Soft Ionization Spectrometry (SIS):

One Step Closer to a "*Magic Box*" for Complete Bev-Gas Testing – *AND Beyond*

Presented at the ISBT Conference – San Antonio - 2007

INTERNATIONAL SOCIETY of BEVERAGE TECHNOLOGISTS

Airborne Labs International

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Background - Review
Industrial Sources of CO_2
+ Unique Distribution Chain

- Natural Wells
- Fuel Combustion
- Bio-Fermentation
- Ammonia Production
- Chem-Process Off Gas

- Feedgas Source – Producer – Transport – Regional Depots –Transport – Storage – Production

Many Potential Impurities

ISBT Bev-Gas Quality Challenges

- As beverage production grows, *continuous* quality testing becomes v important
- CO_2 Quality Assurance is a complex technical challenge
- All dream of a “Magic Box” that can quickly monitor the *entire ISBT Impurity List*

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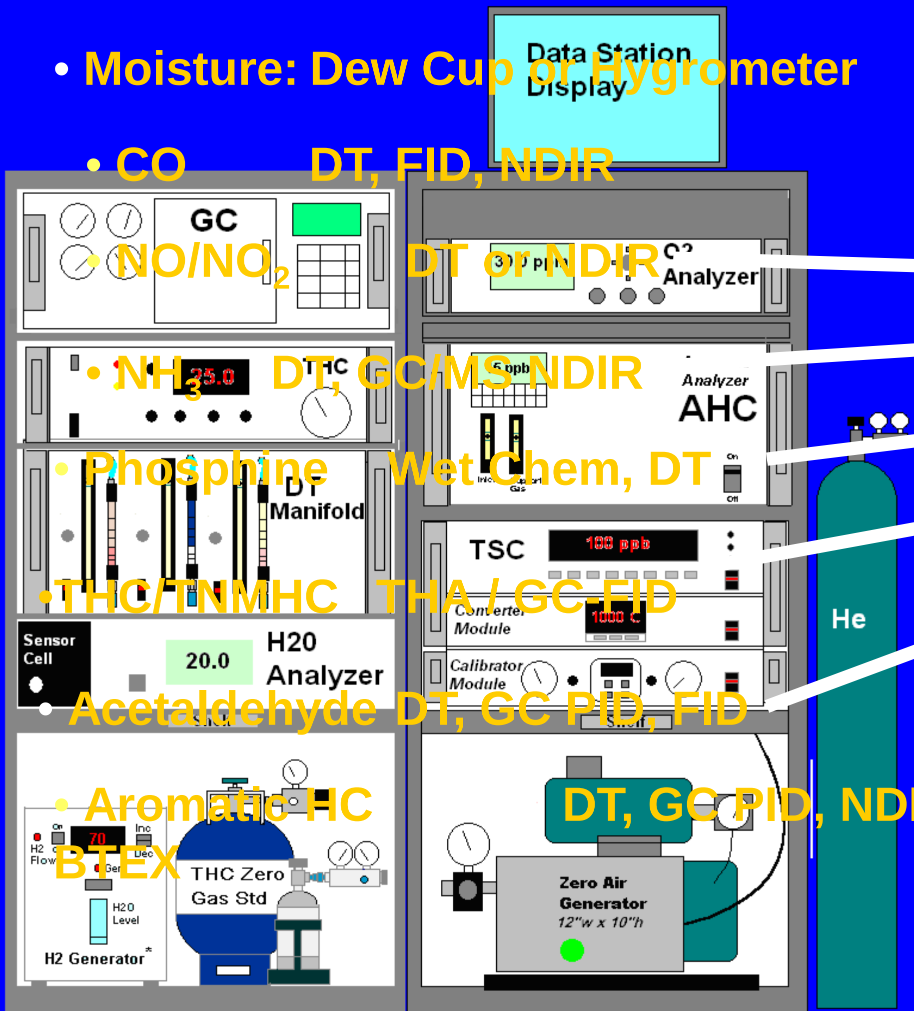
ISBT CO_2 Purity Guidelines

"The List"

CO_2 Purity	99.9% min	Process
Moisture (H_2O)	20 ppm v/v max	Process
Oxygen (O_2)	30 ppm v/v max	Sensory
Carbon Monoxide (CO)	10 ppm v/v max	Process / Regulatory
Ammonia (NH3)	2.5 ppm v/v max	Process
NO / NO_2	2.5 ppm v/v (ea) max	Regulatory
Non-Volatile Residue (NVR)	10 ppm x/x max	Sensory
Non-Volatile Organic Residue (NVOR)	5 ppm w/w max	Sensory
Phosphine (PH_3)	0.3 ppm v/v max	Regulatory
Total Volatile Hydrocarbons (THC) & TNMHC	50 ppm v/v max – including 20 ppm v/v TNMHC	Sensory
Acetaldehyde (AA)	0.2 ppm v/v max	Sensory
Aromatic Hydrocarbon Content (AHC)	20 ppb v/v max (as benzene)	Regulatory
Total Sulfur Content (TSC*) less SO_2	0.1 ppm v/v max	Sensory
Sulfur Dioxide (SO_2)	1 ppm v/v max	Sensory
Odor of Snow	No foreign odor	Sensory
Appearance in Water	No color or turbidity	Sensory
Odor & Taste in Water	No foreign odor/taste	Sensory
Supplemental HCN / Vinyl Chloride	None detectable–best method	Report

Where Does SIS Technology ***Fit-In*** vs Traditional ISBT CO_2 Analyzers?

