Airborne Labs International

CO_2 Feed Gas Dynamics:101

State-of-the-Art Profiling & Monitoring in an Evolving World

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Challenges & Opportunities: CO_2 Feed Gas Source Sampling & Monitoring Programs

Why Feed Gas Monitoring?

1) Feed Gas sources constantly change with new types being added to meet world growth. Not knowing what Feed Gas impurities are present or their levels can lead to inadequate impurity removal & NON-ISBT grade LCO_2 product!

2) Unexpected changes in Feed Gas sources & profiles are a significant cause of CO_2 quality upsets

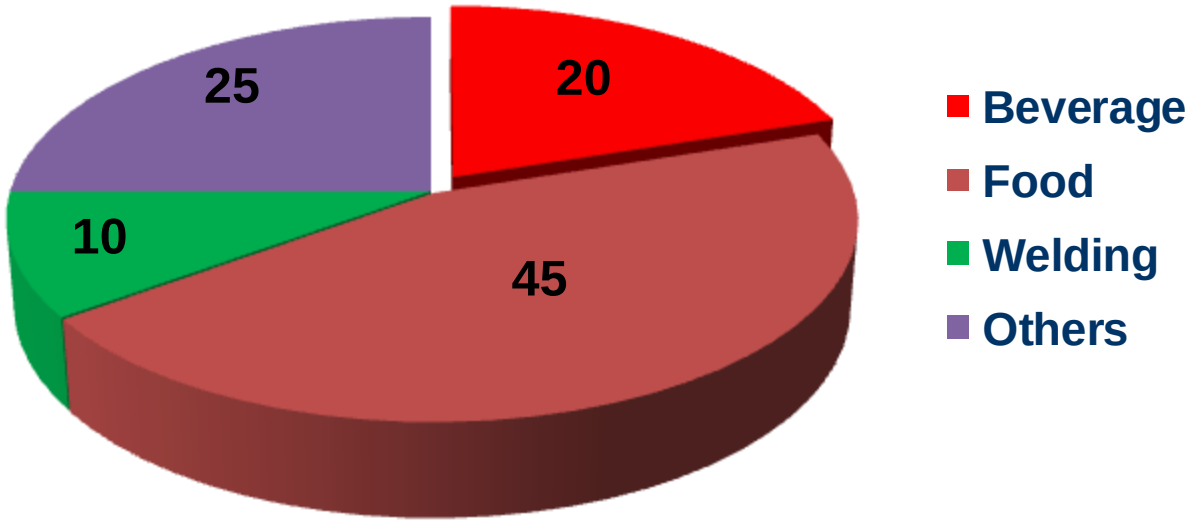
> *Example: Changes in a natural well source can result in big swings in TSC, AHC, THC, etc. This can lead to premature filter & sorbent bed "breakthrough".*

3) Feed Gas impurities above ISBT recommended bev-grade limits can result in undesired Sensory Effects, and/or Health & Safety issues in a carbonated beverage.

4) Knowledge of a Feed Gas impurity profile allows for optimal plant design & defines a Final Product monitoring program. Contracts with a Feed Gas supplier should include the % purity + impurity range limits for proper plant processing.

Commercial CO_2 Markets

World CO_2 Supply - Usage %



Food & Beverage Markets contribute a significant portion to Worldwide CO_2 usage

Step 1: Feed Gas Source Bev-Risk Assessment

HIGH RISK

Many possible **high level** impurities
Significant Feed Gas source variability
Big impact of non-removed Sensory Active and/or Health Concern impurities
Limited experience of CO_2 Manufacturer

MODERATE RISK

Moderate number of impurities at low/med levels
Relatively **stable** Feed Gas source
High – moderate impact of non-removed impurities
Average experience of CO_2 Manufacturer

LOW RISK

Low – moderate number of impurities at low levels
Stable Feed Gas source
Moderate impact of non-removed impurity
High experience of CO_2 Manufacturer

Commercial Feed Gas Sources

Natural Gas Processing: Hydrogen / SNG / Ammonia-Fertilizer Mfg

$CH_4 + 2H_2O \rightarrow CO_2 + H_2$ (A relatively "clean" FG source – but Natgas cost dependent)

Methane

(Impurities: H_2, NO_x, H_2O, CO & THC)

Ethylene Oxide (ETO) Mfg

$CH_2{=}CH_2 + ½\ O_2 \rightarrow C_2H_4{=}O$ (ethylene oxide)

Ethylene

Significant Side Reactions (impurities: Vinyl Chloride, ETO, $COCl_2$ & others?)

