

# **GC-IMS Technology for Efficient Quality Control**

## **VOC-pattern analysis and database related substance identification**

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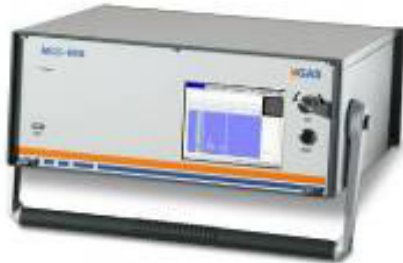
**G.A.S. Gesellschaft für analytische Sensorsysteme mbH  
Dortmund, Germany**

**Booth A1 520 A**



- Interdisciplinary team of specialists from chemistry, physics, electrical engineering and computer science
- Development, production and distribution of gas analysing sensor systems based on ion mobility spectrometry
- Application fields: quantification of odorants in natural gas, trace gas detection for e.g. quality and process control, flavour evaluation, product authentication, breath analysis

## GC-IMS and A-IMS



Detection of traces of VOCs in gases

### Applications

On-line Monitoring  
Process control  
Environment

## BreathSpec®



Detection of traces of VOCs in exhaled human breath

### Applications

Detection of marker Compounds directly in human breath

## FlavourSpec®



Detection of traces of VOCs in the headspace of solid, liquid samples in food

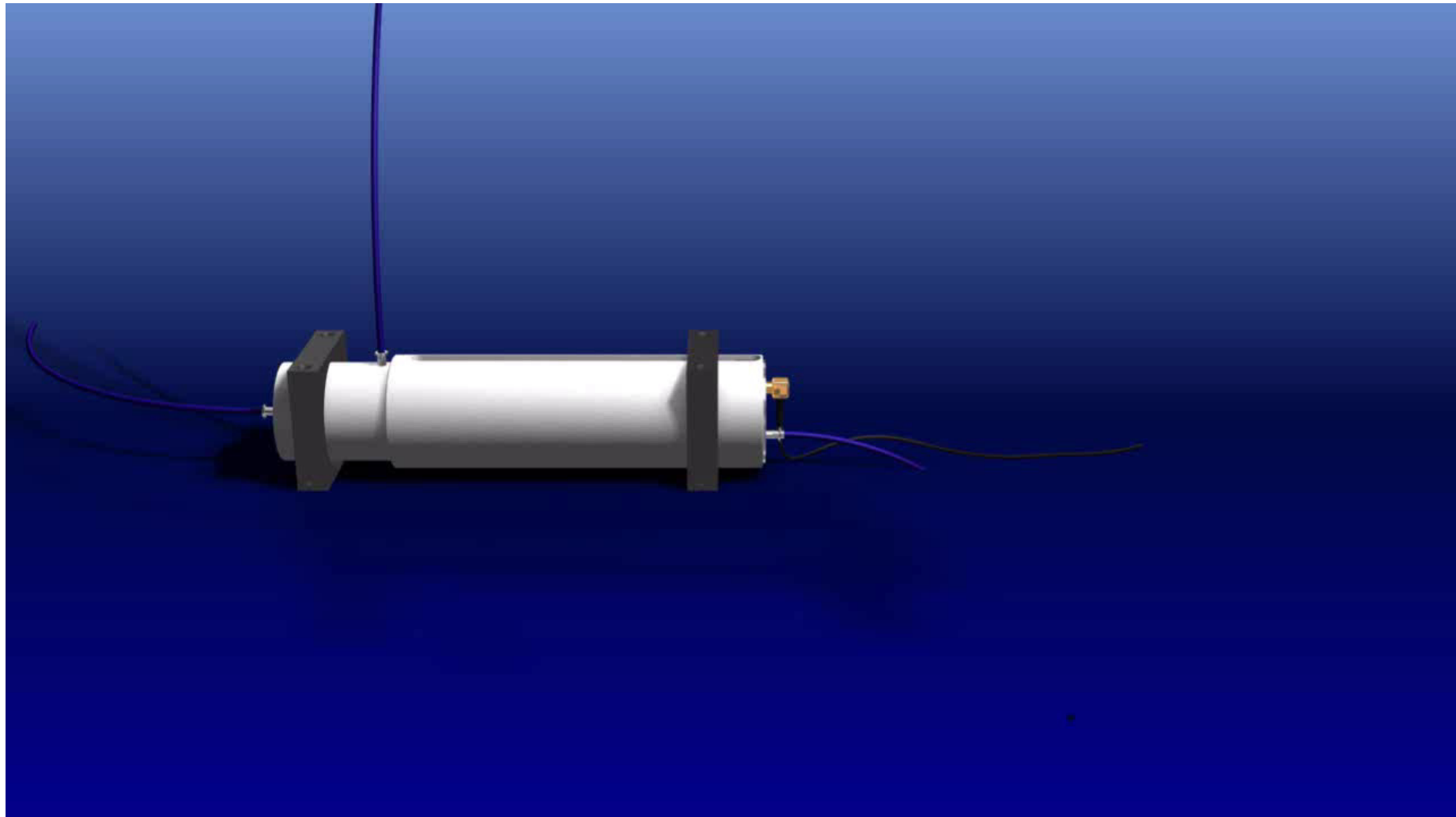
### Applications

“True” electronic nose with physical working principal

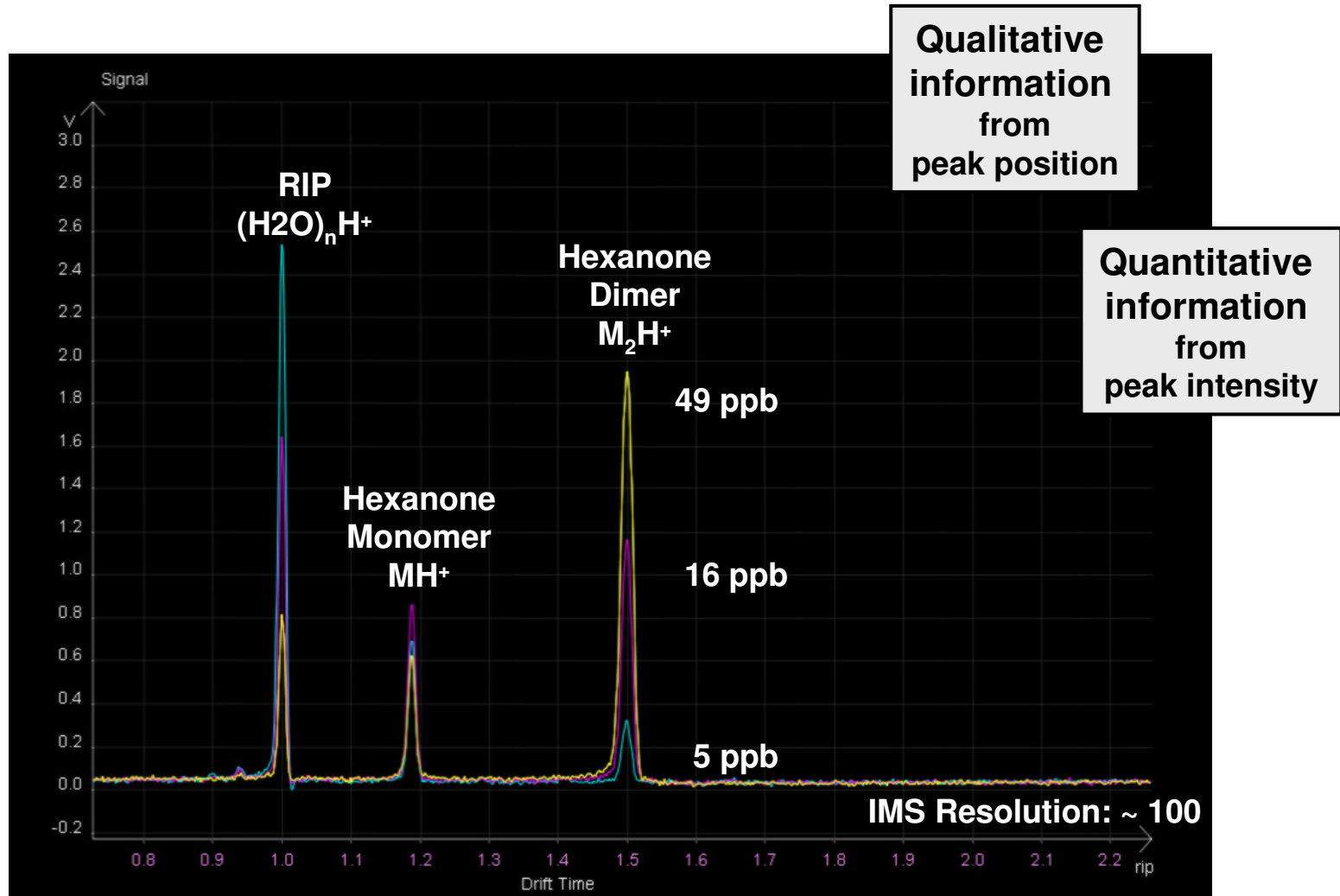
**Advantages** of IMS for the volatile detection (in combination with GC systems):

