V&F Analyse- und Messtechnik GmbH

Airborne Labs International

RECENT DEVELOPMENTS IN ION MOLECULE REACTION – MASS SPECTROMETRY FOR CO_2 QUALITY MONITORING

Front Door to Back Door

BevTech'16, Ft. Myers

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Background & Definitions

- **IMR – MS Technology using a *Dual Capillary* Inlet System**

- **Latest Applications**

  - Final Product ISBT Purity Gas Monitoring
  - Catox Optimization
  - Fermentation Plant Feed- In-Process – Final Product
  - Natural Well Feed Gas Profiles & GC Correlation
  - TSC Reductive Converter *Extended* Feed Gas Applications

Background Applications

Beverages / Foods / Packaging

- CO_2
- Beverages
- Food
- Flavors
- Flavors: good/bad breath + nose-space
- Mold in beverages, jelly
- PET Bottle Contamination Monitoring

IMR-MS Technology

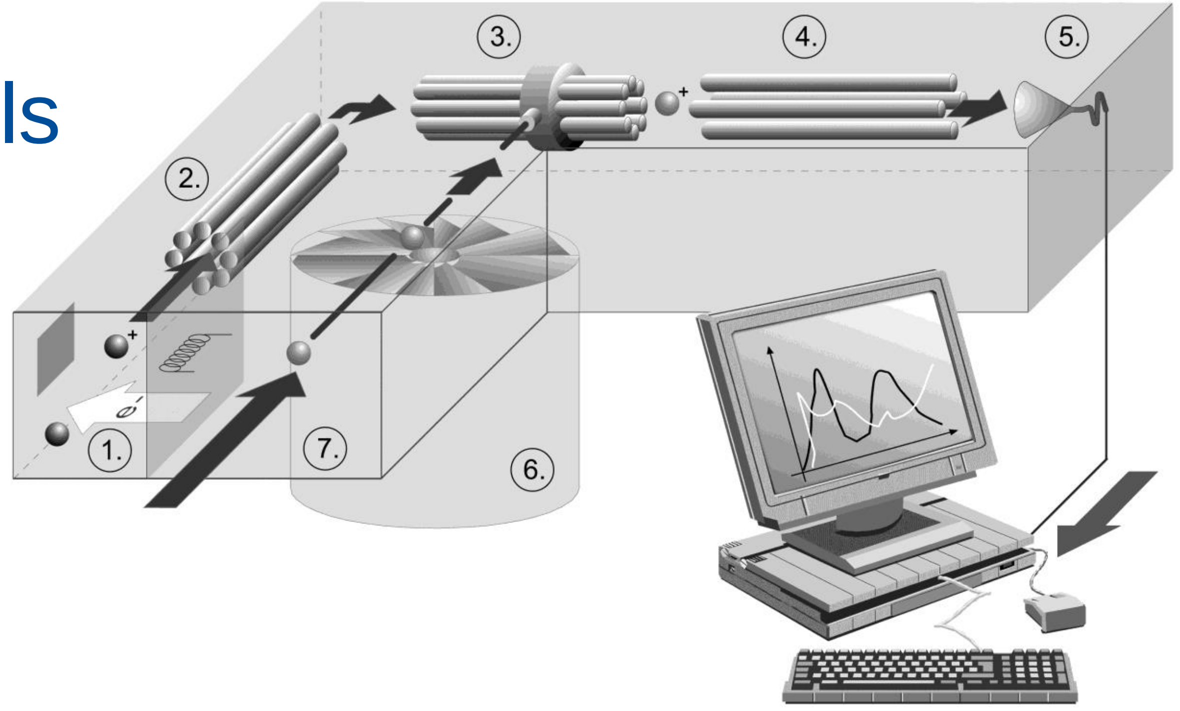
Use of discrete energy levels

LE: 10.44 eV

ME: 12.13 eV

HE: 13.99 eV

followed by



1. Primary Ion Source
2. Octopole Seperation Device
3. Charge Exchange Cell
4. Quadrupole - Mass Filter
5. Particle Detector
6. Vacuum System
7. Gas Inlet System