$CH_2{=}CH_2 + 3O_2 \rightarrow CO_2 + 2H_2O$

$C_2H_4{=}O + 2.5\ O_2 \rightarrow CO_2 + 2H_2O$

Natural Wells

Mostly Piped from "Dome" sources - CO_2 purity from 100% to much less

(ex. potential impurities - VSCs, AHCs, THCs, Radon, pipeline AC additives, etc)

Background Refs: ISBT / EIGA Literature Tables

Commercial Feed Gas Sources cont.

Combustion / Co-Generation (Power Plants – "Coal" Energy = Main Product)

$C_xH_y + n\ O_2 \rightarrow xCO_2 + 1/2Y\ H_2O$ (10-15% CO_2 yield) (HCN, acid gases, metals, VSC etc)
Fuel (gas, liquid, solid) + Air (MEA used to concentrate CO_2)

Combustion - Self-Generators (Small Burners 0.5 – 10 TPD – high use in remote world locations)

$C_xH_y + n\ O_2 \rightarrow xCO_2 + 1/2Y\ H_2O$ (10-15% CO_2 yield) (fuel quality, higher process maintenance)
Fuel (gas, liquid, solid) + Air (MEA used to concentrate CO_2)

(***biofuels also being used***) (Ex. potential impurities: VSC, AA, NOx, HCN, AHC, CO, N_2, O_2 etc) CO_2 is Main Product!

Phosphate / Gypsum / Potash Plants ("Acid Neut" = Batch Reactions)

$3\ NaCO_3 + 2\ H_3PO_4 \rightarrow 2Na_3PO_4 + 3CO_2 + 3H_2O$

$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$

$CaCO_3 + 2\ HCl \rightarrow CaCl_2 + CO_2 + H_2O$

$KCl + HNO_3 \rightarrow KNO_3 + HCl$

$2HCl + CaCO_3 \rightarrow CaCl_2 + CO_2 + H_2O$

(ex. potential impurities : VSCs, acid gas, PH_3, AsH_3, **halogenated HC's, $COCl_2$**, NOx etc)

Other Chem Process (ex. Iron Ore Reduction, many others where CO_2 = by-product)

Background Refs: ISBT / EIGA Literature Tables

Commercial Feed Gas Sources cont.

Ethanol – Fermentation ("BioEthanol" = growing sources + **Beer manufacturing** excess CO_2 use)

$C_6H_{12}O_6$ + **YEAST** → $2C_2H_6OH$ + **$2CO_2$** (impurities: VSCs, VOX, AHC, NOx, others? bio-agents?)
Sugar or starch or cellulosic biomass - ***bioethanol + CO_2***

Each BioEthanol source can have a **unique set** of impurities.

- Some impurities are **"unexpected"**
- Many impurities are sensory **"active"**
- Impurity profiles can **morph & change over** a batch's "ferm-cycle"
- **Several** Feed Gas samples needed (ex. reaction take-off, mid-stage, final phase = min of 3 samples)

Many Biomass types are currently used or being evaluated – however **not much if any Feed Gas data is known about many + YEAST "Compatibility" factors.** Examples include: corn, grains, wheat, rye, beets, sugar beets, potatoes, sorghum, molasses, as well as potential nonedible woods, grasses, yucca fruits, & tobacco plants. This list may include "**genetically modified** " biomass species.

Today, the most widely used biomass types are Indian corn (maize), grains, & rye

Landfill / Sewage BioGas – natural anaerobic decay organic matter – produces CH_4 + CO_2 **BUT can host many potential impurities with high variability = currently banned for bev-CO_2 use! However - some Biogas sources are reportedly being used for beverages!**

