On-site Detection of Siloxanes and other unwanted VOCs in Biogas using Gas Chromatograph-Ion Mobility Spectrometer (GC-IMS)

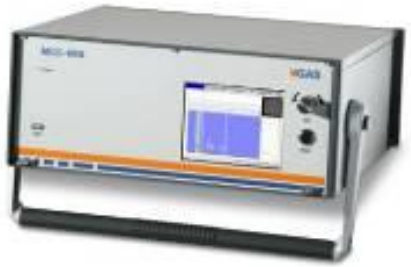
by

G.A.S. Gesellschaft für analytische Sensorsysteme mbH

Hammer Biogastage,
Juli 2015

G.A.S. Instruments with different sampling Techniques

GC-IMS and A-IMS



Measurement
of VOCs in
gases

Applications

Process Control
Environmental monitoring
Gas quality control

BreathSpec®

Detection of
VOCs in exhaled
human breath

Applications

Detection of marker
Compounds directly in
human breath

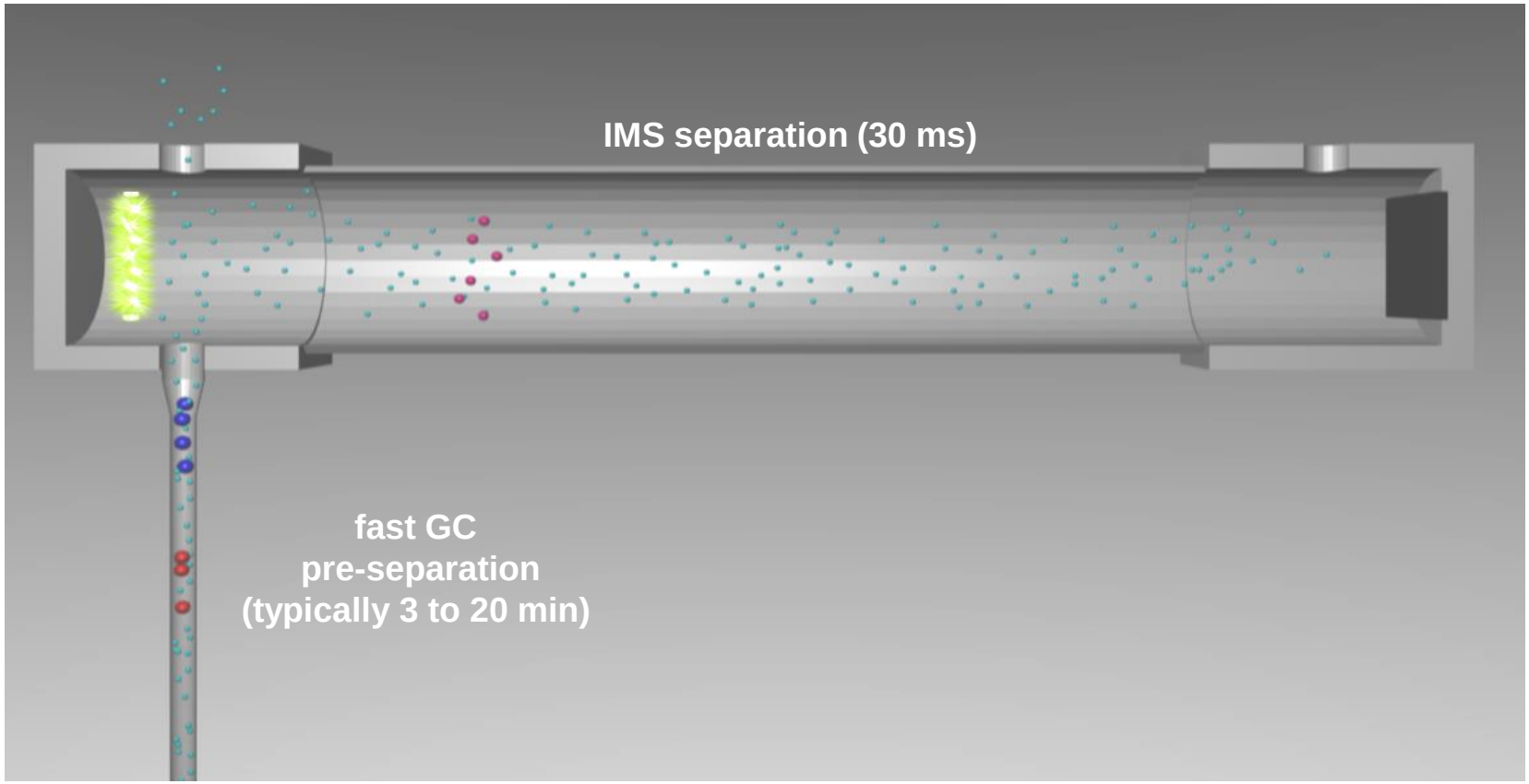
FlavourSpec®

Detection of traces
of VOCs in the
headspace of solids &
liquids in food/beverages

Applications

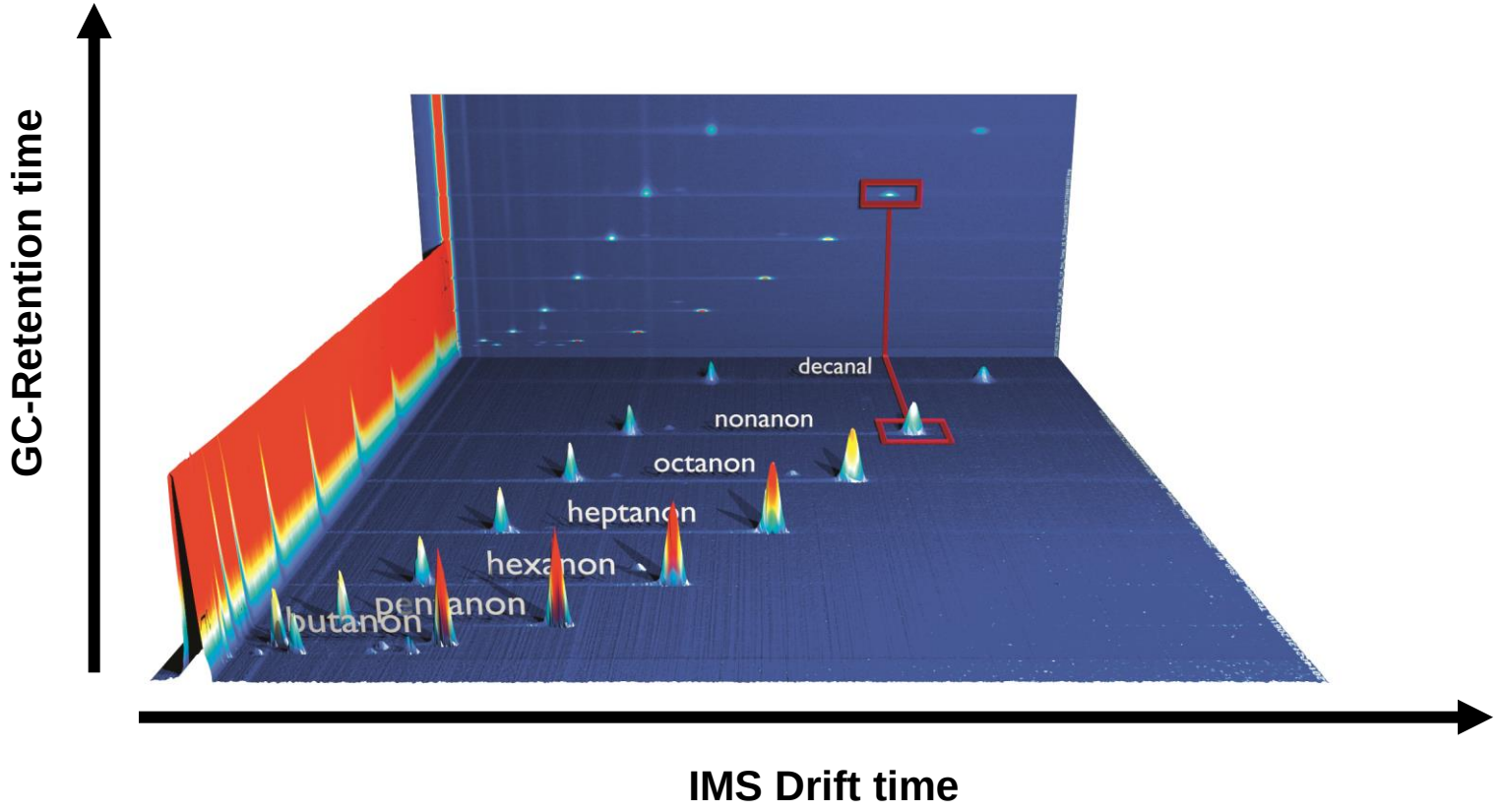
Off-smell monitoring
Raw material and
product quality control