- High sensitivity – no sample pre-concentration necessary
- Good selectivity (quantitative and qualitative determination of single VOCs possible)
- Flavour-/ off-smell inducing substances are detectable (esters, ketones, aldehydes etc.)
- Water no problem (separated by column)
- Fast
- Easy in use

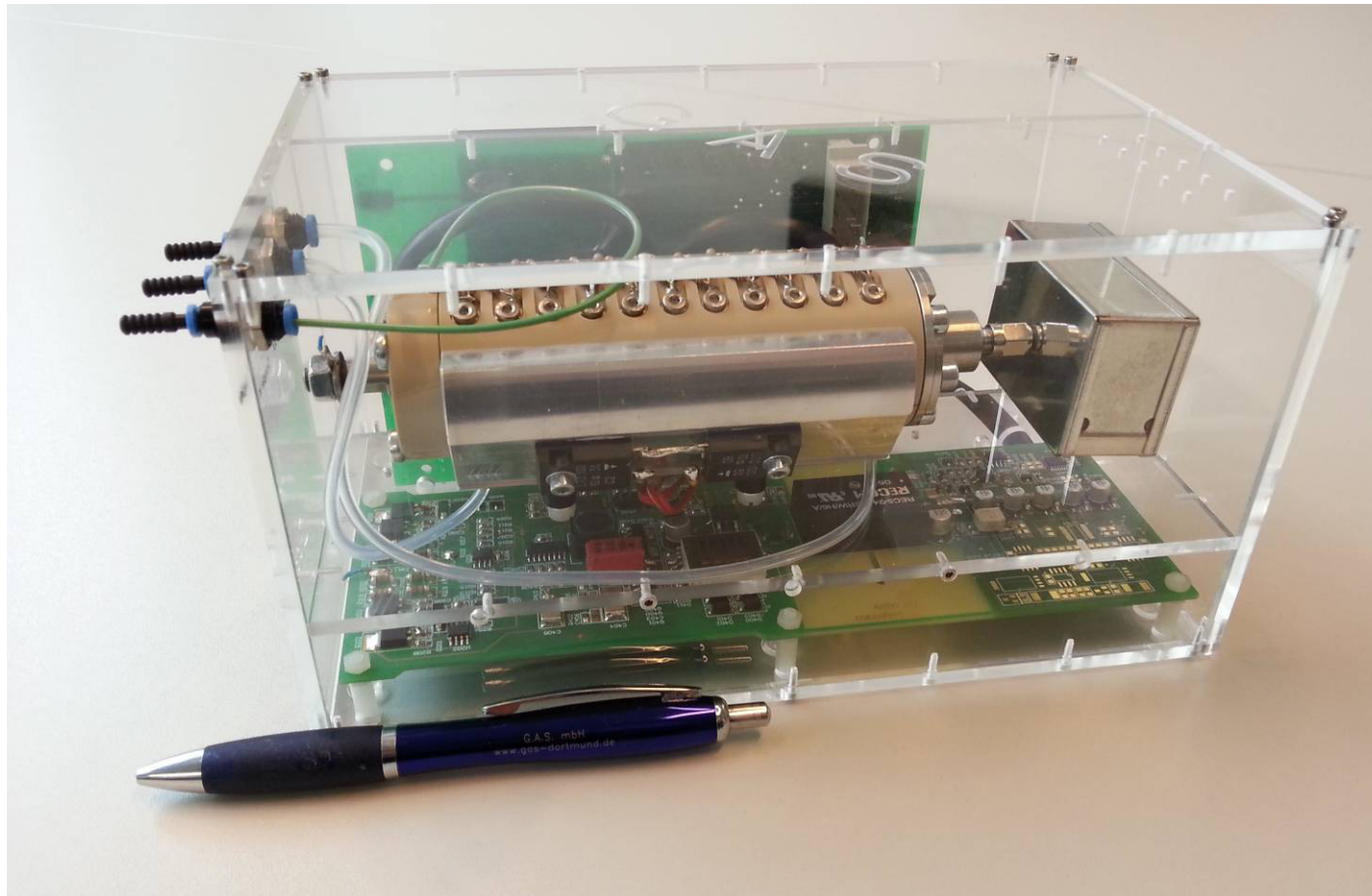
# IMS Working Principle



# Information provided by Ion Mobility Spectra



## IMS made by G.A.S. - Hardware



# Protone Affinities of Volatile Organic Compounds (VOC)



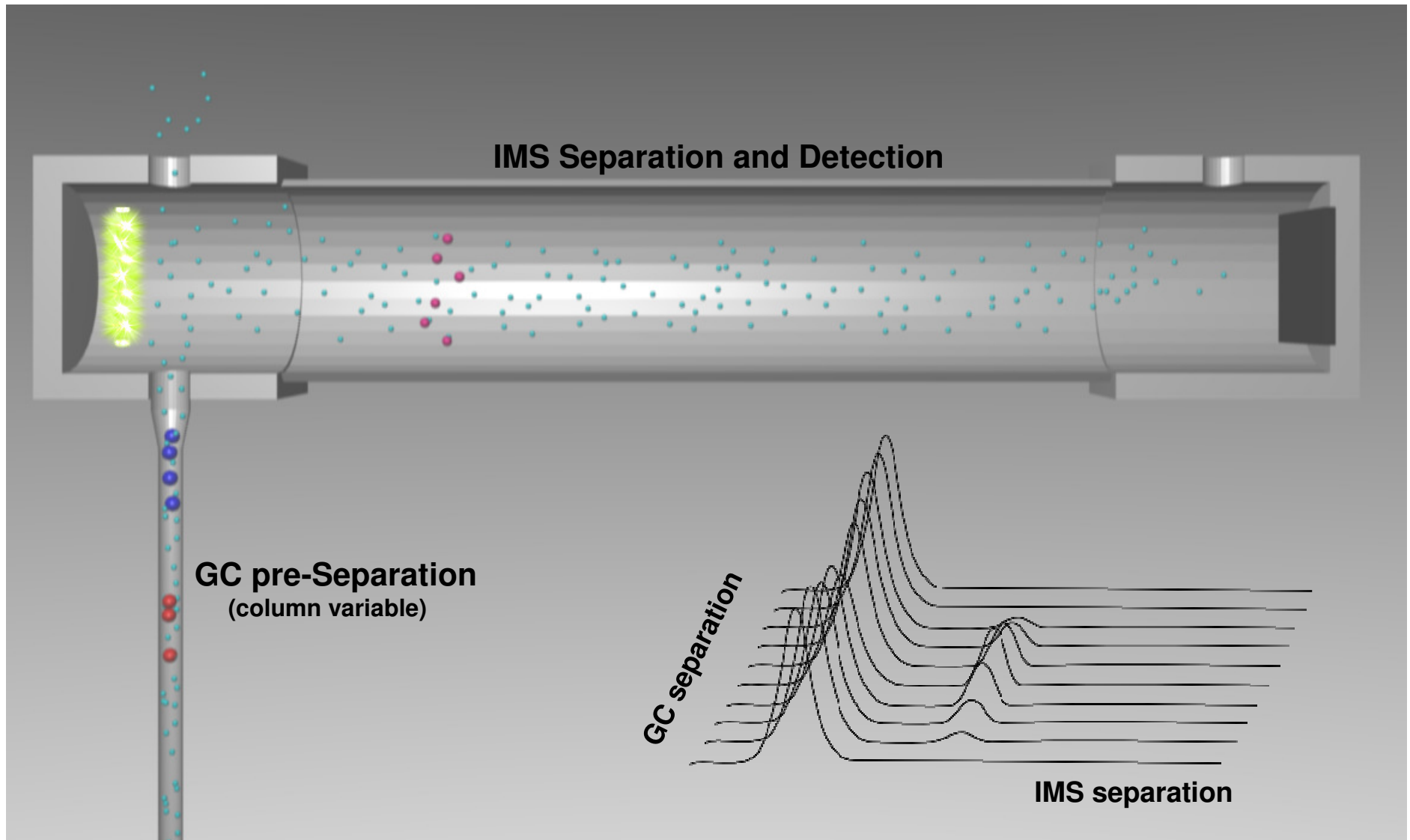
Protone Affinities	Aromatic Amines	930.0 KJ/mol	Pyridine
	Amines	899.0 KJ/mol	Methyl Amine
	Phosphorous Compounds	890.6 KJ/mol	Trimethylphosphate
	Sulfoxides	884.4 KJ/mol	Dimethyl Sulfoxide
		853.6 KJ/mol	Ammonia
	Ketones	832.7 KJ/mol	2-Pentanone
	Esters	821.6 KJ/mol	Methyl Acetate
	Alkenes	805.2 KJ/mol	1-Hexene
	Alcohols	789.2 KJ/mol	Butanol
	Aromatics	750.4 KJ/mol	Benzene
		<b>691.0 KJ/mol</b>	<b>Water</b>
	Alkanes	543.5 KJ/mol	Methane

Source: Gary Eiceman & Zeev Karpas, *Ion Mobility Spectrometry*, CRC Press, 2005, ISBN 0-8493-2247-2