Seasonal Feed Gas Supply vs. Bev Mfg Demand

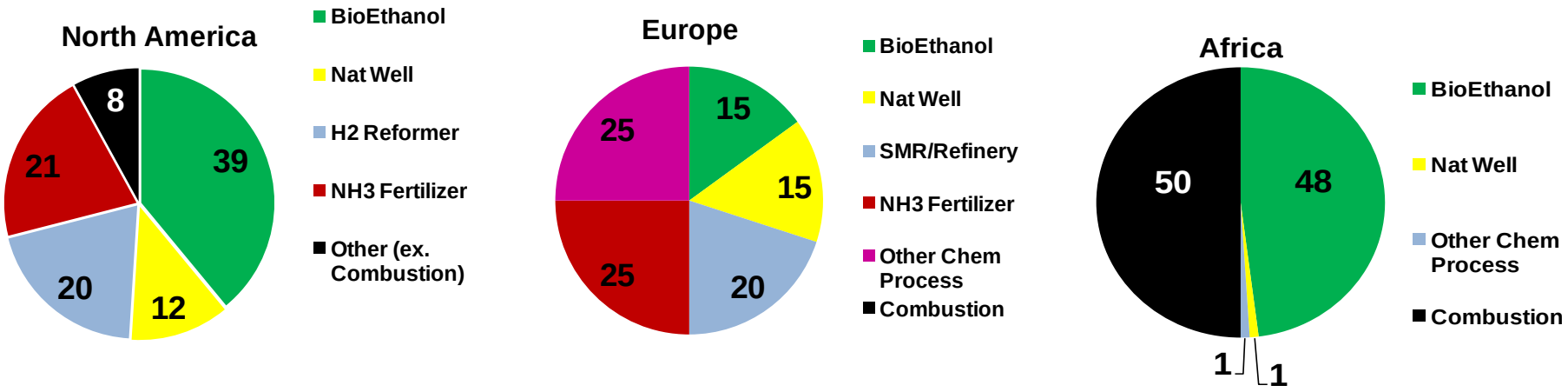
Feed Gas Source Supply vs. Bev Production Timing are often not in-sync; plus there can also be "3rd Party Merchant "dependency" issues.

Examples:

- Major % Feed Gas sources use Natural Gas (Natgas) for Processing or Sub't Natgas (SNG) for NH_3 Fertilizer Mfg / ETO Mfg, where CO_2 is a by-product
    - Seasonal Hi / Lo Mfg Cycles: fertilizer manufacturing is at it's max in fall & winter, however the bev max demand is in spring & summer!
    - Natgas pricing & availability issues: the supply & demand pricing dynamics constantly change in the world
- CO_2 Mfg is often dependent on a 3rd party Feed Gas merchant who can shut down or change direction – with short notice, as CO_2 is not their main revenue market or concern
- BioEthanol = seasonal harvesting + grain source changes + drought + grain prices + food use + regulatory + biofuel future issues? More Beer Mfg sources likely??

Poor Supply - Demand Timing often leads to "swapping" LCO_2 from various plants – so a multiple Feed Gas source (high-med-low risk) of LCO_2 depot supply can be experienced by a bottler!

Feed Gas Sources & Worldwide Variations



…Big variations between each continent!

Feed Gas Sampling Challenges

Physical properties of Feed Gas at desired sampling point:

- **Low pressure (0 – 5 psig) + medium temp (LT 100F)**
  - Ex. **bioethanol** sources
- **Low pressure (LT 0 – 5 psig) + high temp (GT 100F)**
  - Ex. **combustion flue gas** – before MEA step = **NOT** recommended
  - Low % CO_2 sample is **highly reactive** + H_2O saturated)
- **Medium to High pressure (GT 5 – 800+ psig) + medium temp**
  - Ex. pipelines from wells – chem production sources
  - Self gens / combustion sources - **past MEA outlet step** = **recommended**

Feed Gas properties dictate the **sampling equipment / accessories** needed

- Ex. small, battery pump or more powerful AC/DC INERT pumps, hot gas conditioners, etc.

Recommended CO_2 Feed Gas Sampling Points

Representative Sampling Point Selection

Ideal Feed Gas Sampling Location = Key Factor in Test Program!

Objective: Select an early point in the process that represents a maximum impurity "challenge" to the downstream purification system.

Combustion Sources – best after slight compression - just downstream of MEA gas stream outlet (concentrated CO_2 + MEA breakdown released + non-MEA adsorbed impurities monitored)

Alternate Site*: Flue gas stream after positive pressure pump & some cooling = potentially hazardous sampling point + reactive gas changes rapidly!