GC-IMS Technology: 2-dimensional Separation



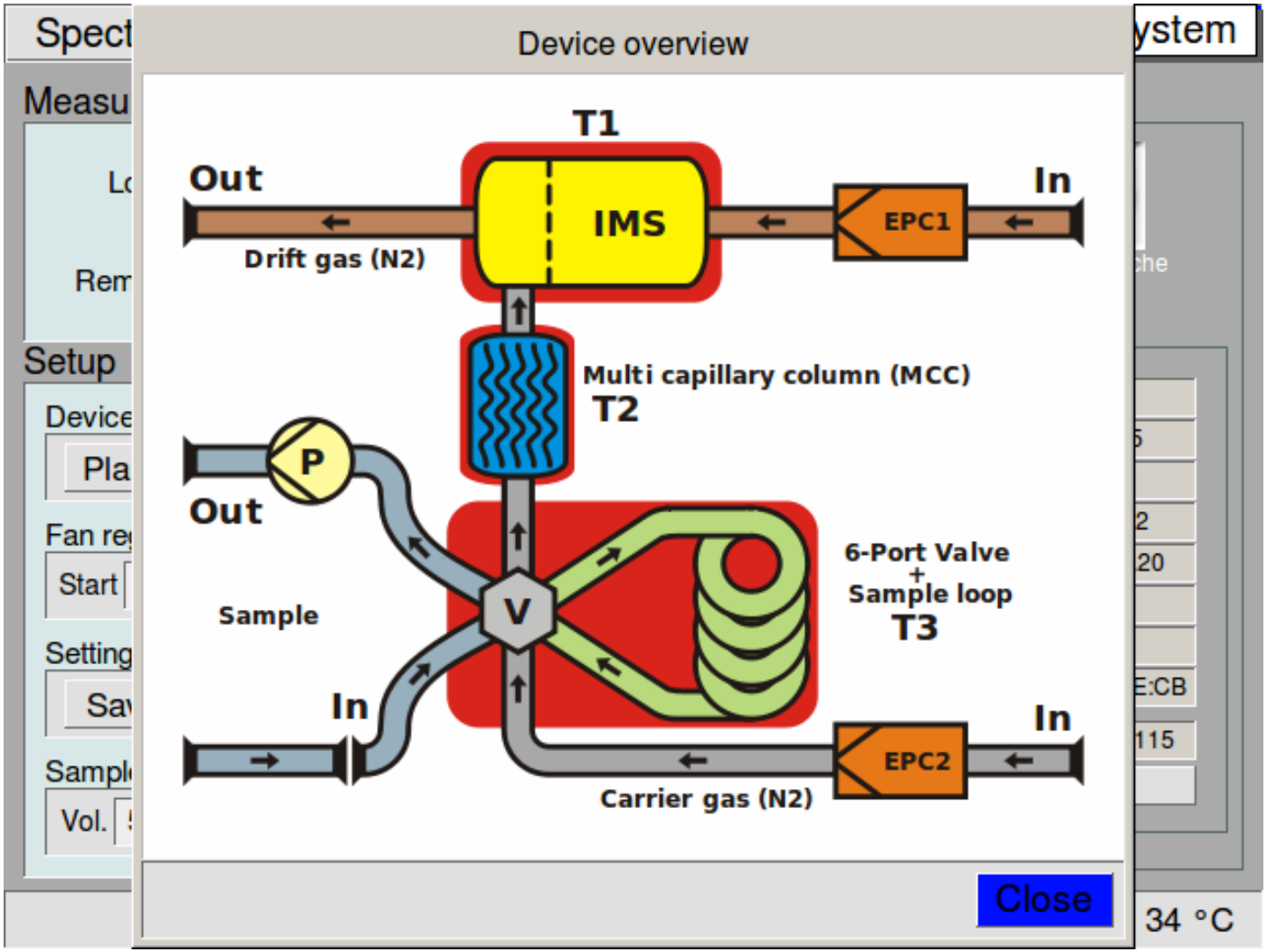
Selectivity of GC plus Sensitivity of IMS to achieve excellent analytical Performance

GC-IMS Technology: 2-dimensional Separation



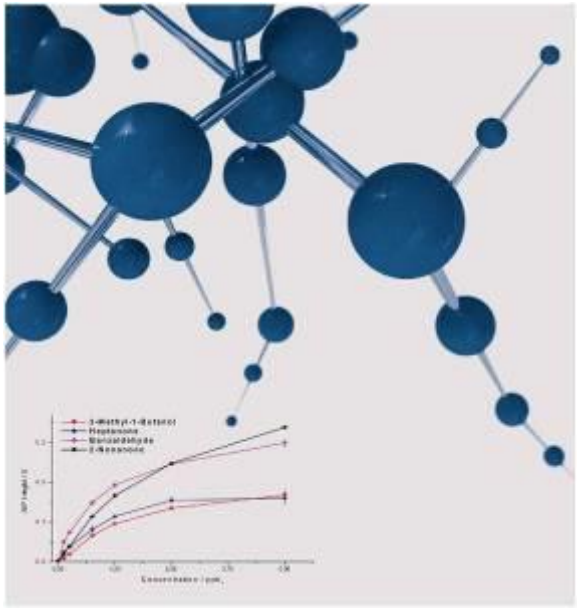
Compound Identification according to NIST-based Library, Validation by test gases

GC-IMS: Flexible System Set-Up



Only power and nitrogen/synthetic air (purge gas) are needed!

Detectable Volatiles using IMS-Technology



IMS is sensitive for a large number of chemical compounds, like:

- ketones
- aldehydes
- alcohols
- ether
- ester
- amines
- aromatic compunds
- organic phosphor compounds
- organic sulfur compounds
- organic nitro compounds
- halogenated compounds
- .....