Ion Molecule Reaction with sample gas

molecules & Mass Spectrometry = IMR - MS

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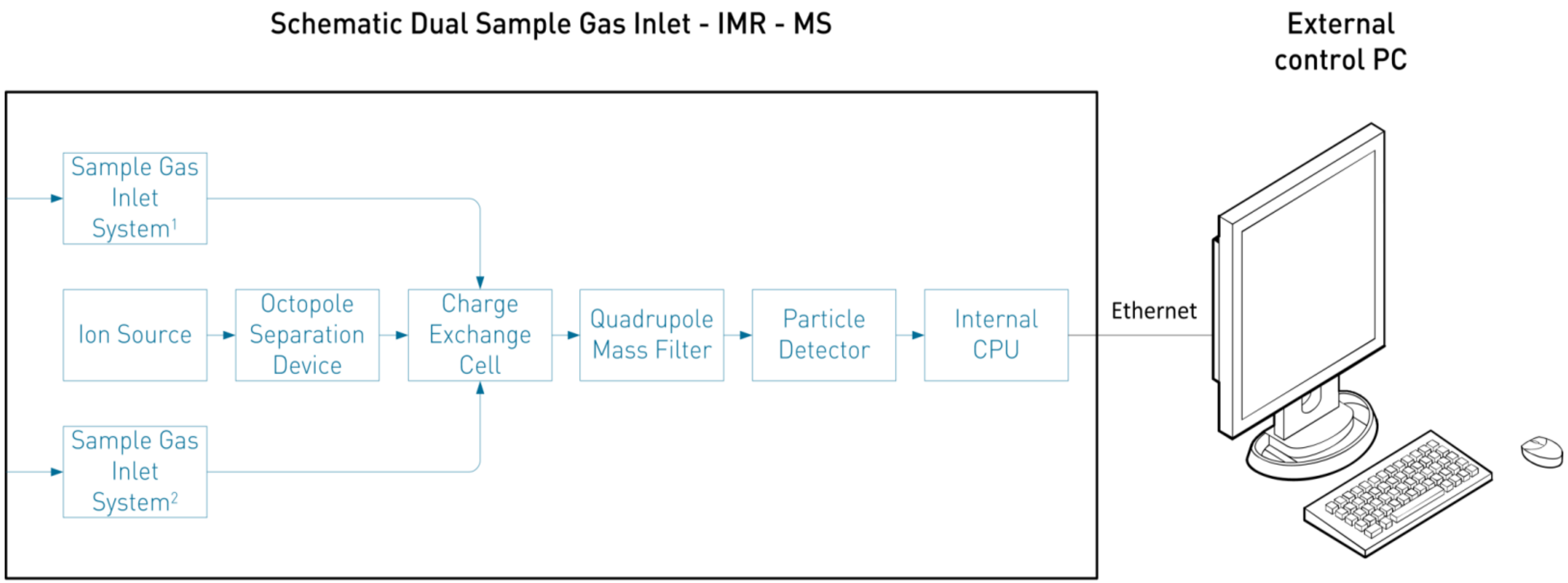
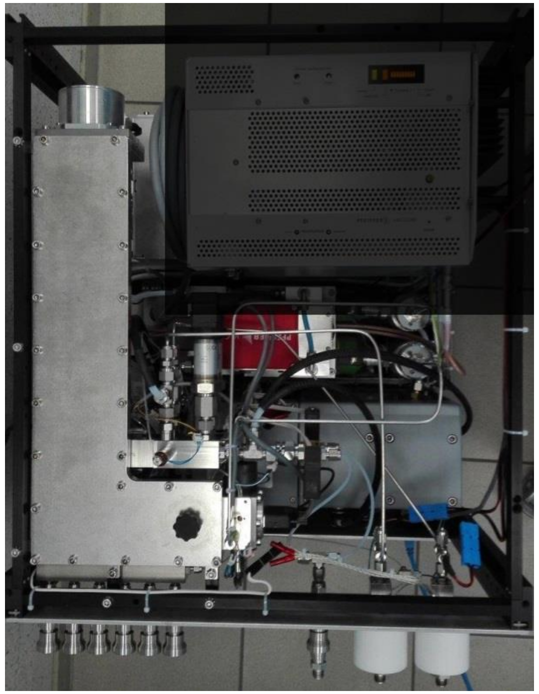
IMR-MS Technology – Dual Capillary Inlet