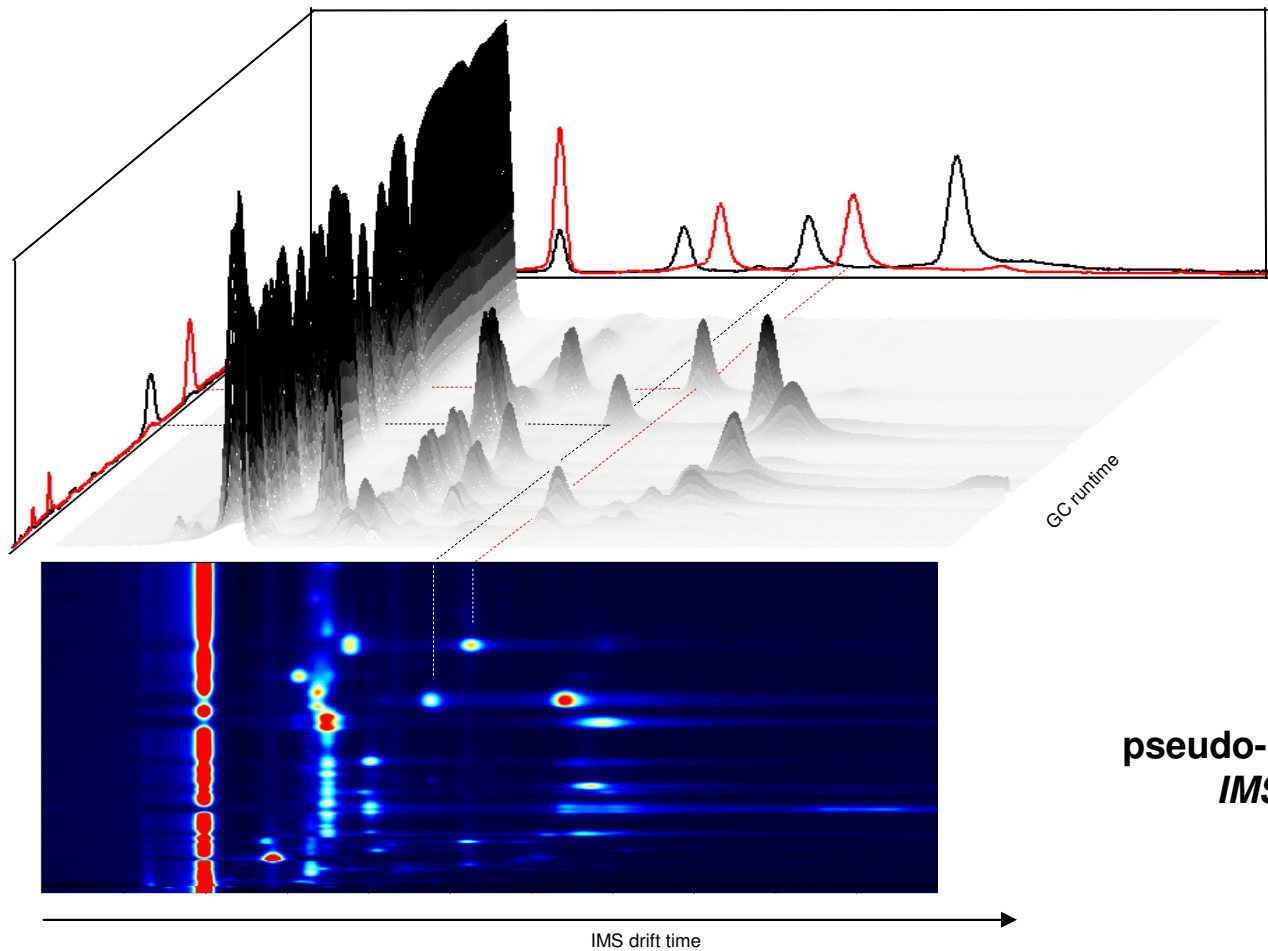
Protone affinities of various VOCs can be found at the NIST chemistry webbook  
<http://webbook.nist.gov/chemistry/>



# Dual separation of GC and IMS for complex Matrices



# Data Output: 2-Dimensional separation by GC and IMS



Single  
*IMS spectra*

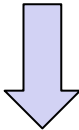
3D  
*IMS chromatogram*

pseudo-colour representation  
*IMS chromatogram*

IMS drift time

**Full GC-IMS headspace analysis**

**Analytical evaluation**



**LAV**  
**- Laboratory Analytical Viewer -**

- Visualisation
- Organisation of measurement data
- List of experimental conditions
- Data analysis:
  - compound calibration → quantification
  - compound identification → comp. Library
- Data export (csv, excel, rapid miner, etc.....)
- Reporting

**Plugin Modules**

**Autonomic reporting**

**Flavour Match**

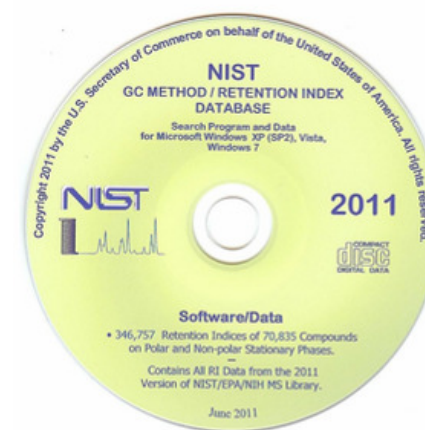
- Automatic pattern analysis
- Similarity analysis:
  - Quantification
  - Quality control
  - Identification
  - Classification
  - .....
- Reporting



# GCxIMS Library Search



- Based on the current NIST method / Retention Index Database with ~300.000 annotated Kovats retention indices and ~70.000 compounds
- Supports the identification of unknown compounds with respect to their Kovats indices after column normalization
- Additional identification certainty by G.A.S. mbH relative drift time database (under continuous development)
- Provides various search options (CAS, name, retention index...)
- Generation of customer specific data bases possible



# GCxIMS Library Search



GCxIMS Library Search 0.0.3

File Edit Libraries GC-Column About

Actions

0.0[M] 1.0[M]

**"2-Ketonmix7-C4-C10"**

RT: 292.0  
RI: 1208.4  
Dt: 1.539 x RIP-position

measurement run [sec]

drift time [RIP relative]

RIP: 8.06ms

Column normalization: C:\Users\sanders\GAS GCxIMS Library\data\1H1\_00038\_50.dat

0%

Click Position RI Rt Dt 1208.7 292.664 1.5339 208

Compound CAS#

Name Fragment

Elements present / absent C,H S,N,Si

Retention Index RI 1208.7 ± 3

Drift time / RIPrel 1.5339 ± 0.03

Molecular Weight MW ± 999

Clear Search

- GC Retention Index
  - CUSTOM ov-5
    - Decanal / C112312 / C10H200 / 156.3
    - NIST 5proz Phenyl methyl siloxane
    - NIST DB-5
    - NIST DB-5MS
    - NIST HP-5
    - NIST HP-5MS
  - GC x IMS
    - CUSTOM ov-5
    - NIST 5proz Phenyl methyl siloxane
    - NIST DB-5
    - NIST DB-5MS
    - NIST HP-5

Selection

Count	Com...	CAS#	For...	MW	RI	Rt [s...]	Dt [R...]	Com...
1	Dec...	C11...	C10...	156.3	1207...	291...	2.05...	
2	2-no...	C82...	C9H...	142.2	1095...	112...	1.88...	
3	2-Oc...	C11...	C8H...	128.2	1001	48.0...	1.76...	
4	2-he...	C11...	C7H...	114.2	892.2	22.3...	1.63...	
5	2-He...	C59...	C6H...	100.2	784.2	11.8...	1.507	
6	2-Pe...	C10...	C5H...	86.1	688.6	7.645	1.37	