➢ **detection limit typically low ppb$_v$ range**

Composition of Biogas

Biogas is produced by the anaerobic digestion or fermentation of biodegradable materials such as biomass, sewage, waste …

Methan	50 – 60 %
CO_2	30 – 45 %
N_2	< 5 %
O_2	< 2 %
H_2S	2 % (200 – 2000 ppm)

I. Application: Detection of Siloxanes in Biogas

Different Applications regarding Siloxane Monitoring need to be addressed

I. Sources/Types of Siloxanes as Contaminants in Biogas

Due to the presence of……

Washing Agents
Cosmetica
Skin Care Products
Silikone Oils
Waterproofing Materials
Shoe Cream
……

... induced presence of siloxanes

Tetramethylsilane (TMS)
Trimethylsilanol (MOH)
Hexamethyldisiloxane (L2)
Hexamethylcyclotrisiloxane (D3)
Octamethyltrisiloxane (L3)
Octamethylcyclotetrasiloxane (D4)
Decamethyltetrasiloxane (L4)
Decamethylcyclopentasiloxane (D5)

Generated (typical) Siloxanes

I. Consequences/Effects of Siloxanes/Silicon

….different parts of the engine can be damaged resulting in:

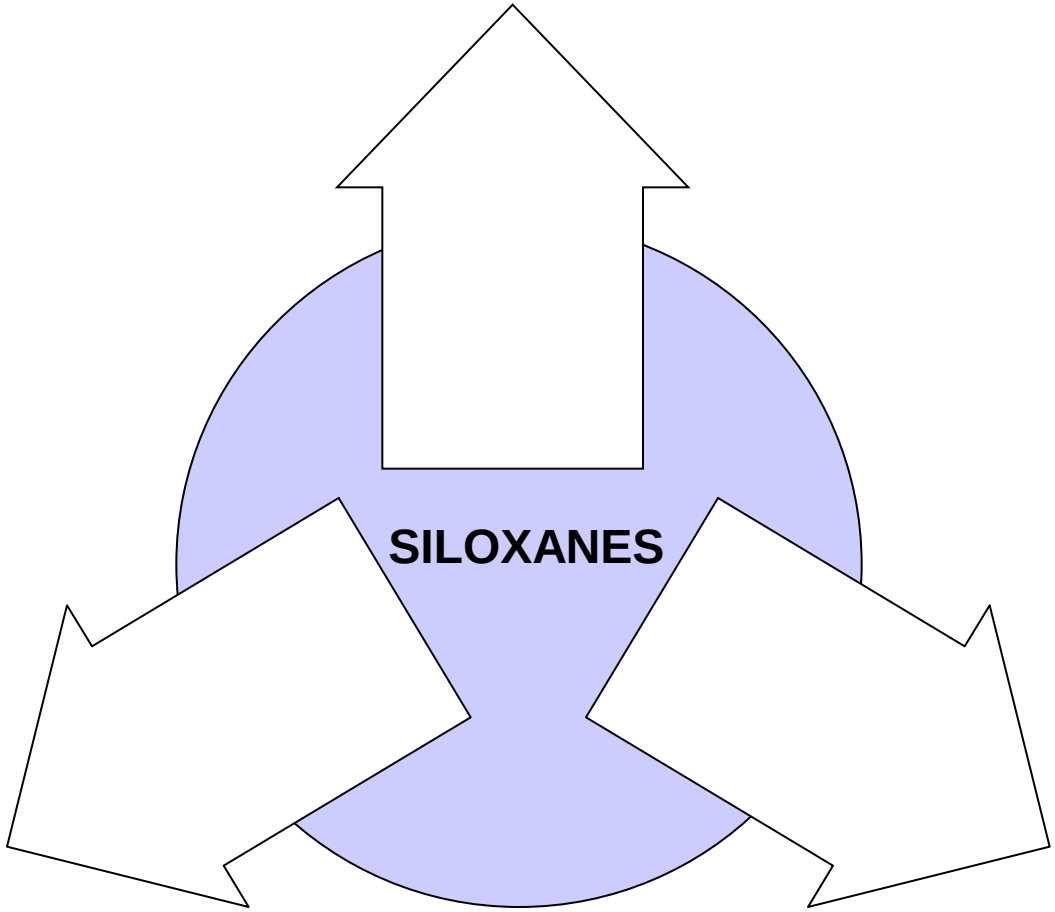
1. Cost intensive break downs of the engine and …

2. and significant secondary costs: Repair and Down Times!