[1] Sample gas inlet for final CO_2 product quality
[2] Optional sample gas inlet for CO_2 feed- and process gas analysis



IMR-MS Technology

- Single two-body reactive collision conditions in charge exchange chamber

    - Neutral, purely kinetic collisions → no change of ion mass number

    - Very low operating pressure → long mean free path between particles → Avoidance of bulk gas ionization

- Simultaneous detection of organic and inorganic compounds resp. compound classes (online or offline)

- Concentrations: ppt – ppb - ppm - Vol%

- Time of analysis: > 1 msec per compound

IMR-MS Technology - CO_2 Applications

Feed Gas

- Sources: combustion, natural wells, fermentation, geothermal emission, ammonia, coal gasification, ethylene oxide, phosphate rocks, etc.

- CO_2 Impurities: ppb – Vol %
- Online monitoring of impurity profiles & time variations

In-Process

- Online monitoring of CO_2 purification steps of catox, hydrocat, hydrolyzer, carbon beds, scrubbers, filters, etc.

Final Product Quality Control

- Product to Storage, Storage Tanks, Truck filling stations

IMR-MS Technology – Catox Monitoring Applications

- **CO_2 Feed Gas - Petrochemical Plant – Background:**
  - Catox malfunction in contrast to its design specs
  - Time-Related decrease in Catox conversion rate
  - Regeneration of Catox activity at lower temperatures
  - Breakthrough of small organics in the CO_2 feed gas
  - IMR-MS Monitoring of major impurities: O_2, H_2O, methane, ethylene, propylene, acetaldehyde, ethylene oxide, etc.

IMR-MS Technology – Catox Monitoring Applications

A. Original CATOX: 0.3% Pt on Al_2O_3

- T-in Catox from 390 – 360 C: 1.5 – 7.5 ppm ethylene (maximum desired value: 1 ppm)
- Addition of adsorbent → no better performance
- Possible solution: higher operating Catox temperature
- Catalytic oxidation: exothermal → too high temperature → high risk for damage of Catox

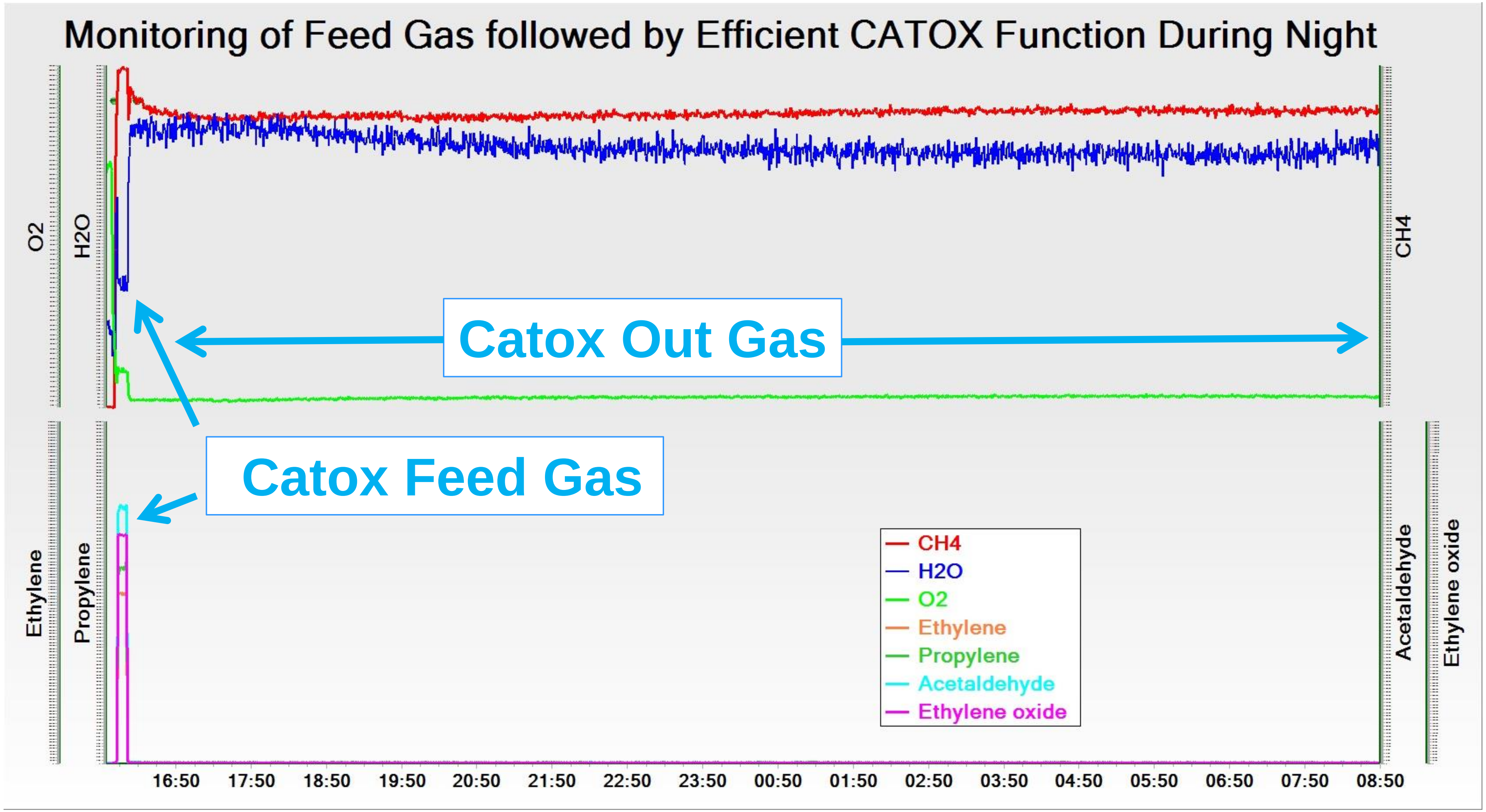
B. New Catox: 0.15% Pt + 0.15% Pd on Al_2O_3