# Application Field



Classification of Tea



Quality Control of Solvents

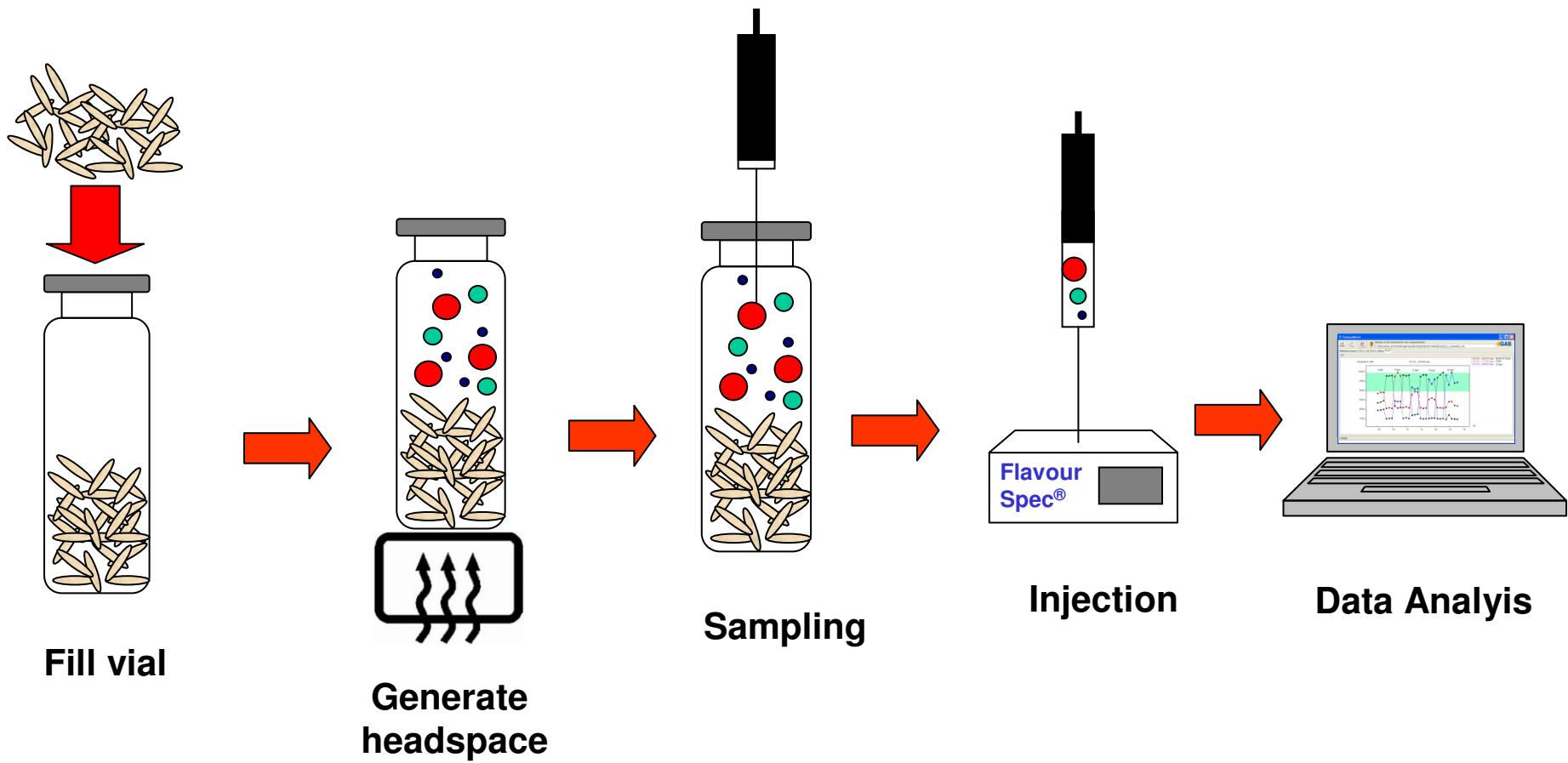


Quantification of Diacetyl and Pentanedione in Beer

# System Workflow



## Sampling using the FlavourSpec®

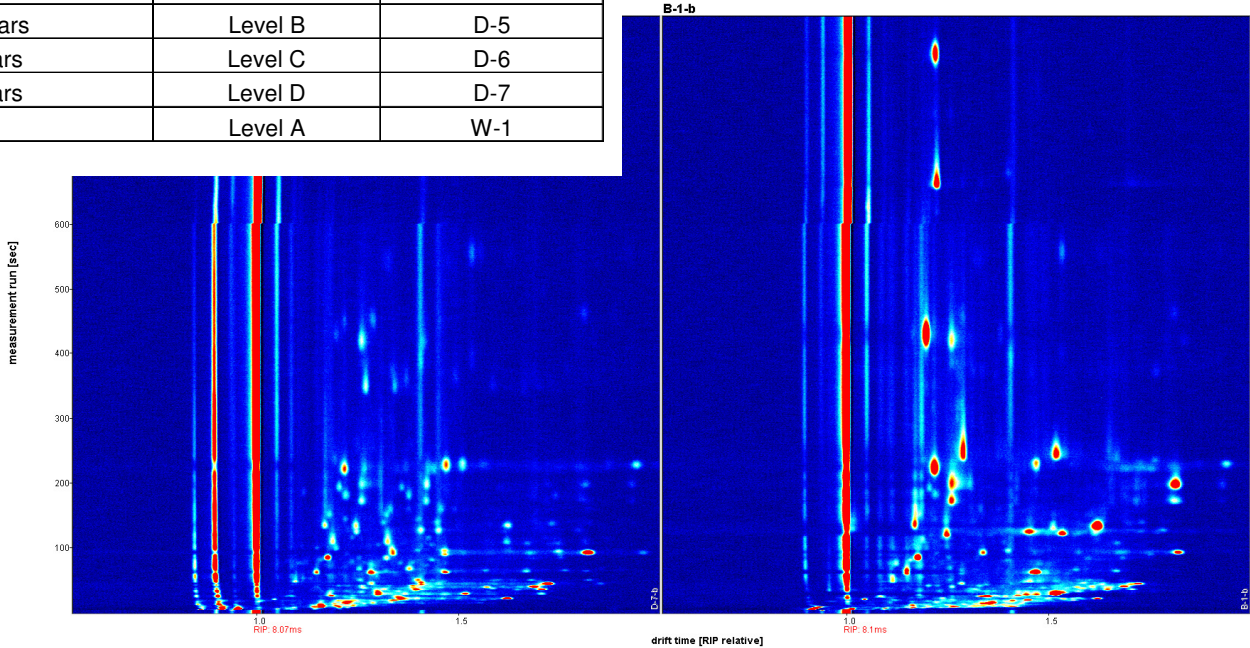


# Differentiation of Tea



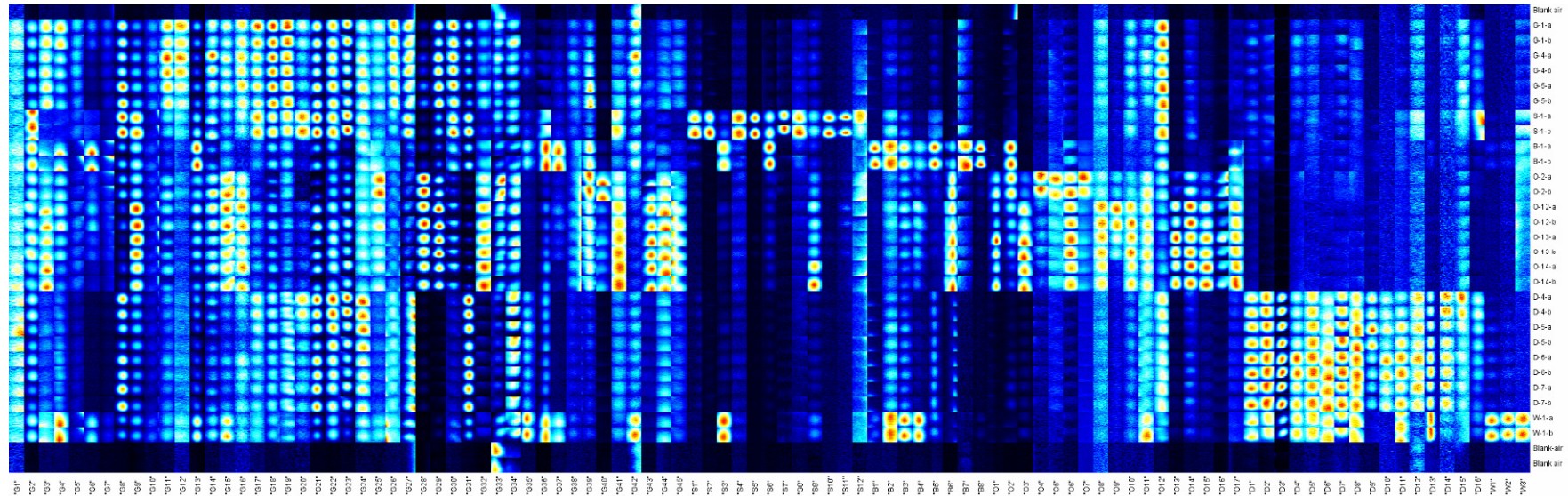
## Analysis with to habitants, quality and storage years

Tea samples			
NO.	Sample name	Grade	Category number
1	2012 Sichuan Green Tea	Special Grade	G-1
2	2013 Ningde Green Tea	Special Grade	G-4
3	2013 Anhui Green Tea	Special Grade	G-5
4	2013 Fuding Jasmine Tea	Special Grade	S-1
5	2013 Wuyi Black Tea	Special Grade	B-1
6	2013 Jianou Narcissus Tea	Level A	O-2
7	2013 Anxi Tie Guanyin Tea	Special Grade	O-12
8	2013 Anxi Tie Guanyin Tea	Level A	O-13
9	2013 Anxi Tie Guanyin Tea	Level B	O-14
10	Pu'er Tea-20 years	Level A	D-4
11	Pu'er Tea-15 years	Level B	D-5
12	Pu'er Tea-8 years	Level C	D-6
13	Pu'er Tea-5 years	Level D	D-7
14	White Tea	Level A	W-1





## Gallery view of the peaks



- A series of 101 peaks are selected using the software tool *LAV*
- Only peaks which vary between the samples are selected
- The work has to be done only once and the area set can be saved