I. Customers‘ Applications regarding Siloxanes

2. Portable/flexible Instrumentation to test for

Siloxanes/Silicon Concentration



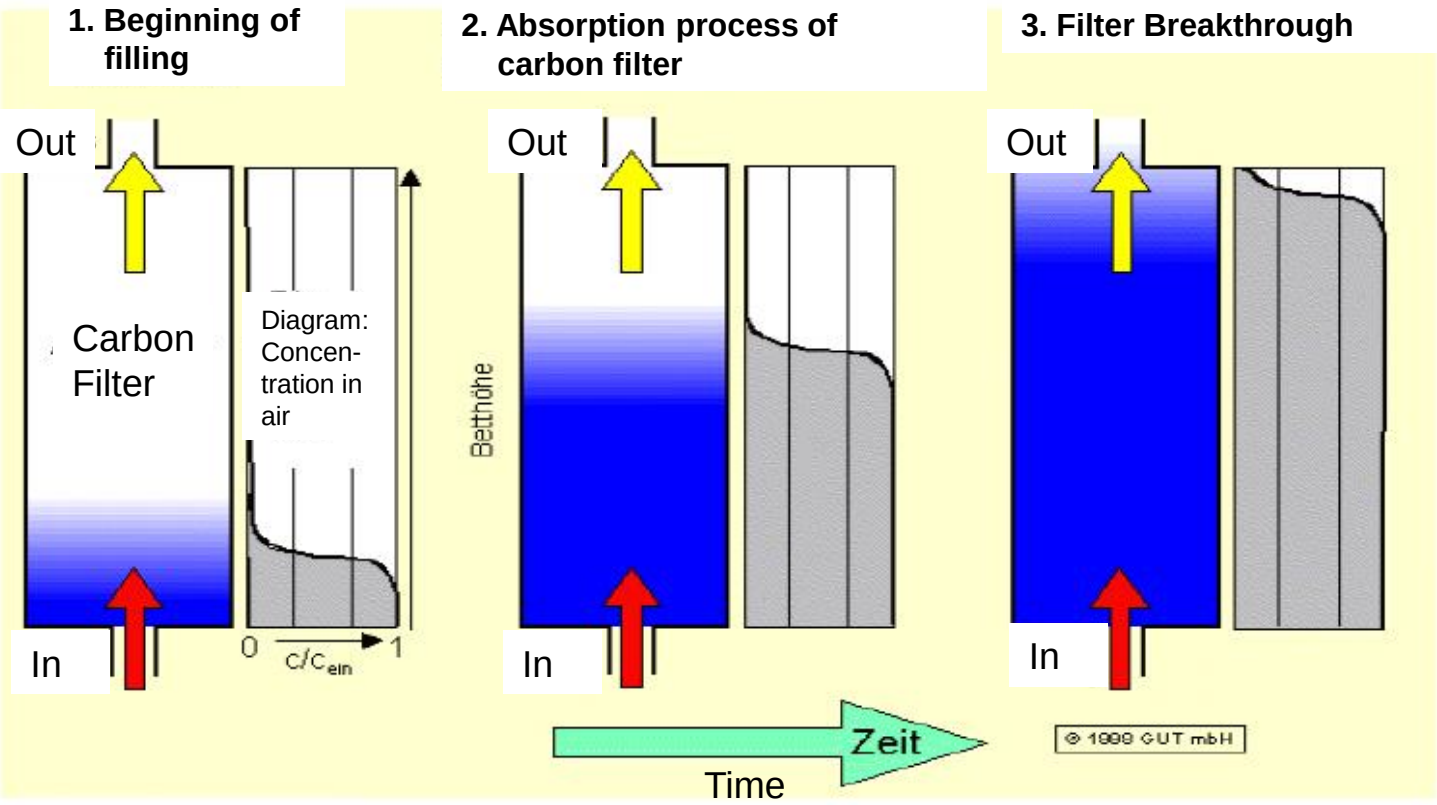
1. On-line Monitoring

Filter Breaktrough

3. Online Monitoring

Siloxane/Silicon Concentration

I. Cleaning Procedure of Biogas

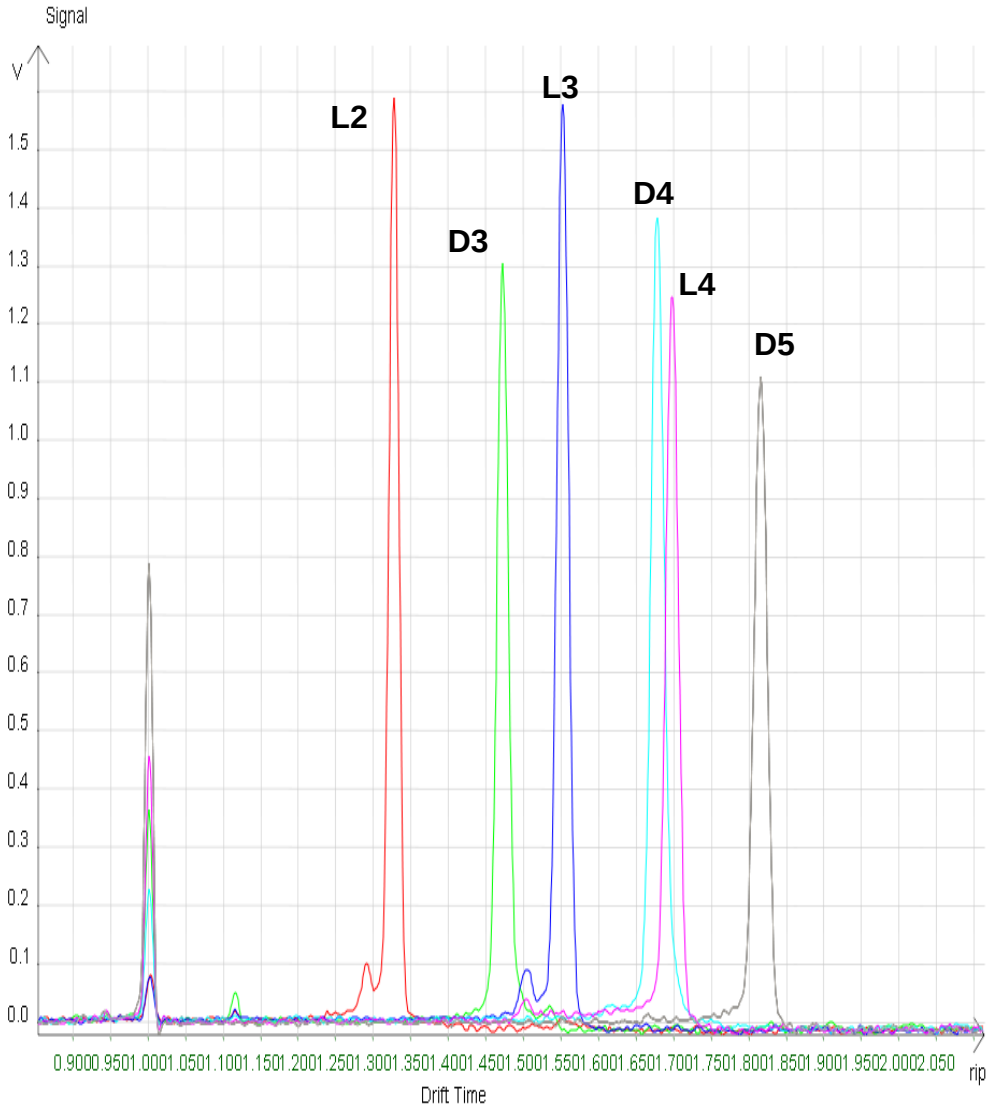


Crucial question for on-site Responsibles: When is the filter saturated?

I. On-site Solution: GC-IMS-SILOX

Sensitive, rugged and easy to use on-site and on-line tool !

I. Chromatogram of L2-L4, D3-D5

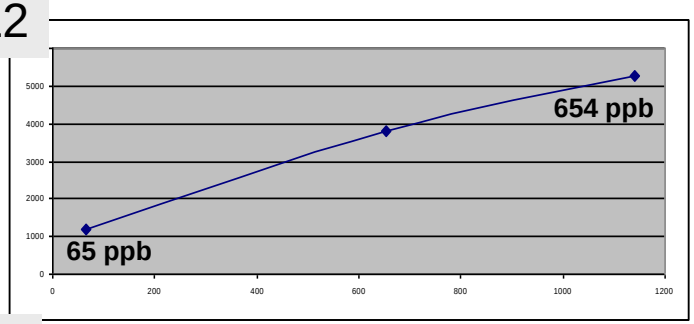


Reliable detection of individual Siloxanes!

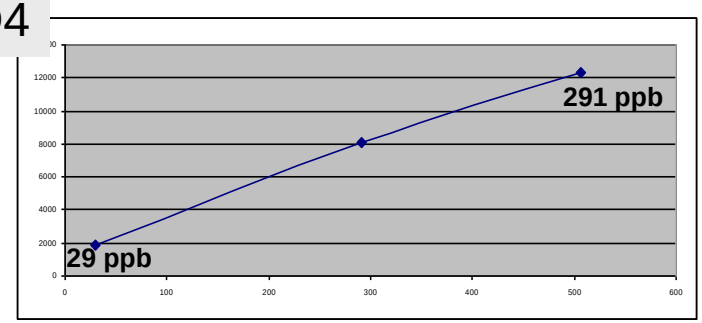
I. GC-IMS-SILOX: Calibration using Permeation Tubes

Calibration with test gases of L2, D4 and D5.

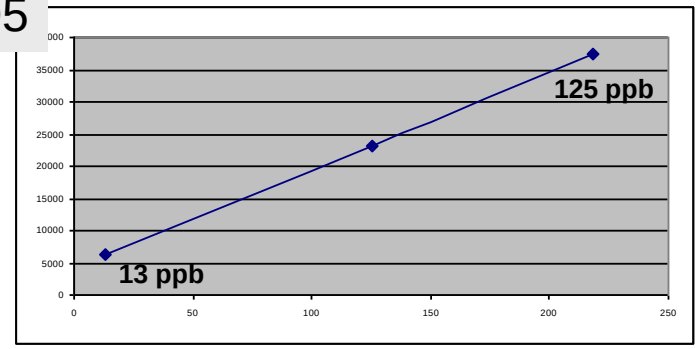
L2



D4



D5



Detection limit requirements in NL for siloxanes are:

L2: 31 ppb, D4: 16 ppb, D5: 13 ppb

Total silicon: 0.8 mg/m^3

I. Customized ‘Siloxane Solution‘: Set-up on-line Monitoring

Certified test gas
or permeation
stand

Ambient pressure

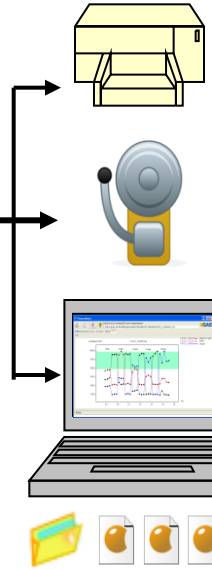
GC-IMS-SILOX

Power

Control Room

Reporting

4-20 mA, Lan, USB



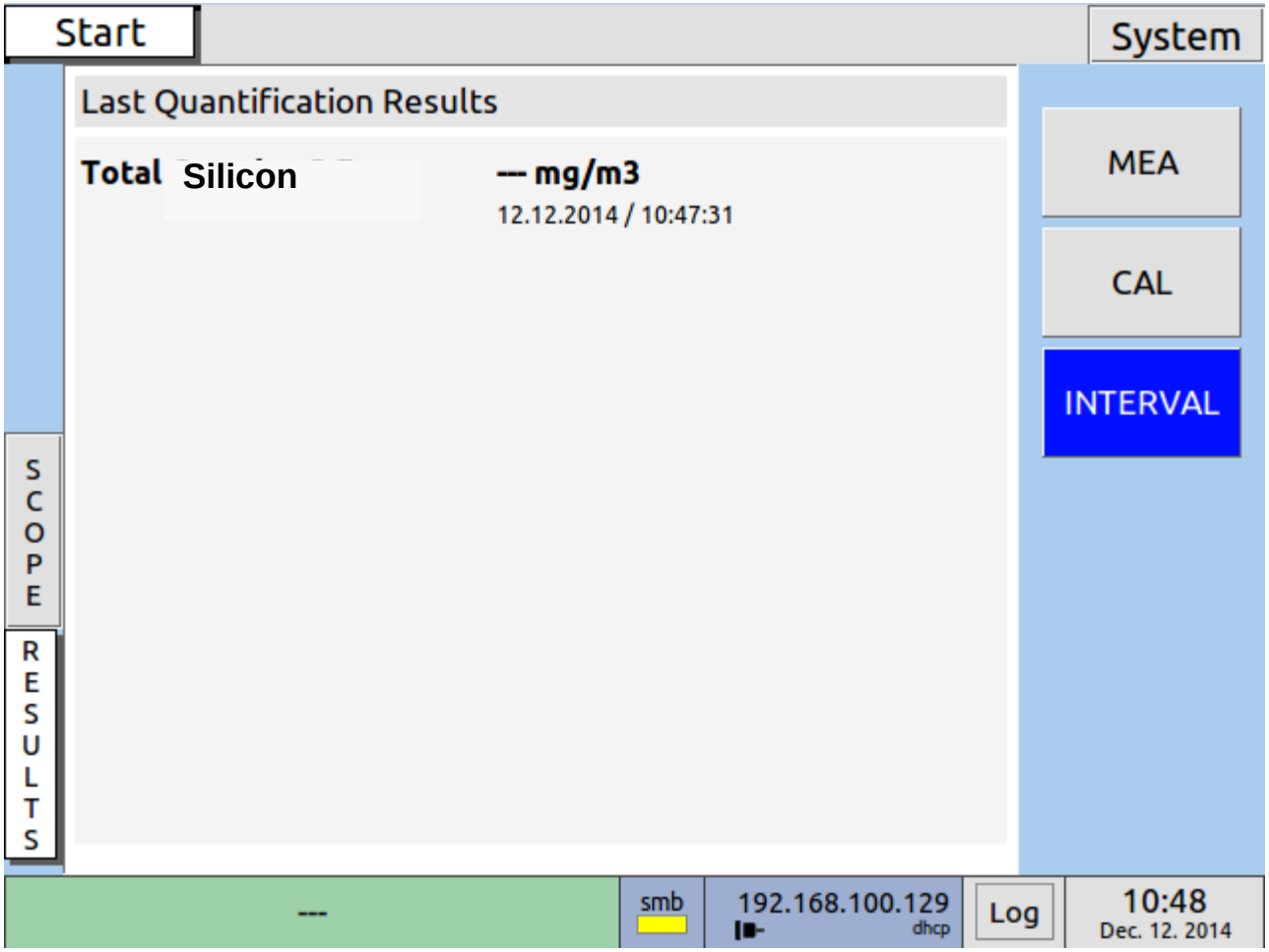
3mm Swagelock

Stainless Steel
Pressure Reducer

Nitrogen, quality 5.0
(Drift-/carrier gas, typically 0.5-3.0 bar)