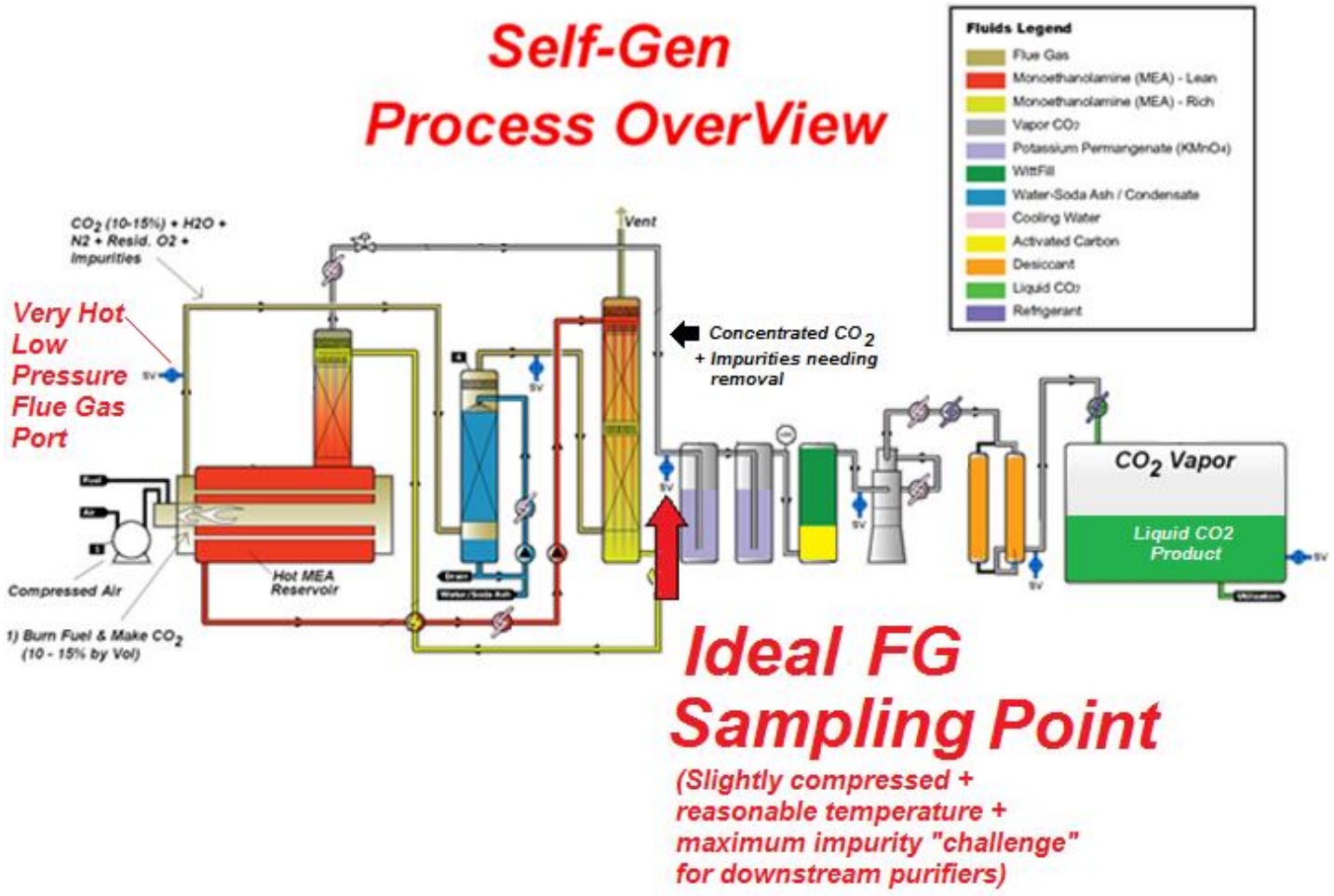
*Only viable for on-site analyzer systems & quick chemical tests due to high reactivity & high H_2O vapor content of flue gas stream!

Flue gas impurities (ex. NO_X / SO_X, unburned / partially oxidized VHCs) are unstable & cannot be accurately analyzed after shipment to a lab – due to their reactive changes during transit including H_2O condensation-solubility effects).

Other Feed Gas Sources: After slight compression – if possible & just before 1st stage (ex. "Water Wash Tower" for removal of H_2O soluble impurities.) For Highly variable sources – (ex. fermentation) several samples are suggested to capture "profile swings"

You need to know ALL Types & Max "Spikes" + Typical Levels of Feed Gas impurities present!

Example: Feed Gas Sampling Combustion Source



Slide courtesy of The Wittemann Co.

Non-Hazmat Feed Gas Sampling & Shipping

Gaseous CO_2 samples UN 2.2 can be legally shipped as non-hazardous goods @ LT 29 psig = non-compressed