- At T-in 360 – 380 C: worse performance than original Catox
- At T-in > 430 C: better performance than original Catox

Solution:

Installation of *1st layer* of original Pt catalyst + *2nd layer* of Pt + Pd catalyst with appropriate gas hourly space velocity

IMR-MS Technology – Catox Monitoring Applications



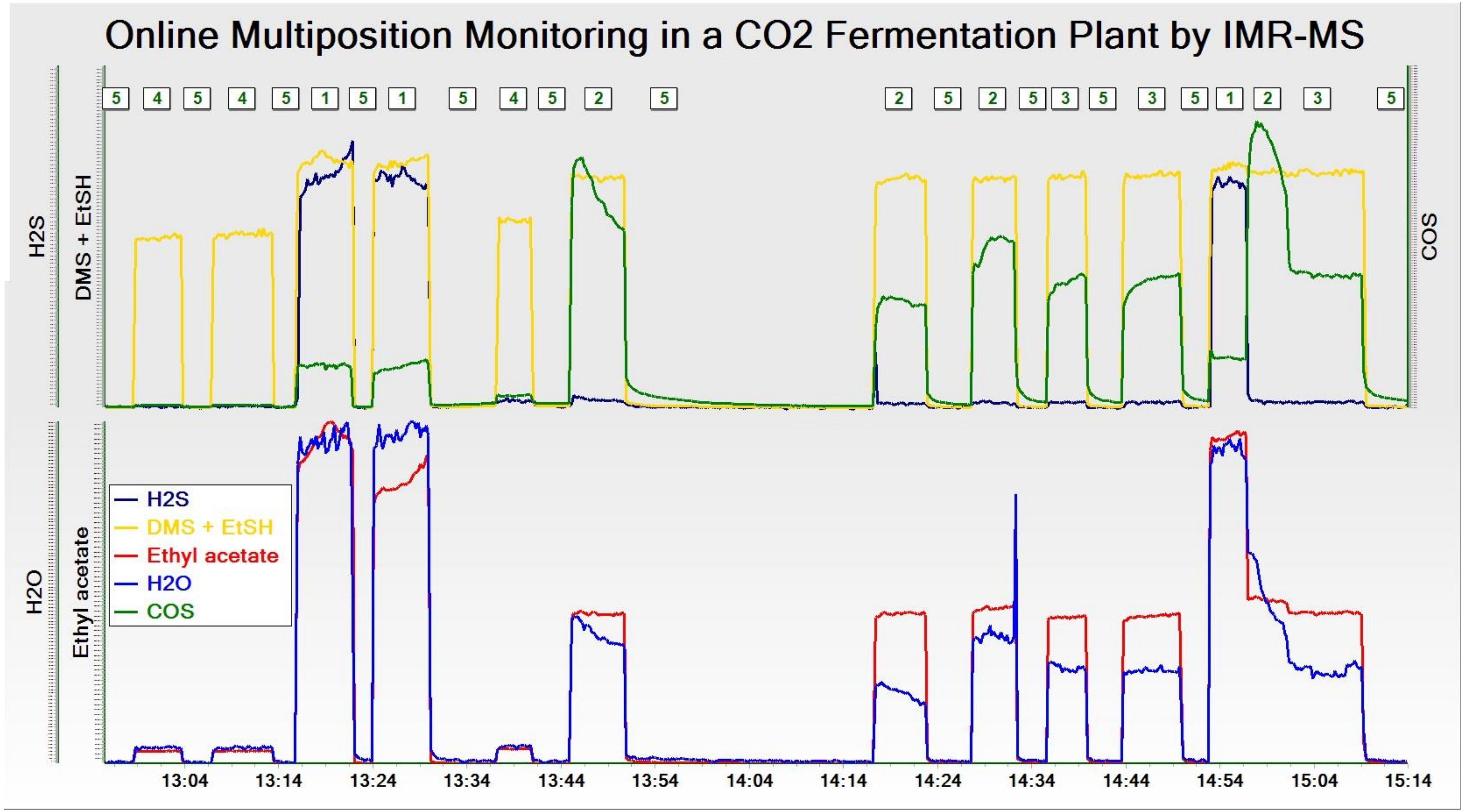
- **In-Process Monitoring @ Key locations**

Requirements

- *Fast respond* to process & *concentration changes* from Feed Gas - In-Process - Final Product
- Rapid Sample location switching.
- Adequate temperatures of wet gas streams
- Regulated / equal pressures & flow rate for each sample location

IMR-MS Technology – Fermentation Plant In-Process Monitoring

1…Feed Gas
2…Post Hydrocat
3…Post Hydrolyzer
4…Post Scrubber
5…Product Gas to Storage



IMR-MS Technology – Natural Well Monitoring vs GC Data

Compounds	GC Result	IMR-MS Result	Difference GC vs. IMR-MS [%]
Methane [ppm]	3,100	3,140	1.3
Ethane [ppm]	1,200	1,300	8.3
Propylene [ppm]	0.20	0.23	15.0
Benzene [ppb]	18	15	-16.7
Toluene [ppb]	4,310	4,310	0.0
Hydrogen Sulfide [ppm]	0.54	0.54	0.0
Carbonyl Sulfide [ppm]	1.7	1.4	-17.6

Total Sulfur Converter

- It is important to monitor Total Sulfur Content (TSC) in both feed and final product CO_2.
- TSC is present in most CO_2 feed gas sources.
- High TSC has caused many beverage recalls.
- Unexpected increases of TSC in feed gas can cause liquid CO_2 quality upsets.
- Most on-line analyzers do not have the wide measurement range and H_2O tolerance for single instrument TSC analysis for both feed gas and final product.

ISBT Bulk Carbon Dioxide Quality Guidelines and Analytical Methods Reference 2010
(Method 13.0, recommends a TSC Limit = 0.1 ppm v/v (IMR-MS [SIS] is an acceptable method for this application)

Background & Definitions

Carbonyl Sulfide (COS) is the most important Volatile Sulfur Compound to monitor.

- COS is odorless.
- COS can be created during the CO_2 manufacturing process and is very common in feed gas sources.
- COS slowly hydrolyses into highly odiferous H_2S (rotten eggs smell) in acidic conditions such as carbonated beverages.
- High COS is historically responsible for most sulfur related odor complaints and packaged beverage recalls.