Result is displayed

I. GC-IMS-SILOX: User Interface on Touch-Screen



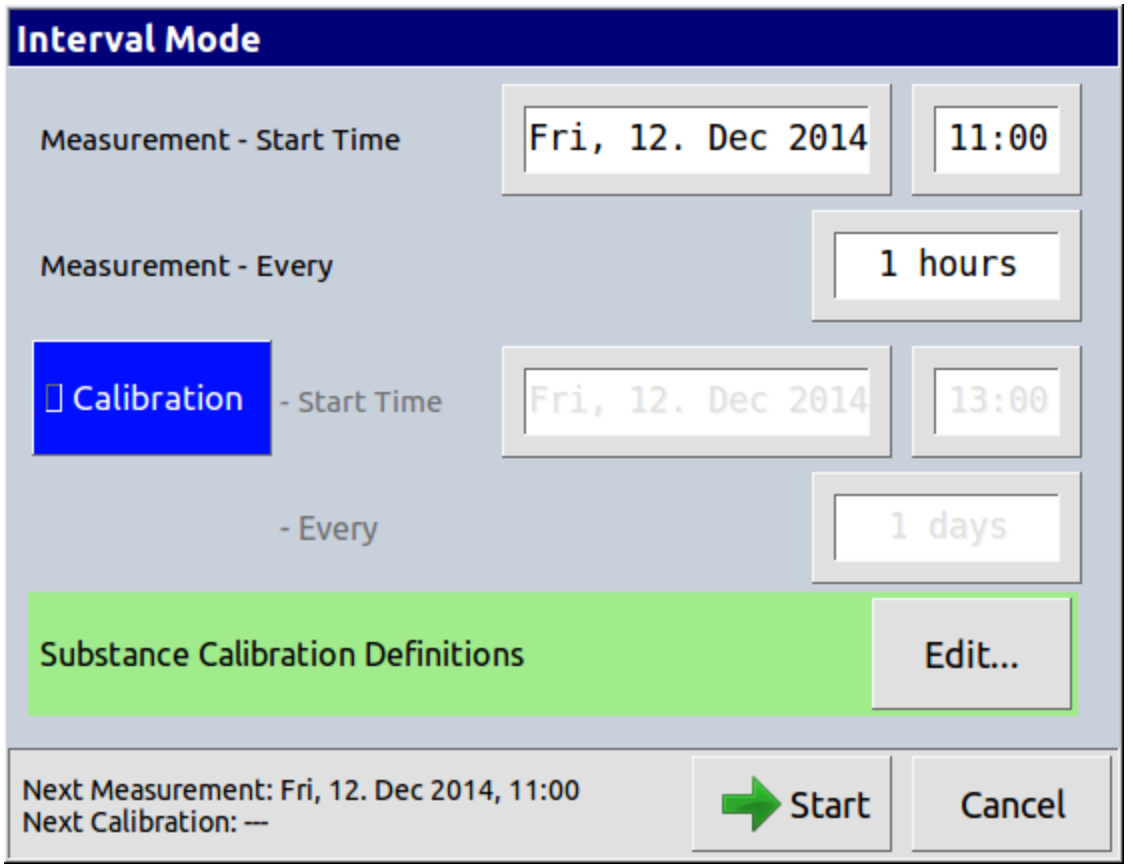
Start measurement manually

Start calibration manually

Start automatic measurement cycle

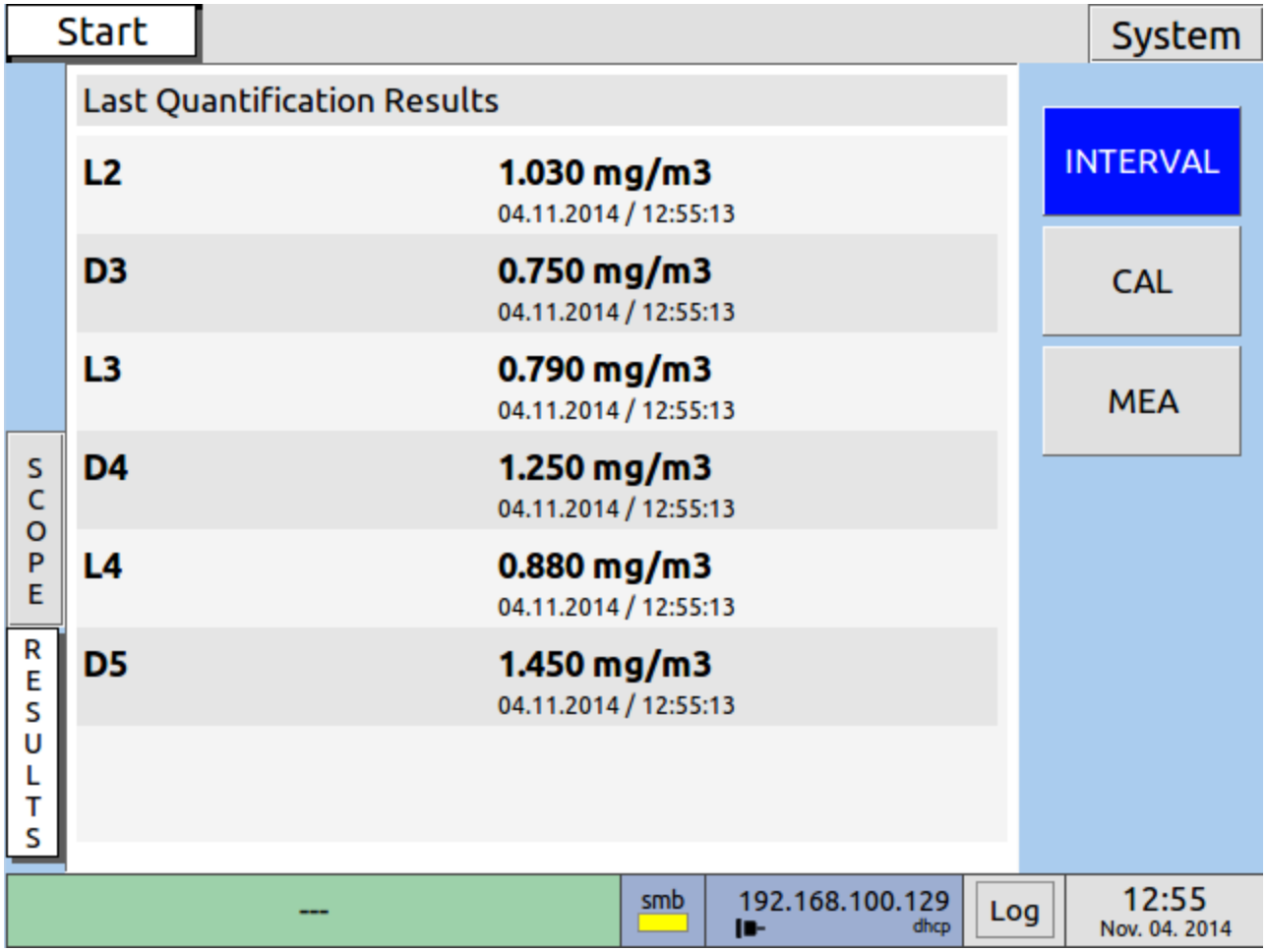
100% remote and continuous Operation using 'INTERVAL' Mode!