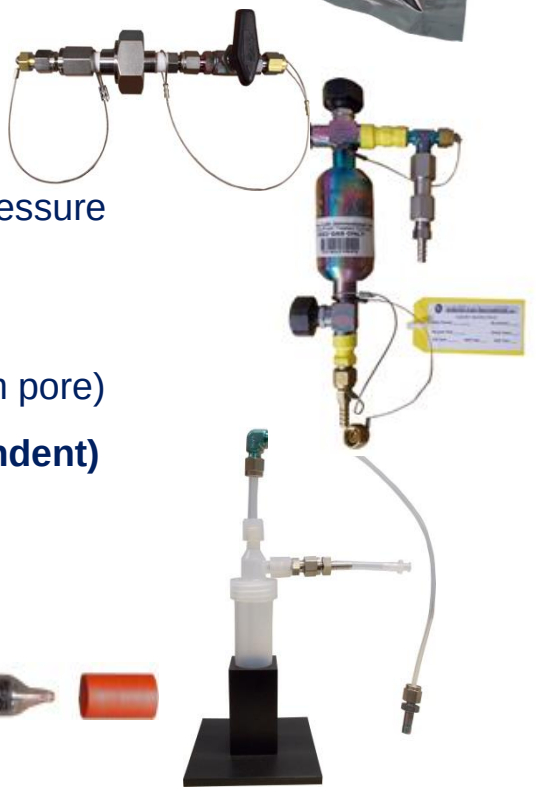
This greatly simplifies the shipping process – especially International shipping

Recommended Sample Containers:

- Polymeric bags (2 or 3 x 2L MLB-type for inertness & ruggedness)
    - NO outer shipping can needed!
- Passivated small cylinders (75 – 300 cc dual valved – with 25 psig pressure inlet check valves!)
- Sorbent Tubes Charcoal or Silica-type (high capacity)
- Filter Assemblies – 25 mm nylon or PTFE filter patches (ex. 1 - 0.5 um pore)

Special Apps Containers (may require hazmat shipping – case dependent)

- Impinger solutions (ex. 40 cc H_2O or dilute acids)
- Bioagent traps (ex. agar gel plates / fine filters / sticky plates / oils)



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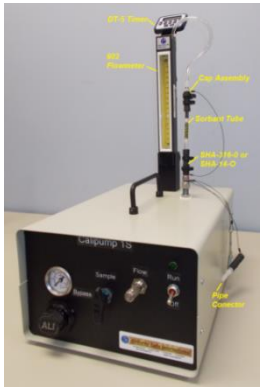
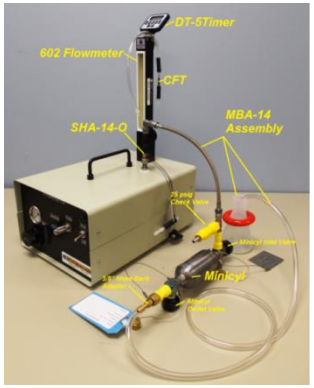
Feed Gas Sampling Equipment



Sorbent Tubes
(ex. Charcoal Tubes)



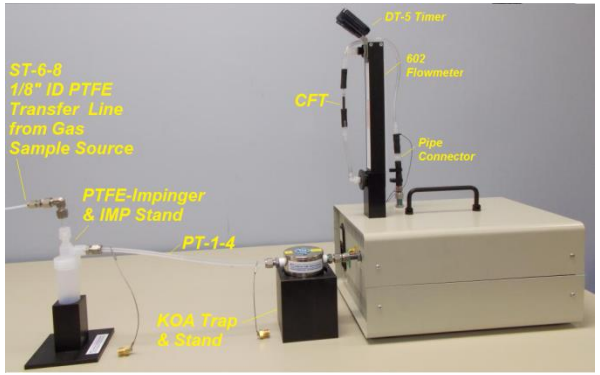
Small Passivated Cylinders

Inert AC/DC Hi Flow Portable Pumps

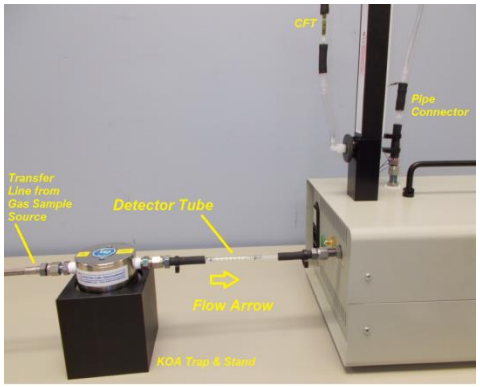
Pump Inlet
H_2O ***Knock-Out***
Trap

MLB Polybags

Small Battery-Powered – Low Flow /Lo Pressure Inert Pump



PTFE Impingers
(solvent collection)



Detector Tubes
(high range)