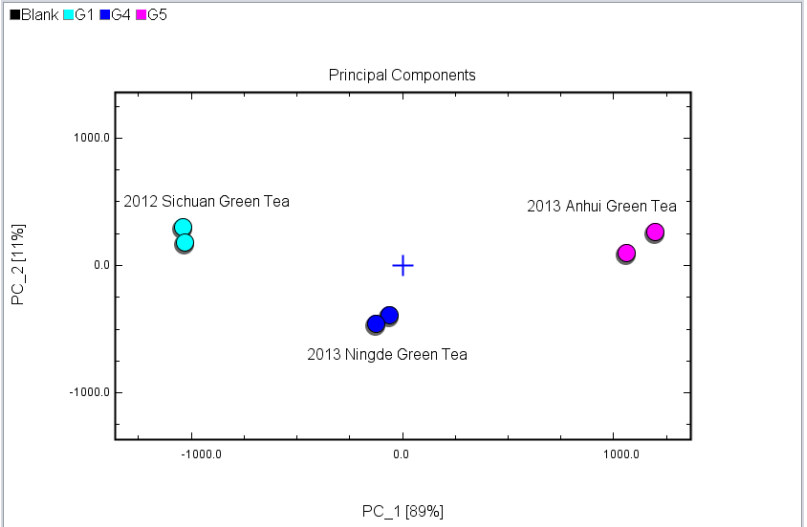
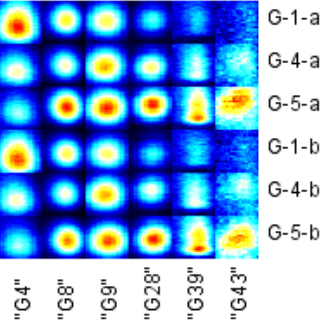
# Differentiation of Tea



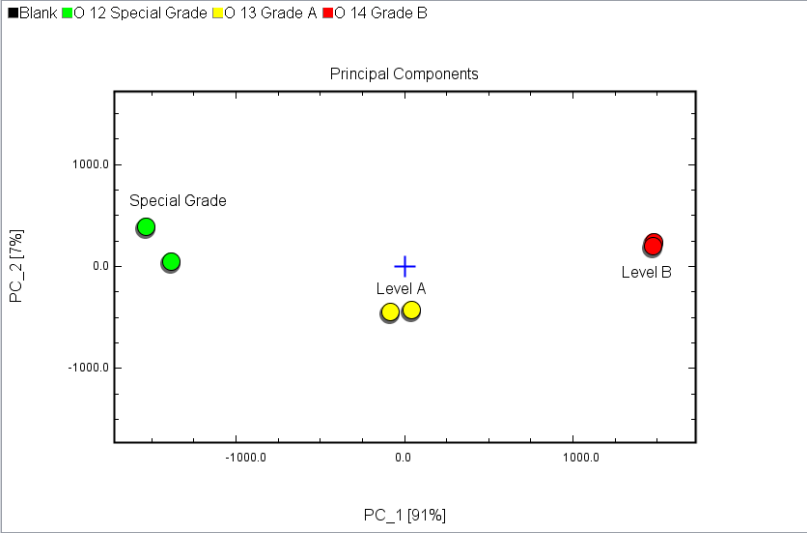
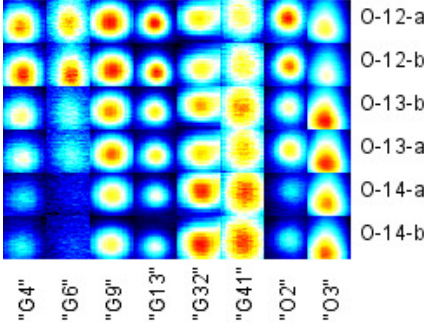
## Gallery view of the peaks

Peaks were a variation was recovered:

Different Habitants



Different Qualities

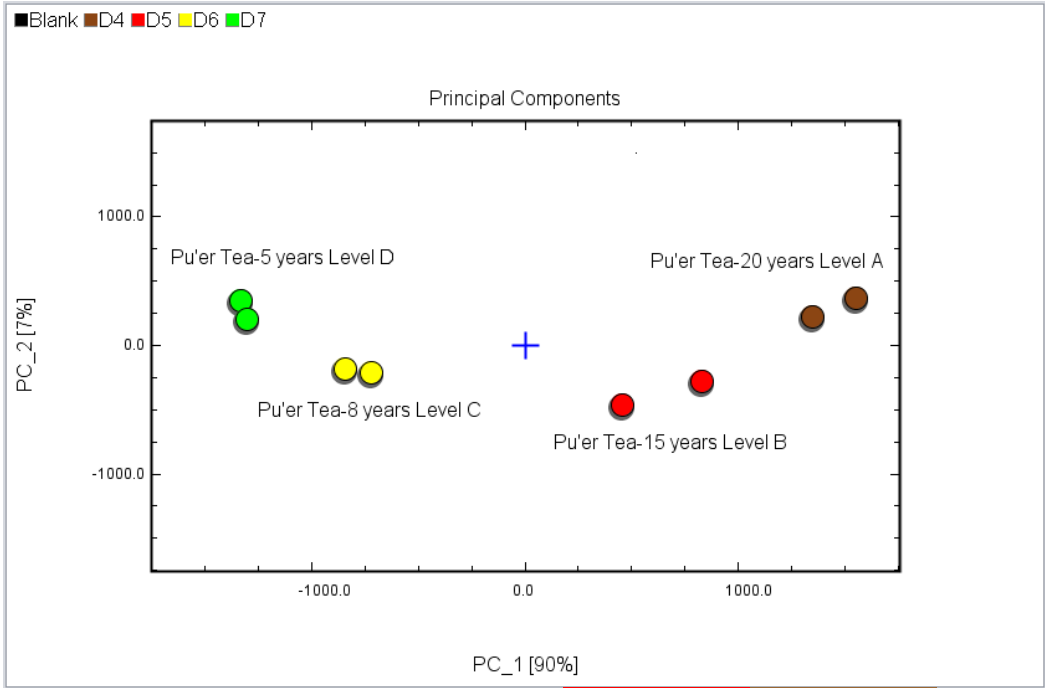
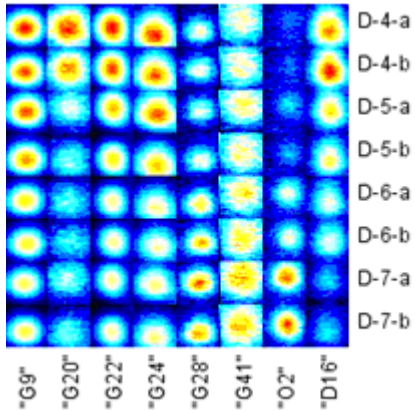