Background & Definitions

TSC Objective: ISBT Method 13.0 – Convert all forms of Volatile Sulfur Compounds (VSC) in CO_2, into a single form for measurement as Total Sulfur Content. This can be achieved by either a reductive or oxidative conversion.

Reductive TSC Reactor

(Ni Catalyzed + Δ T=1000 ˚C)

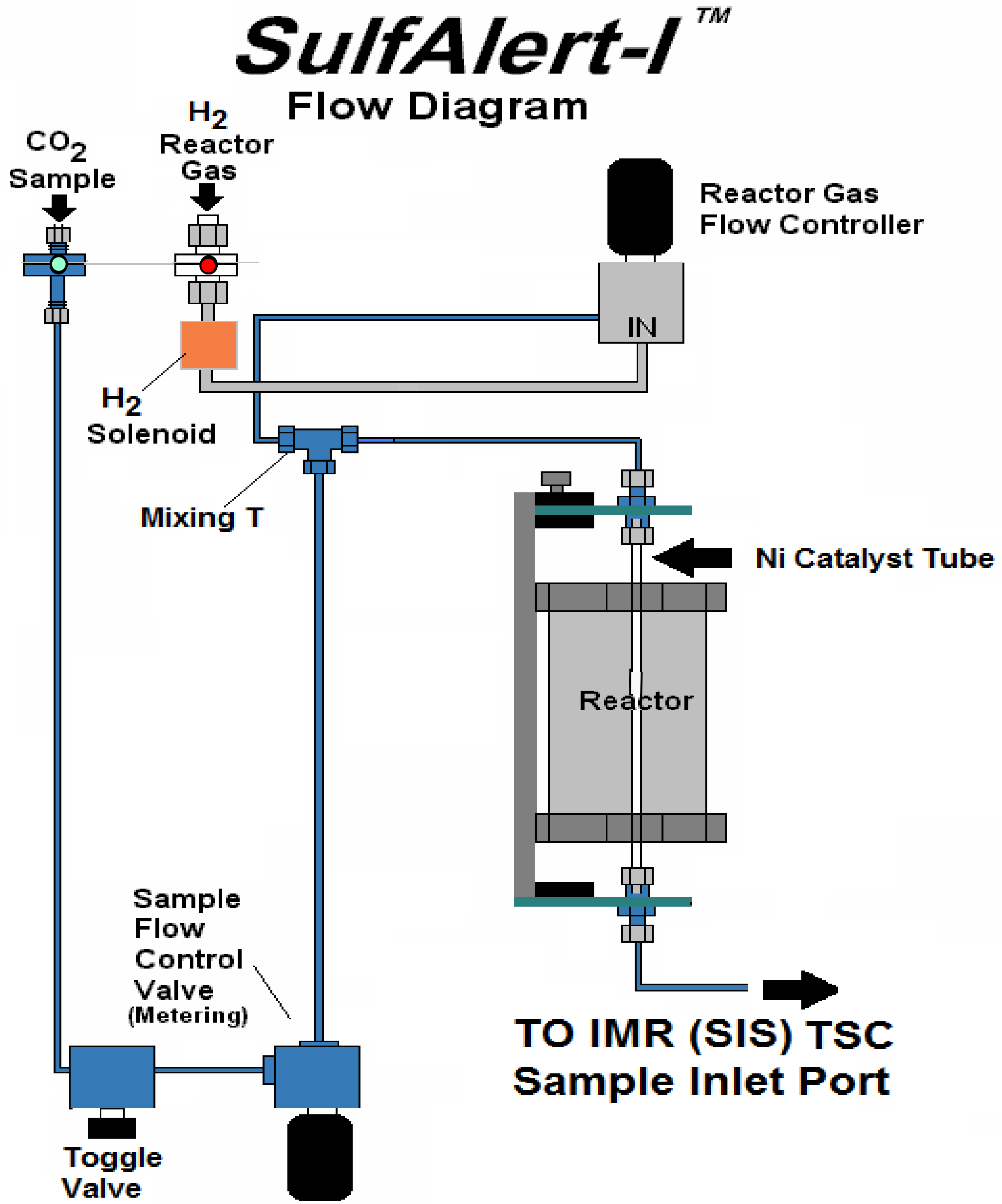
CO_2 + VSC + xH_2 → **H_2S*** + CH_4 + C_xH_y