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Feed Gas Sampling Equipment

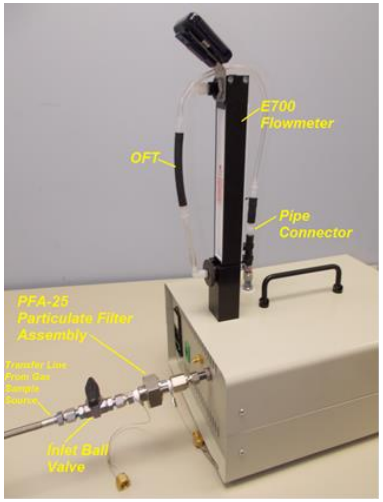
Non-Pump Contact Vacu-Fill of Polybags

Hot Flue Gas Conditioner

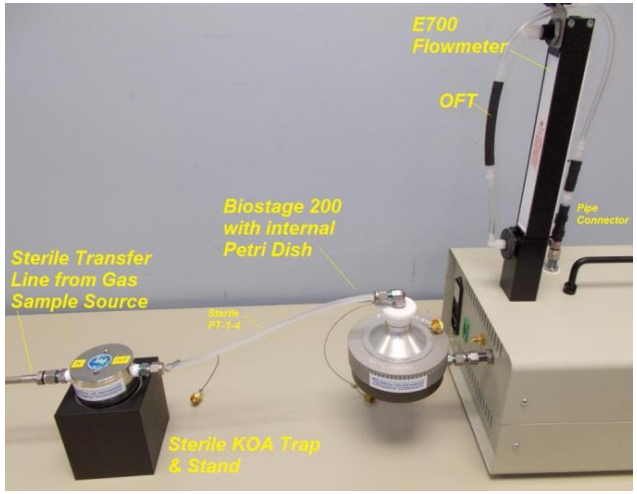
Passivated ss 1-Stage PR

Passivated ss 2-Stage Mini-PR

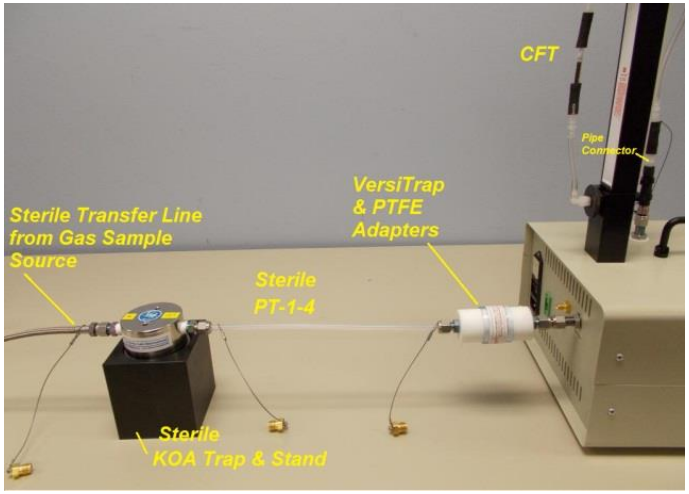
Passivated Flash Vaporizer - PR



Feed Gas Particulate Filtration



BioStage 200 for
Intact / Viable Bacteria & Fungi
FG Bioaerosols (agar plate)



VersiTrap for
Bacteria & Fungi
(Sticky Microscope Slide Trap)

No-Haz Feed Gas Sampling & Shipping Kits

Advanced & Standard Test Program Kits

Currently, ISBT general sampling methods & best lab practices adapted = no specified ISBT Feed Gas sampling methods

Advanced Feed Gas Test Program Kits + Accessories

- For initial Feed Gas or complex, variable Feed Gas sources
- Polymeric Sampling bags, small pressure-limited sample cylinder(s), possible sorbent cartridges, filter assay's & possible special apps containers (ex. impingers)

Upper MLB Tray

Standard FG Test Program Kits + Accessories

- For routine testing of well documented, low – med risk Feed Gas streams
- Polymeric sampling bags only

MLB only Kit

Analytical Lab Monitoring

(Some recommended programs are source specific)

Non-condensable gases: H_2, N_2, O_2, Ar, CO_2

CO, NO_x, HCN, SO_2 , PH_3, ETO (ex. combustion & other sources)

THC & TSC = rough "order of magnitude" indicators = ***good Feed Gas screening!***