I. GC-IMS-SILOX: Interval and Calibration Settings



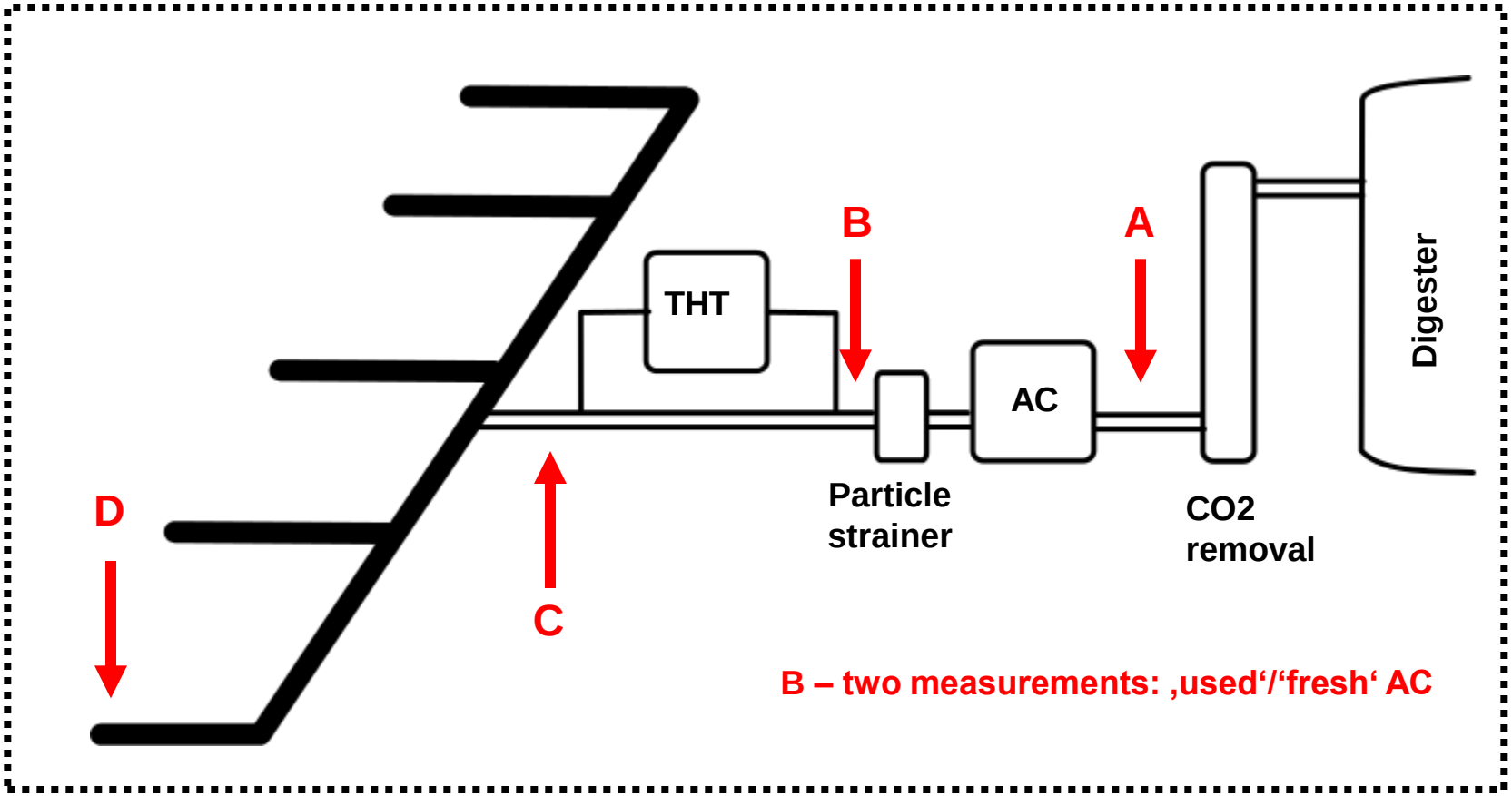
Measurement interval defined by user

I. Exemplary Results of Siloxane: Range 0.1-5 mg/m³



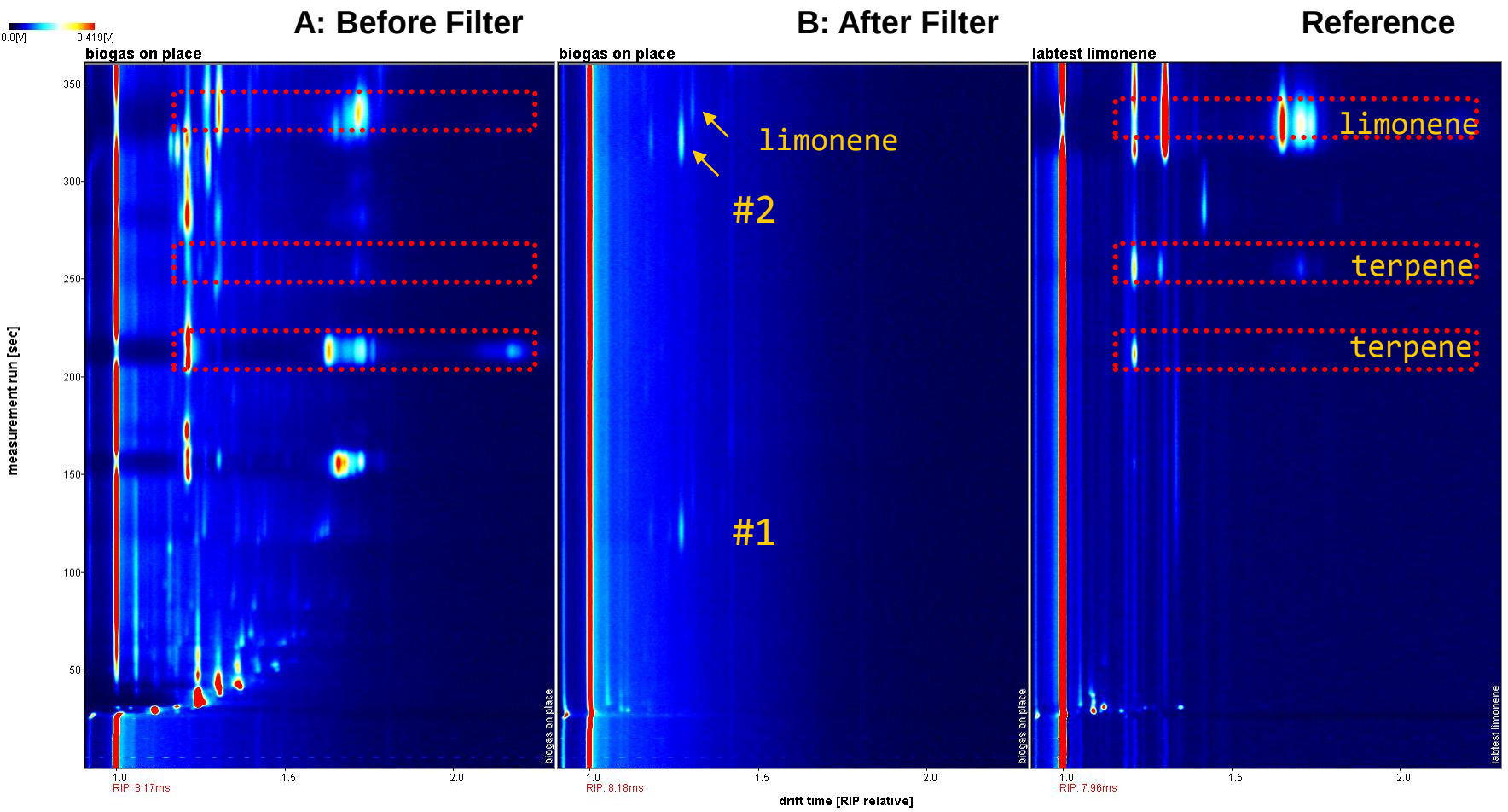
Displayed Concentrations of Siloxanes plus Total Silicon!

II: Biogas from Food Waste with Off-Flavour



Sampling points of interest at customer's biogas plant

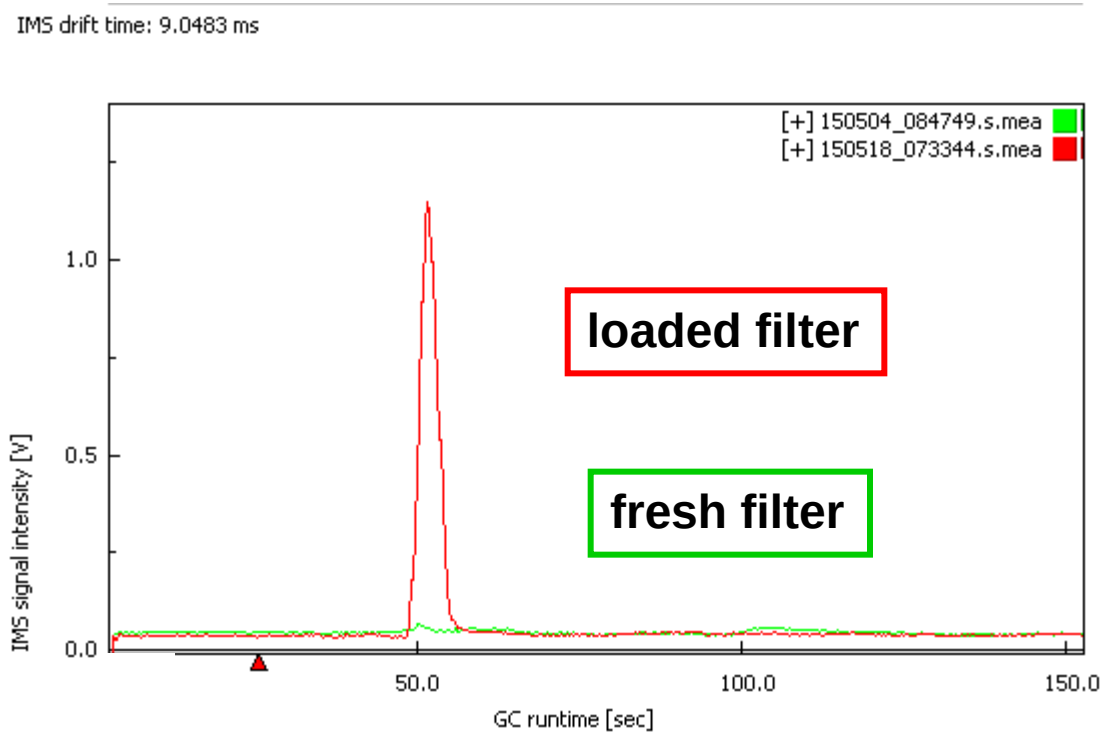
II: Chromatograms: Results from Case Study