Undesired Side Reaction at > 1010 ˚C

$CO_2 + 4H_2 \rightarrow 2H_2O + CH_4$

*Atomic Mass (AM) = 34 amu

TSC-SIS Hardware / Plumbing



- Sample
- Hydrogen
- Total Sulfur

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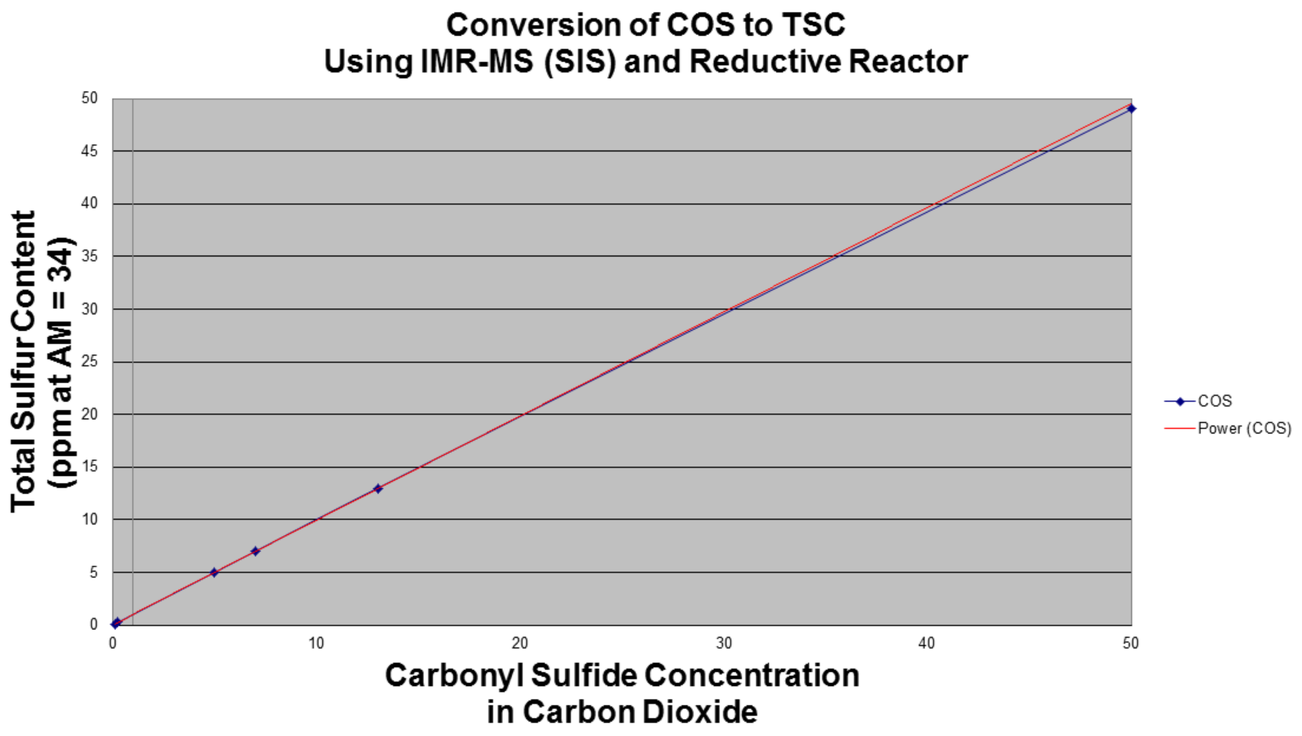
TSC Performance Data

TSC Measurement Range

- ISBT Method 13.0 recommended working range: 0.00 – 1 ppm v/v
  - Limits: 0.1 ppm v/v TSC and 1.0 ppm v/v SO_2.
- Current range is 0.00 ppm v/v to ≈50 ppm v/v*.
- Most commercial feed gas sources have TSC < 50 ppm.



* Higher ranges not studied to date.