# Differentiation of Tea



## Gallery view of the peaks

Different Storage Age



Increasing Storage Age



# Verification of Regional *Huangjiu* wines



Analysis of the aroma composition to validate origin



High priced wines with regional background are often copied

- Detection of markers for regional origin directly from the wine samples

**Parameters:**

1 ml Huangjiu wine in 20ml headspace vial

**Conditioning:**

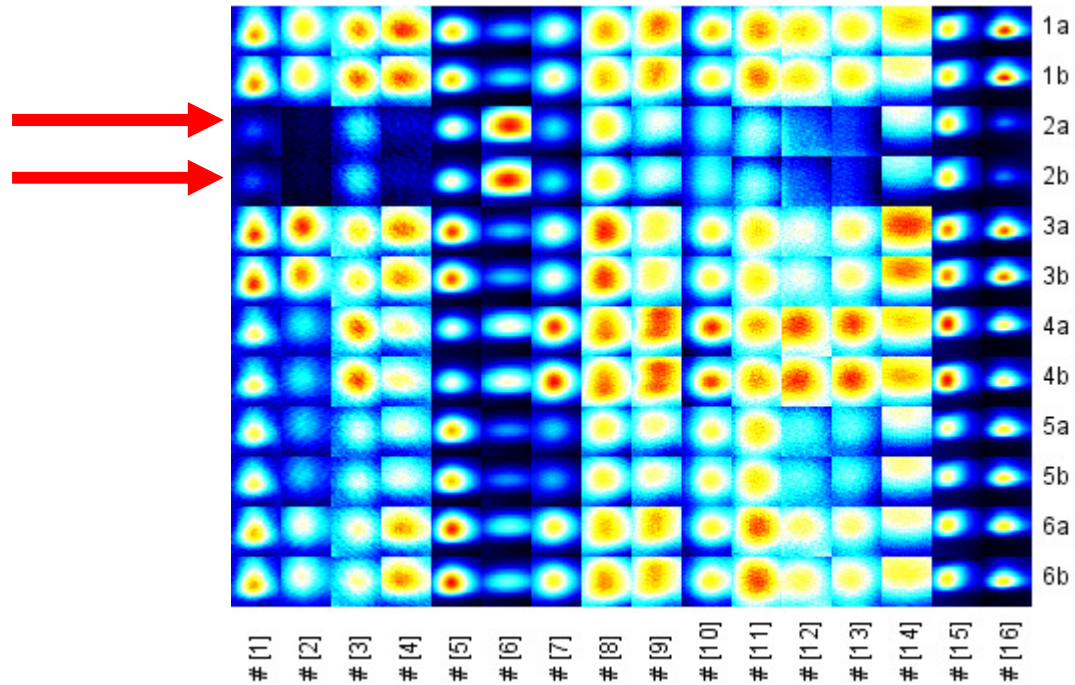
20mins @ RT



# Verification of Regional *Huangjiu* wines



Analysis of the aroma composition to validate origin



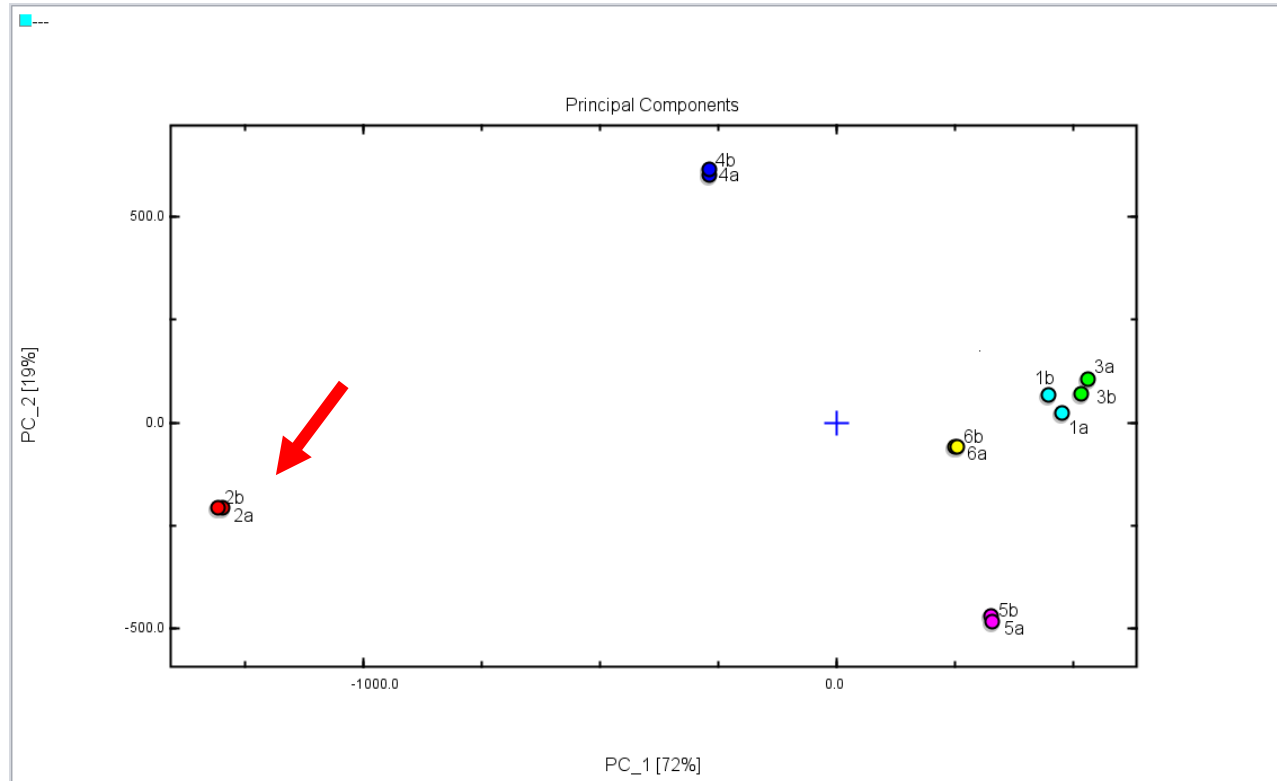
One sample exhibits unique pattern -> produced in other chin. province



# Verification of Regional *Huangjiu* wines



## Analysis of the aroma composition to validate origin



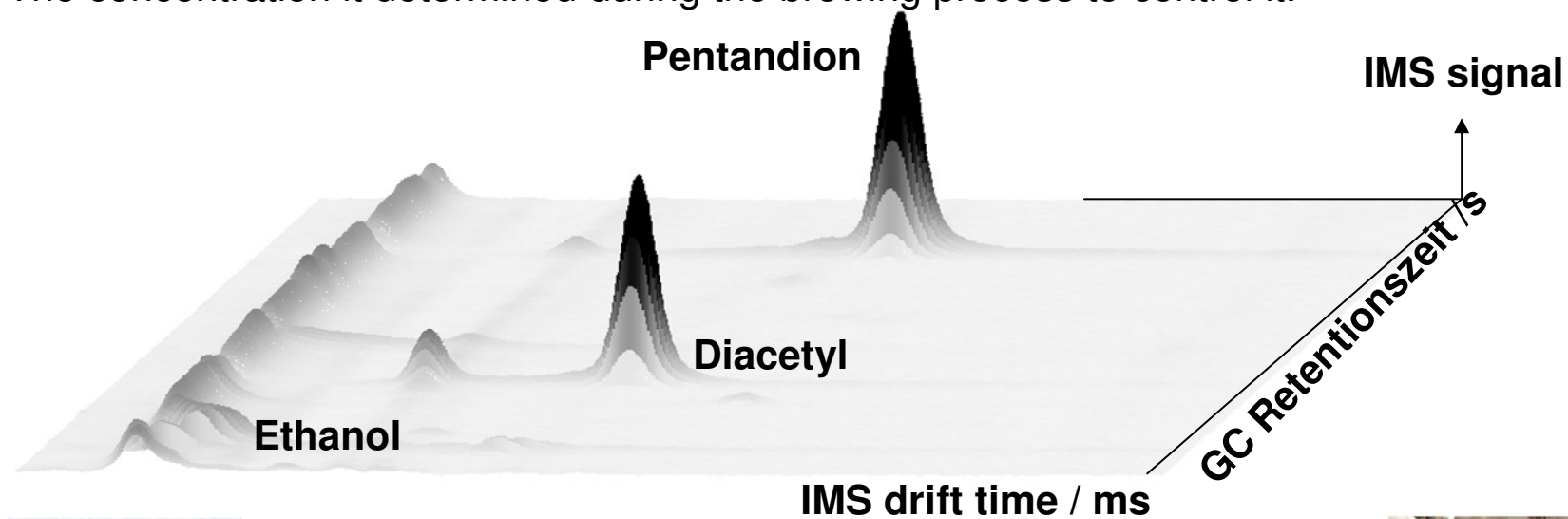
**One sample exhibits unique pattern -> produced in other chin. province**



# Application: Diacetyl and Pentandion in Beer

## Background

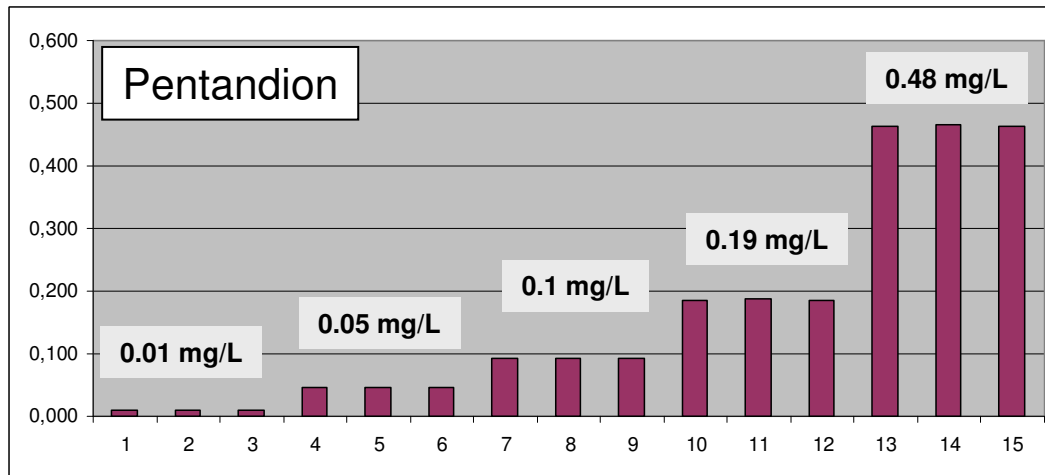
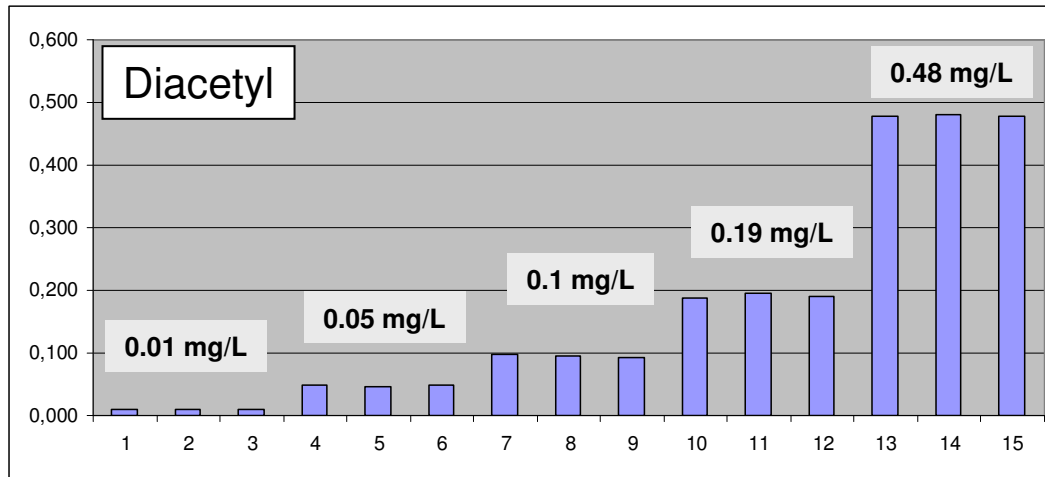
- Diacetyl as well as Pentandione are the most well-known marker flavours related to brewing.
- They are produced during the fermentation as a by-product.
- Diacetyl has a butterscotch like aroma. The detection threshold for diacetyl in beer is typically between 10 and 40  $\mu\text{g/L}$ .
- The concentration is determined during the brewing process to control it.



