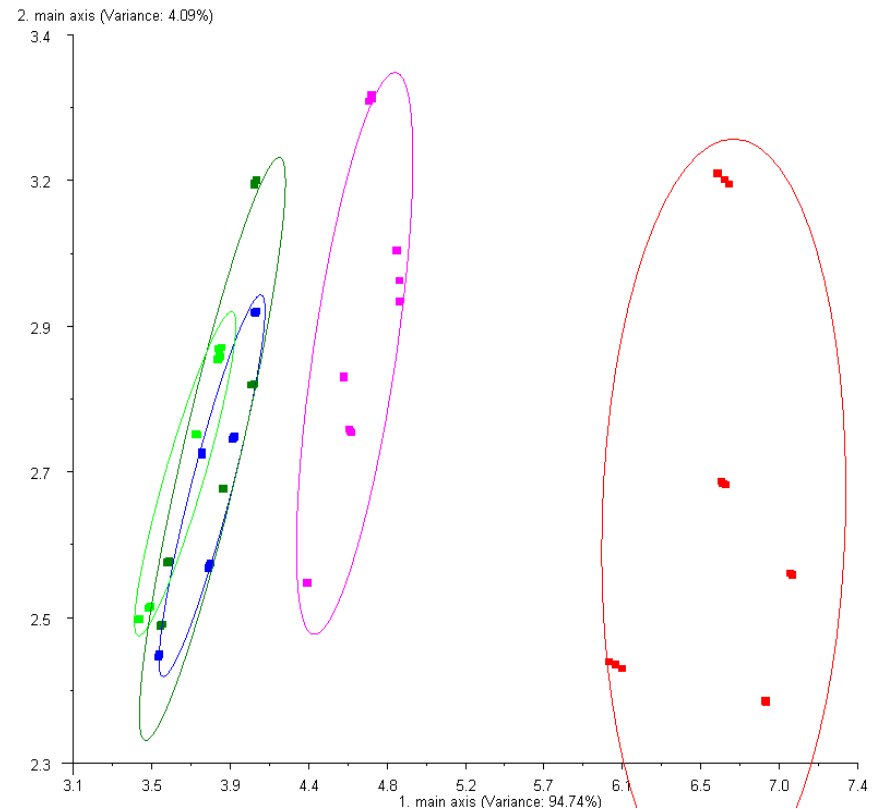
# PEN3: Biogas Generation

- PLS - descriptor
- quantification on Propionic Acid in Fermenter



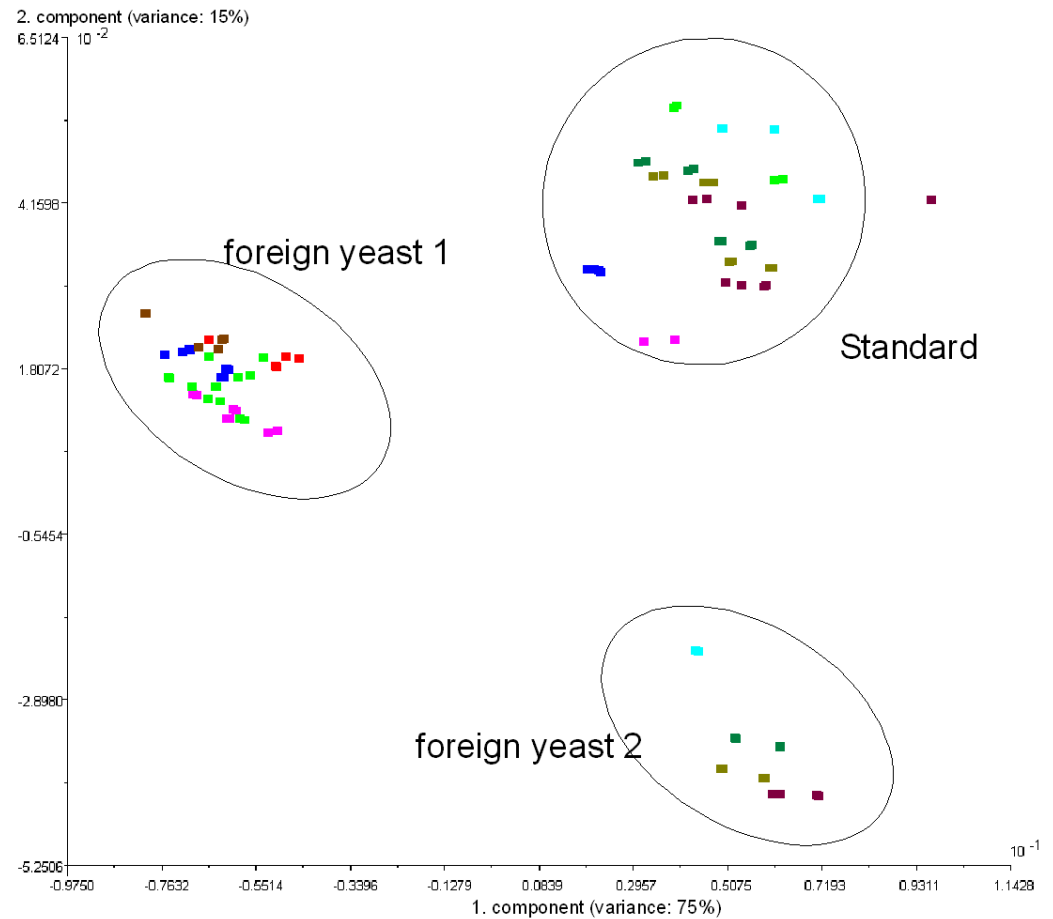
# PEN3: Fungi in Grain Storage

- Test samples containing different Fungi, Aspergillae
- Compounds of interest
  - 1 Butanol
  - 2 Octen -3- ol
  - Dimethyldisulfid



# PEN3: Foreign Yeast in Joghurt

- Early detection of potential spoilage before delivery
- Yeast tested:  
(JB20.11.-2)  
(QMa29.11.-1)