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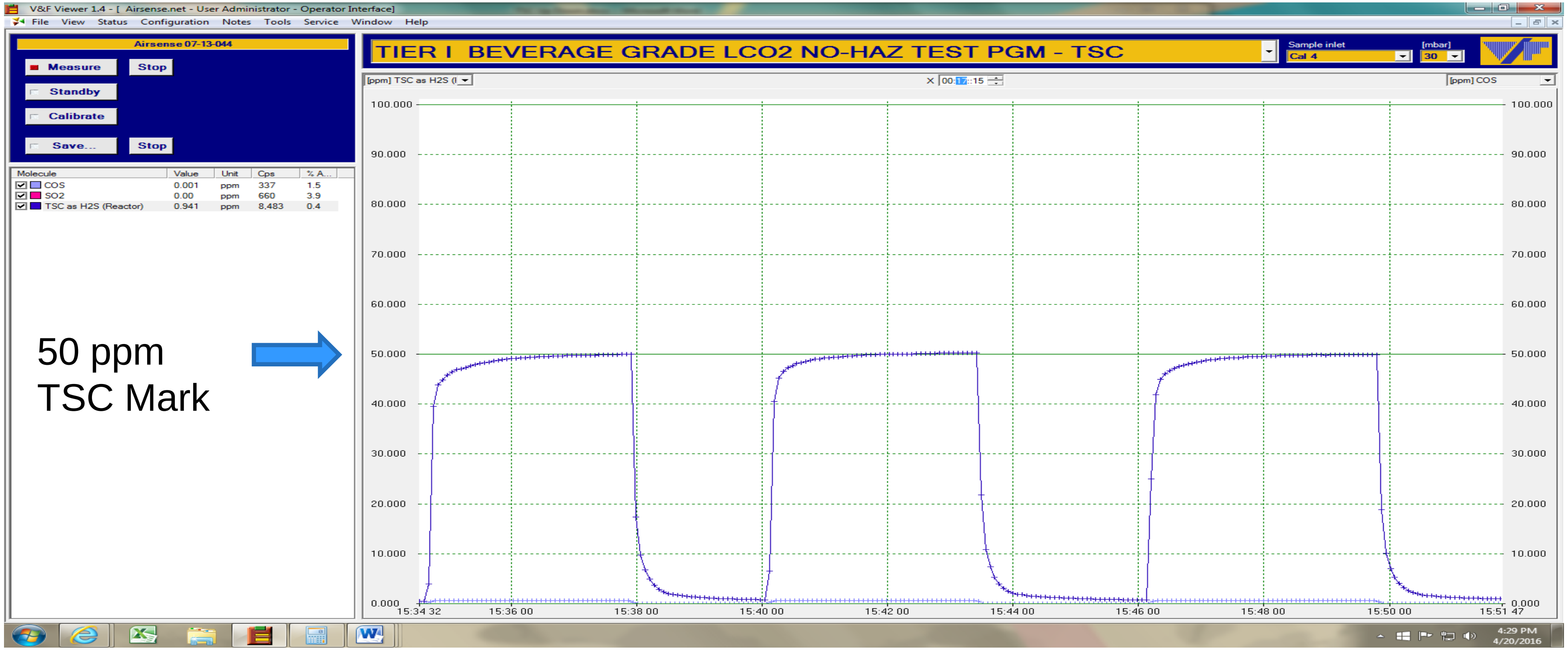
TSC Performance Data

TSC Measurement @ 50 ppm Level



Alternating analysis from 50 ppm COS to Zero CO_2

% COS conversion to TSC ≈ 98+%

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TSC Performance Data

Key Sulfur Species currently being Studied at Feed Gas Impurity Levels

- Carbonyl Sulfide (COS)
- Hydrogen Sulfide (H_2S)
- Dimethyl Sulfide (DMS)
- Ethyl Mercaptan (EtSH)
- Carbon Disulfide (CS_2)
- Sulfur Dioxide (SO_2)

Advantage:

- Both TSC & speciated VSC are *simultaneously* monitored by the IMR-MS (SIS) with TSC reactor outlet.

Summary

IMR-MS (SIS) analyzers equipped with dual capillary inlets and reductive TSC converters exhibit a wide measurement range which is required for:

- Continuous CO_2 feed gas monitoring.
- Continuous in-process CO_2 composition.
- Continuous monitoring of beverage grade CO_2 for TSC and other key parameters.

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Questions?

Thank you for your Interest!

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