- Biogas before filter exhibits VOCs, among them min. eight terpenes
- Biogas after filter contains few compounds at low concentrations. Two terpenes (limonene and #2_unidentified) and ghost peak (former test) can be observed
- Min. three terpenes occurring in biogas can be found in technical limonene reference

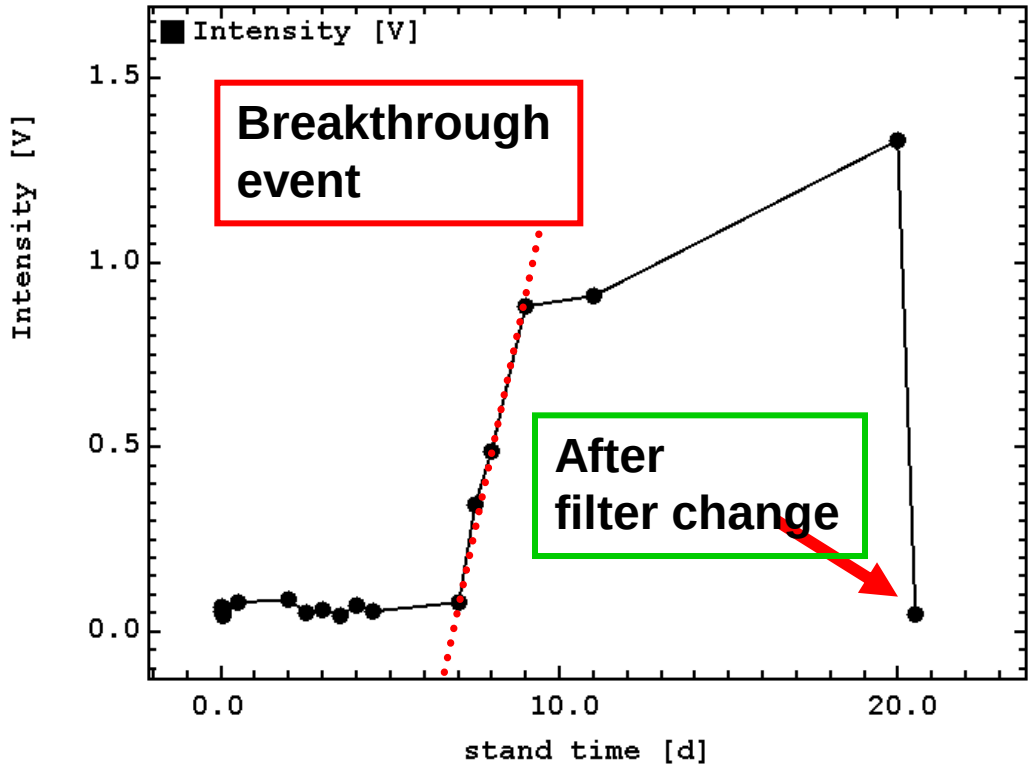
II. Filter Efficiency in Biogas via VOC-Marker

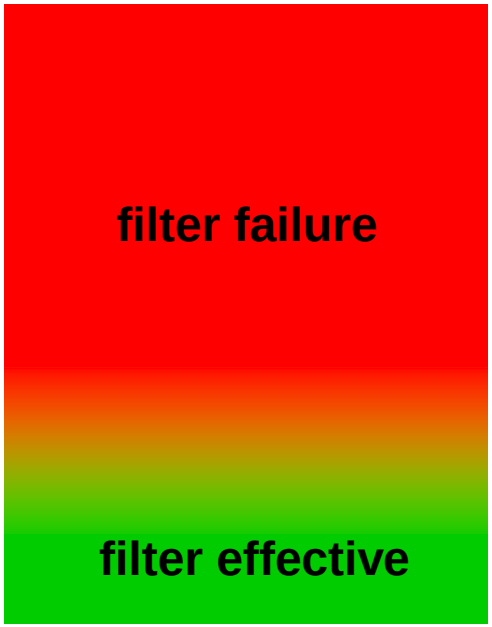
Total Ion Current Chromatogram of biogas marker compound



- Marker compound detectable only in traces for fresh filter media
- IMS signal intensity corresponds to compounds concentration
- Compounds selectable, multiple compounds possible (e.g. siloxanes, sulfur compounds, terpenes)

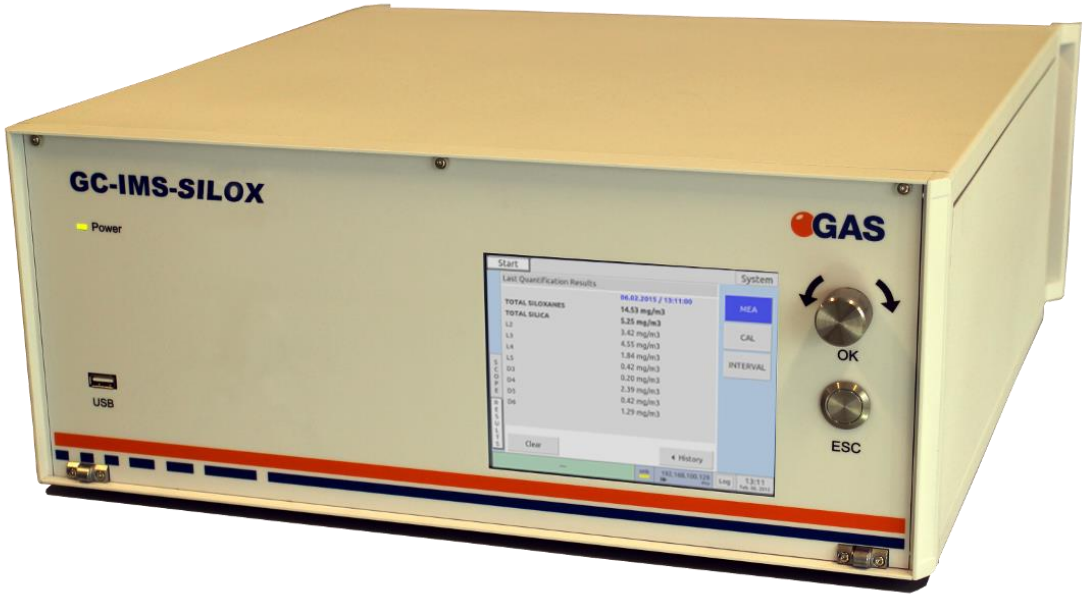
II. Filter Breakthrough via VOC-Marker





- Biogas (after filter) is monitored for selectable compounds
- Increase of concentration maps filter breakthrough

Technical Summary – GC-IMS



- **Easy to operate – no analytical specialist needed**
- **Precise (<10% at span)**
- **Fast: Typically <15 minutes run times**
- **Online and/or portable on-site Operation**
- **Fully automatic measurement at user defined intervals**
- **Digital Documentation**

Siloxanes/VOCs in Biogas, Filter Efficiency using GC-IMS

1. Most relevant siloxanes in biogas L2-L5, D3-D6 can be measured and quantified on-site and on-line using GC-IMS-SILOX in the range of 0.1-5mg/m^3.

2. Several other volatile organic compounds are detectable and can be identified (terpenes, sulphorous compounds, …).

3. Filter breakthrough can be detected and full filter capacity can be used.

4. Reasonable investment and operational cost .

Thank you for your attention!

For further questions

please contact

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