- Special sampling tool



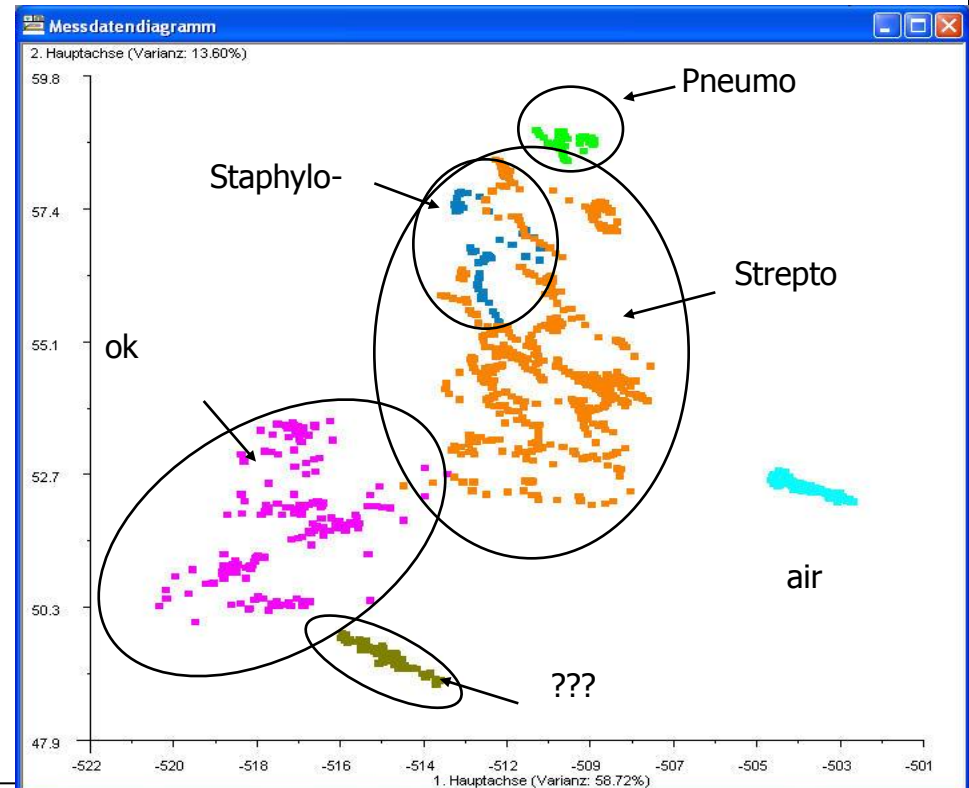
# PEN2: Otitis media

- Differentiation of Infectia for enabling a specific treatment

Many lab samples and patients have been investigated within 6 months

Strepto- Staphylo,  
Pneumokokkae H. influenzae

PCA Analysis  
Normalization



Sensor Array Technology offers an affordable quality supervision

Enoses have a huge field of applications

Sampling Set Ups have too be optimized

Medical applications are widely in Research State