- **Volatile Sulfur Compounds** (speciated target list ex. H2S, COS, DMS, CS2, RSH, etc)
- **Volatile Hydrocarbons** (speciated target C1 – C6+ alkane / alkenes list)
- **Volatile Oxygenates** (speciated target list ex. AA, MeOH, EtOH etc)
- **Volatile Aromatics** (ex. BTEX)
- **Volatile Halogenates** (target list ex. $COCl_2$, MeCl, $MeCl_2$, $CHCl_3$, CCl_4, VCL etc)
- **Semi-Volatiles** (polyols = glycols, glycerols, phenols, pipeline additives, natural oils, MEA?, Fatty Acids, vegetable oils?)
- **Radon^{222}**? (natural well sources = Lucas "Scin Cell" Method suggested)
- **Bio-agents**? (big unknown - no current "std" method = experimental – based on ambient / compressed air methods)
- **Trace Metals**? (ex. Hg, As, Sb? Others? no "std" methods = NIOSH ***impinger / sorbant tubes?***

Recommended Instrumental Methods that can detect "unknown / unsuspected" impurities
(ex. GC/MS, Gas Cell FTIR, High Res GC's with selective detectors, Ion Chromatography, Osmotic [H_2O Sample] Detector Tubes)

Analytical Feed Gas Methods

(Wide range of ISBT-adapted & proprietary test methods used)

- No specific ISBT methods currently offered – many methods used are ISBT-adapted CO_2 final product methods or proprietary lab-based methods based on Feed Gas experience
- Feed Gas samples are often highly complex & require sophisticated instrumentation + extensive sample preparation methods. Knowledge of potential chemical interferences is essential – especially for DT-related data + proper GC/MS peak or FTIR profile ID interpretation!
- Lab staff experience in CO_2 Feed Gas profile characterization is highly recommended for proper test program design & reliable result interpretation
- Short holding times between sampling date & analysis date are required for maximum result accuracy (LT 14 days recommended).

Typical Feed Gas Impurity Ranges

ISBT List PLUS Feed Gas Source Dependent = ALI Experience

% CO2 Purity = 10 – 99+%
H_2 = nd 1 – 10,000+ ppm
N_2 = nd 1 - 150,000+ ppm
O_2 + Ar = nd 1 – 50,000+ ppm
CO = nd 1 – 1,000+ ppm

TSC = nd 0.01 – 20,000+ ppm
THC = nd 0.5 – GT 25,000+ ppm
Methane = nd 0.5 – 15,000+ ppm

Benzene = nd 1 – 500,000+ ppb (500 ppm)
Toluene = nd 1 – 500,000+ ppb (500 ppm)
Ethyl Benzene = nd 1 – 15,000+ ppb (15 ppm)
Xylenes = nd 1 – 100,000+ ppb (100 ppm)

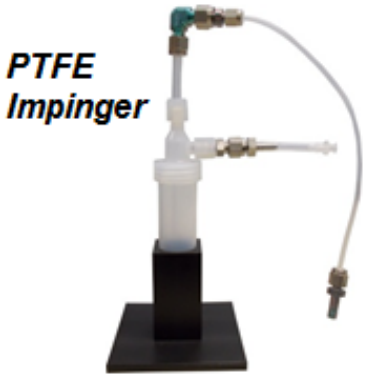
Acetaldehyde = nd 0.05 – 300+ ppm
Ethanol = nd 0.1 – 20,000+ ppm
Methanol = nd 0.1 – 200+ ppm

On-Site Feed Gas Monitoring

Risk Management Driven – Key Feed Gas Stream Analytes

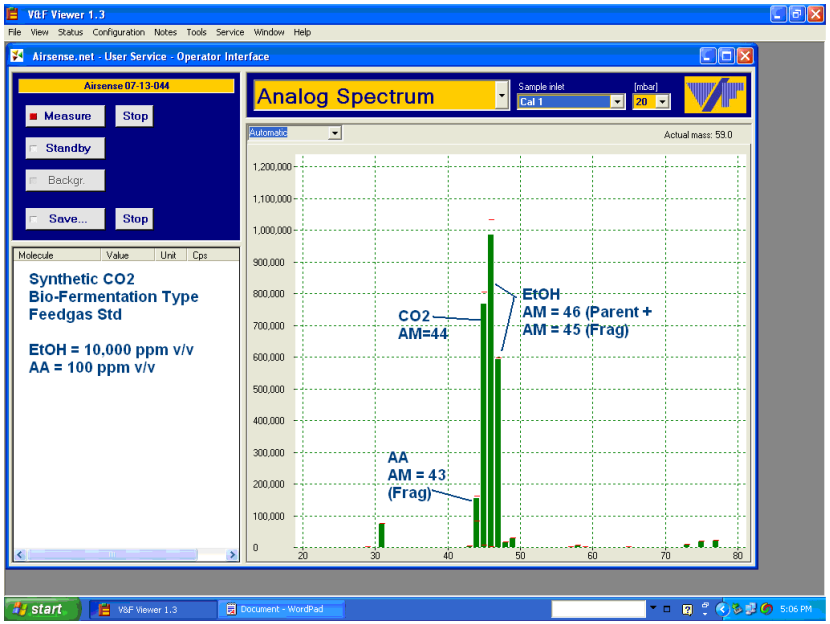
Examples – Critical Feed Gas Impurity Load - Routine Monitoring Recommendations:

- **% CO_2 Purity** = Zahm-Nagel Models – GC/TCD - SIS based units
- **TSC** Measurement by DT – GC/FPD – SIS based units
- **AHC** (BTEX) Measurement by DT – GC – SIS based units
- **THC** by THC analyzers – low gain settings / possible precise dilution
- **Key Analytes / Families** (ex. Total Alcohols – CO – AA / Total Aldehyde by DT or GC or SIS based units
- **NOX & SOX & Other Acid Gases** by DT or SIS or specific analyzers
- **% O_2** by Fuel Cell Analyzers – Pyrite Kits – self gen / combustion only?
- **Rn^{222}** = RadioChem Methods – natural wells only?
- **Trace Metals** (Hg / As / Sb) – coal combustion / bioethanol sources only?
- **Bioagent** testing = bioethanol sources only if needed?

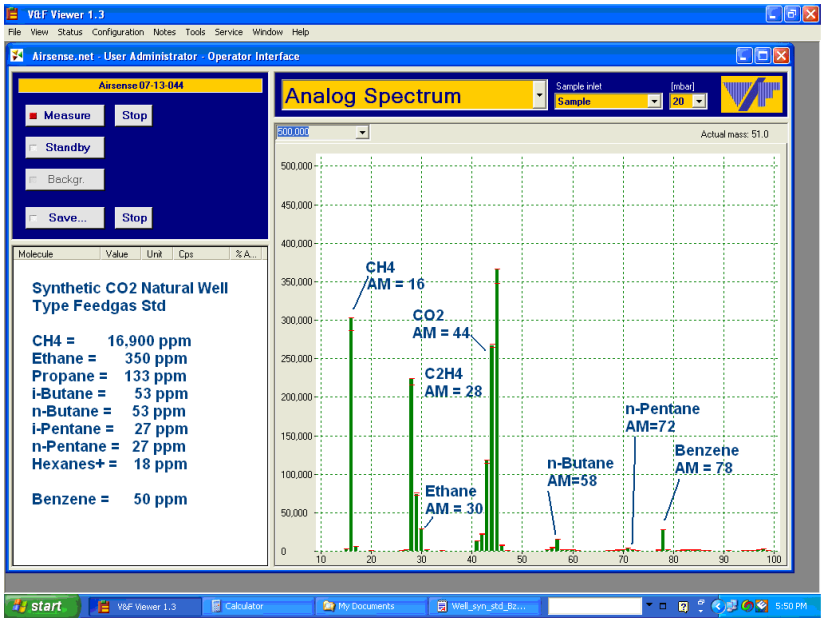


Continuous Feed Gas Monitoring Systems

Feed Gas + In-Process + Final Product Multi-component Analyzers



Continuous SIS
BioEthanol Monitoring
Key Impurities – Wide Range



Continuous SIS
Natwell Monitoring
Key Impurities – Wide Range

Fermentation Impurity profiles "Morph" over Fermentation Reaction Cycle!

Key To Success for Feed Gas on-Line Monitoring: Initial Detailed Feed Gas information (for Interference Correction) + Feed Gas line conditioning (proper pressure + sample gas flow + H_2O knock out control + possible transfer line heating)

Future Feed Gas Monitoring & Industry Challenges

Based upon potential use of new "uncharted "Feed Gas Sources

- R&D need for an acceptable bio-agent screening test(s) for Feed Gas Monitoring?
- R&D need for an acceptable Rn^{222} test?
- R&D need for Trace Metal tests – Feed Gas & Final Product Monitoring?
- Need for ISBT recommended Feed Gas test program(s) + recommended sampling frequency for NEW or existing CO_2 Sources?
- Need for ISBT recommended Feed Gas analytical methods?
- Need for simple Feed Gas tests (DT?) + Advanced Feed Gas on-line monitoring analyzers?
- Need for a set of industry criteria guidelines for acceptance of a NEW Feed Gas source for beverage production
- Need for CO_2 Merchant – CO_2 Producer ISBT Audits & Good Communications about "Changes" that could influence impurity profiles & plant removal capabilities?

Questions?

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