drift time / msec

# Repeatability

## Calibration for Diacetyl and Pentanedione

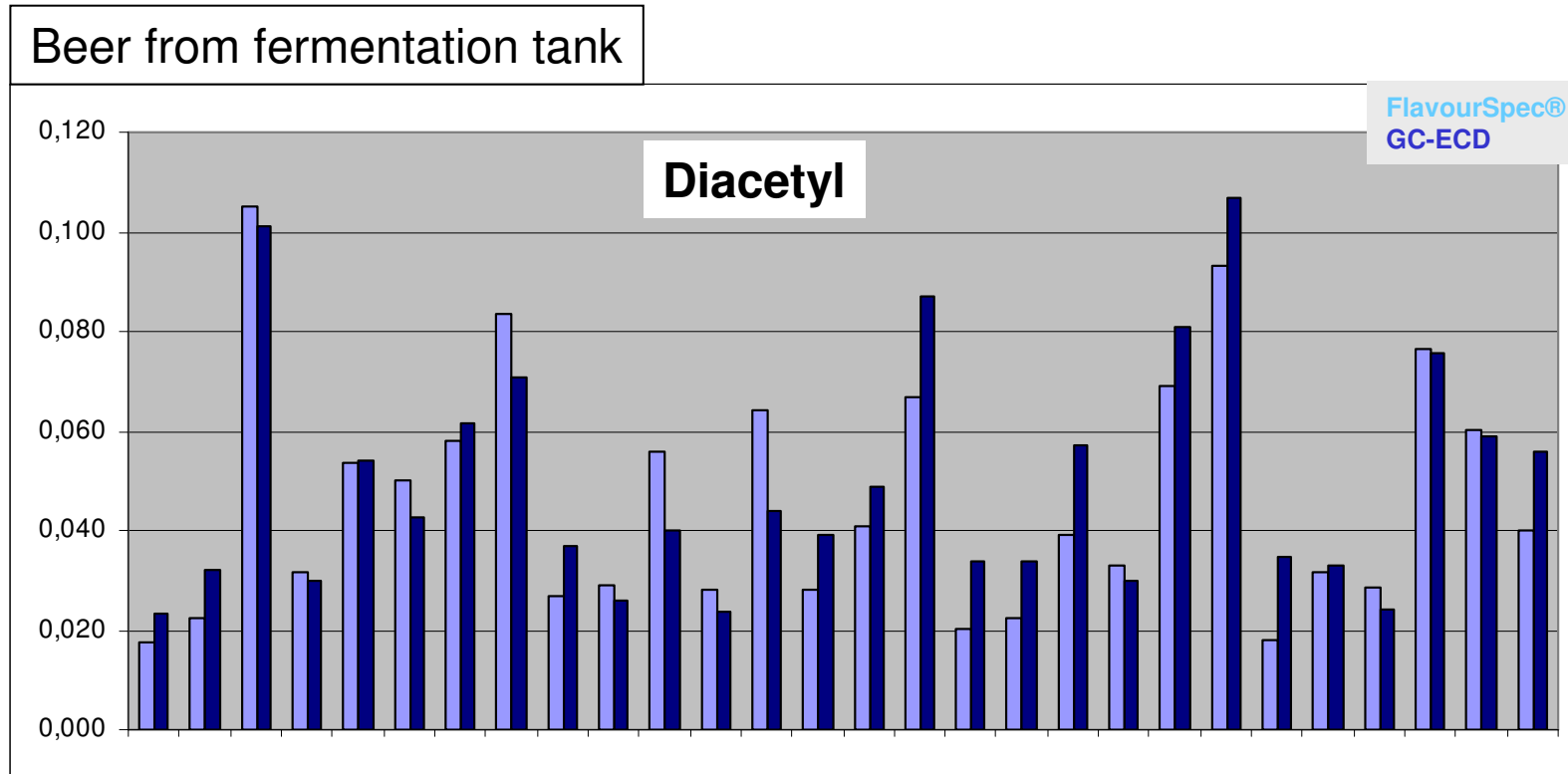


Standard deviation  
in the concentration range  
0.01 – 0.5 mg/L:  
**< 0.003 mg/L**





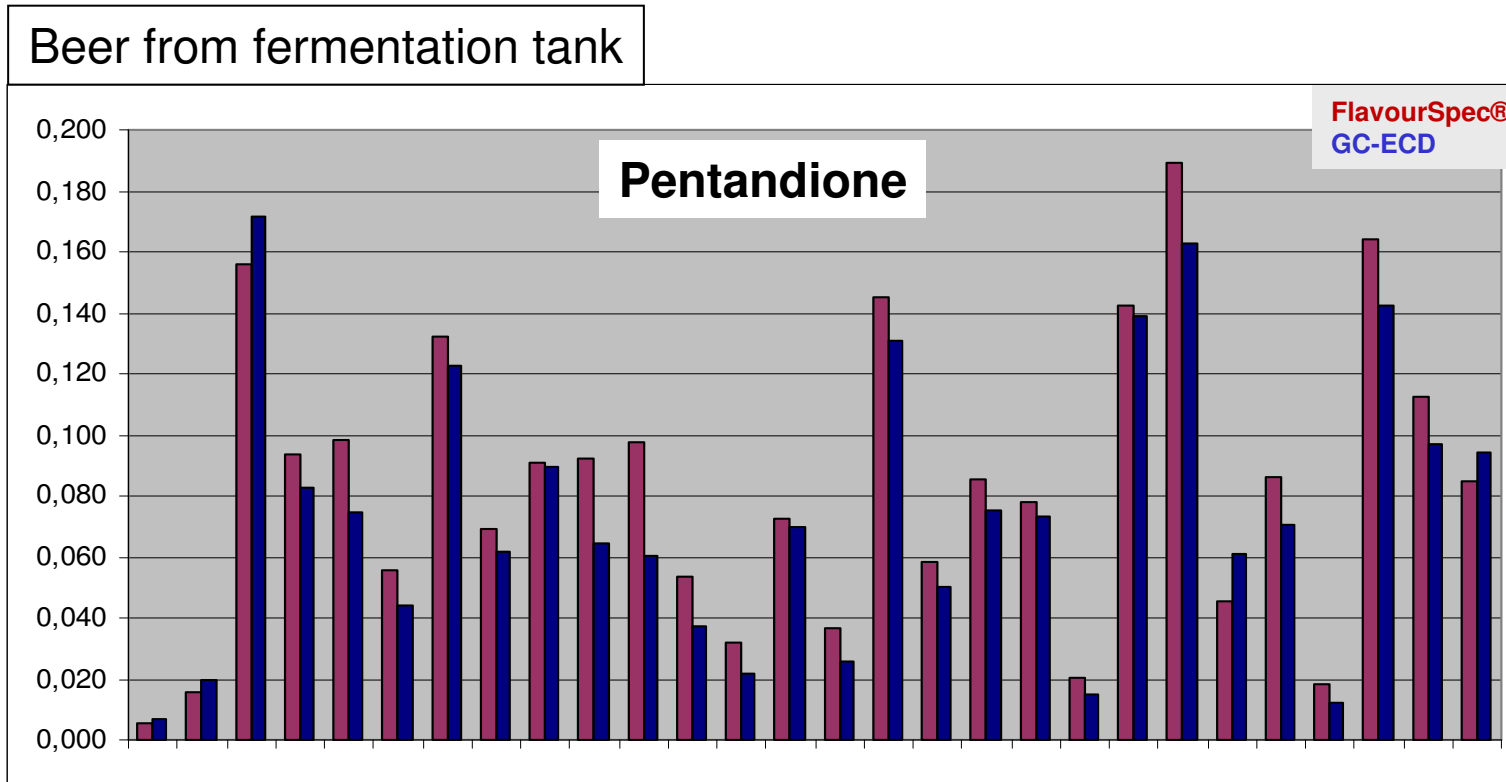
## Comparison of the GC-ECD Results



Deviation to GC results for Diacetyl (mean value):  
**0.003 mg/L**  
(min: - 0.02 mg/L / max: 0.02 mg/L)



## Comparison of the GC-ECD Results



Deviation to GC results for Pentandione (mean value):  
**0.009 mg/L**  
(min: - 0.016 mg/L / max: 0.038 mg/L)



# Application: GC-IMS to detect Impurities in Solvents



## Sampling

Nine samples (sample ID 1,2,3, 4,5,6,7,8, 9) were provided in aerosol cans.



### Sample Introduction

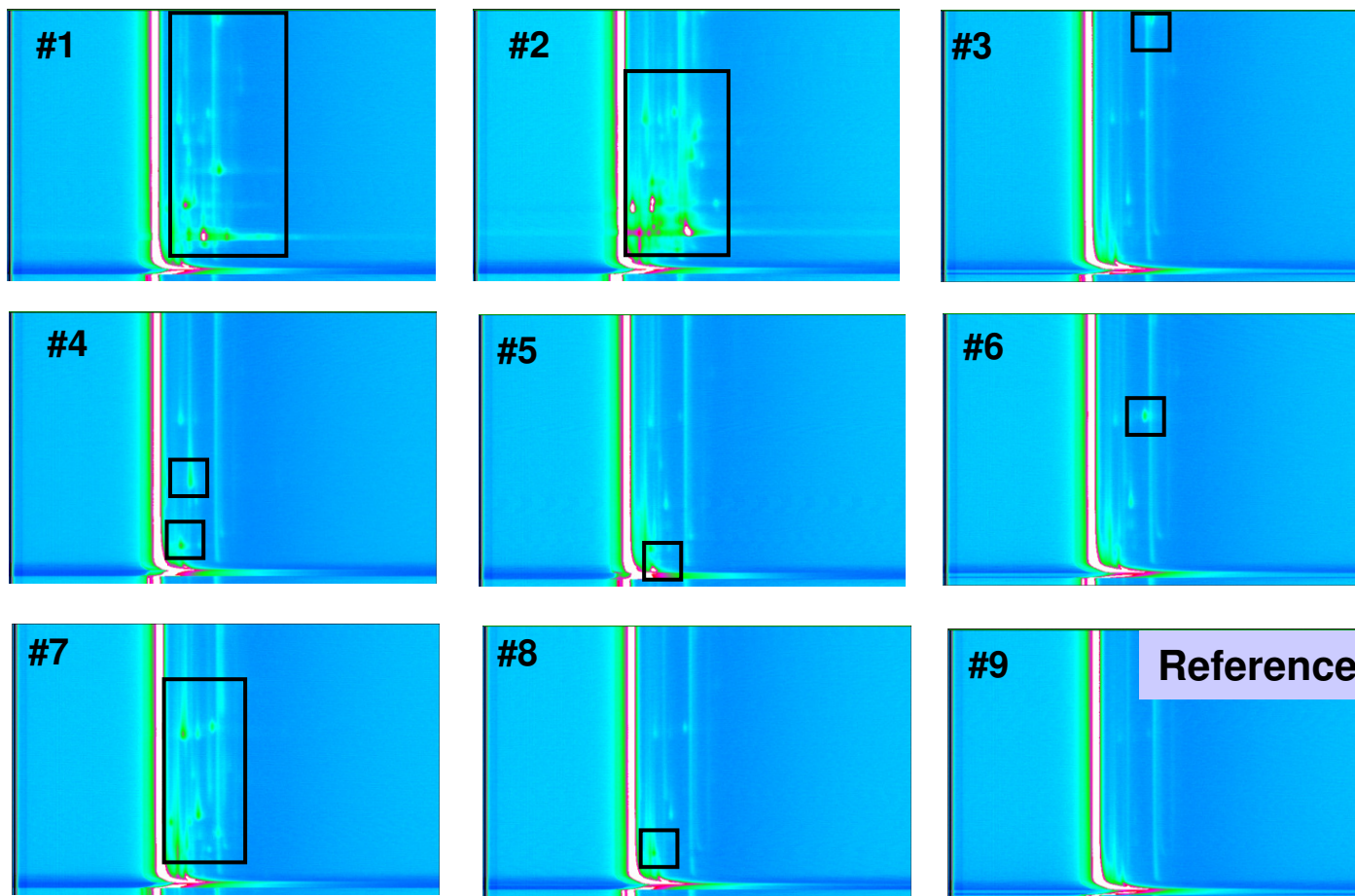
A shot of each sample aerosol can (~1sec.) was sprayed into a sampling bottle. The bottle then was connected to the GC-IMS system. The sampling for analysis was performed automatically by the internal pump of the GC-IMS.



# Impurities in Solvents

## Results for different solvent qualities

Compilation of the IMS chromatograms\* of the samples under investigation:

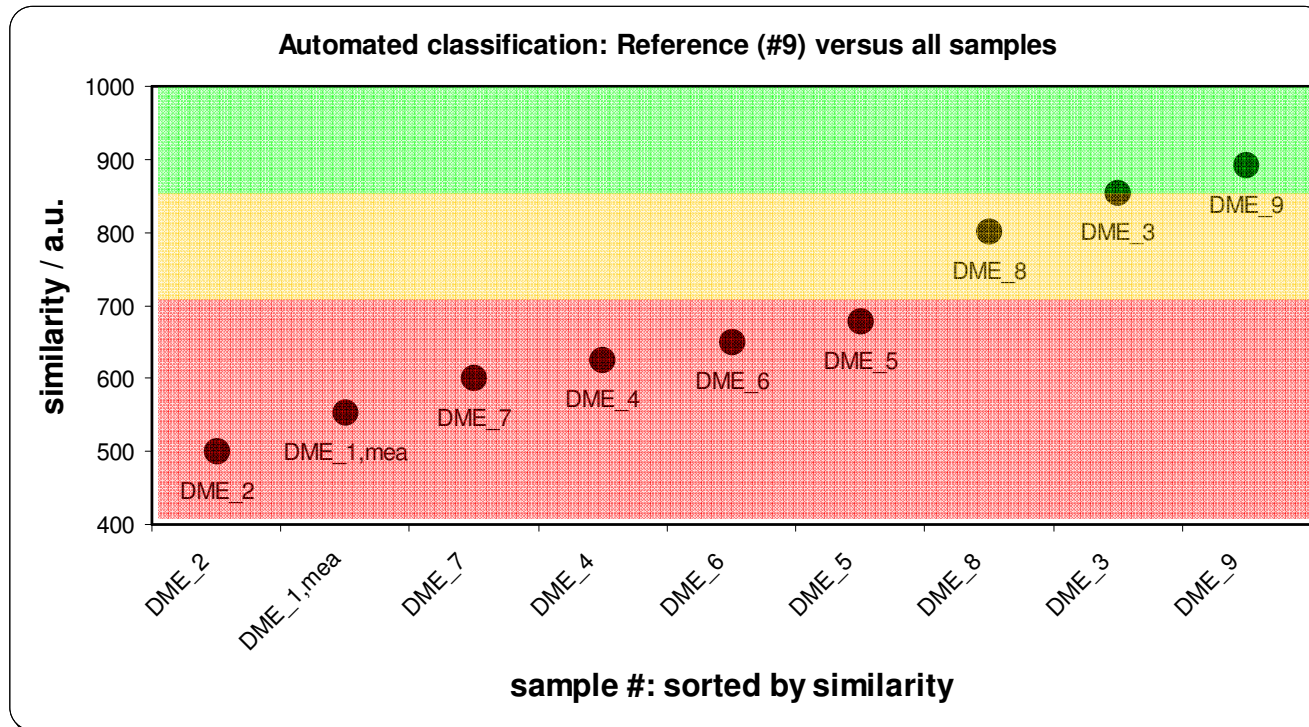


Marked areas show additional signals for samples # 1 to # 8



# Automatic Classification of Results

Classification based on headspace composition: Reference sample vs. all samples



Most similar to reference (#9): 3 > 8      Most unlike: 2 > 1

# Applications for FlavourSpec®/GC-IMS

- Process control (unwanted smell from production,...)
- Quality control of commodities and products (olive oil, ham,...)
- Impartial prove of product flavours
- Support of sensory panels
- Early Detection of Off-smells (impurities, diacetyl in beer etc)
- Blending (green tea, coffee, cigarettes, wine, etc)
- Optimisation of manufacturing process
- VOCs in plastics/papers (packaging materials)
- Residual solvents in polymeres, leather, etc.
- Environmental pollution (contaminants, bad smell ...)
- ...





## Summary

- FlavourSpec can work “at-line” (no lab environment needed)
- GC-IMS is extremely rugged and can operate on-line (coupled to process incl. automatic sampling)
- Results: Pattern /”Fingerprint” for a certain class/attribute (good, bad, fresh etc.)
- Results: Single substances can be identified due to characteristic IMS chromatogram
- Detection limits for VOCs in the low ppb<sub>v</sub> / µg/L range
- Short total analysis run times of 3-10 minutes
- No sample preparation necessary
- Easy to use



Thank you for your attention!

**Your are welcome to visit us at our Booth:  
A1 520 A**

For further questions please contact

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