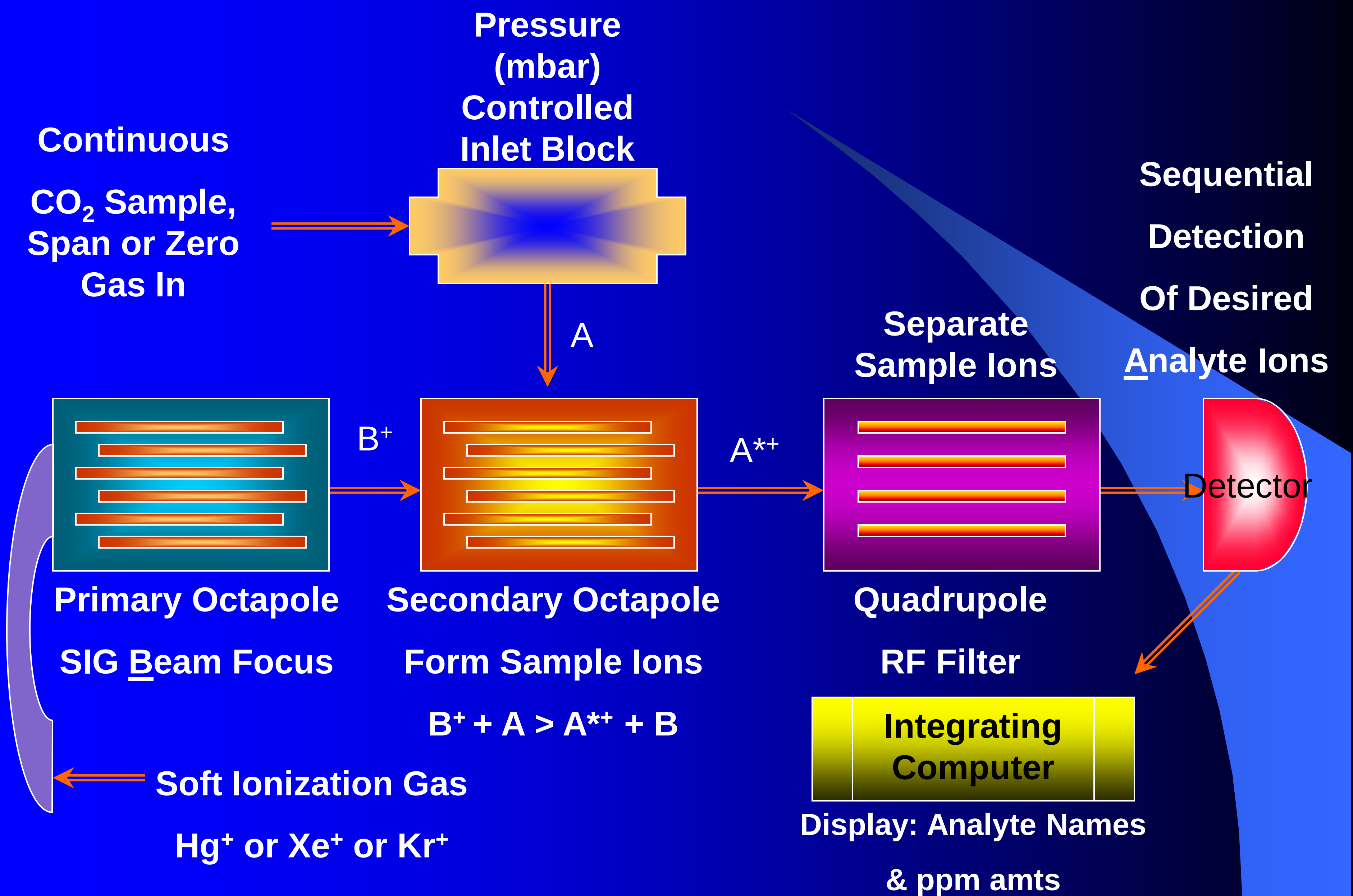
- CO_2 Purity: Zahm/Nagel or GC/MS
- Moisture: Dew Cup or Hygrometer
  - CO DT, FID, NDIR
  - NO/NO_2 DT or NDIR
  - NH_3 DT, GC/MS NDIR
  - Phosphine Wet Chem, DT
- THC/TNMHC THA / GC-FID
- Acetaldehyde DT, GC PID, FID
- Aromatic HC BTEX DT, GC PID, NDIR
- HCN/VCL DT or Wet Chem
- SO_2 or TRS DT, SCD, CLD



What Is Soft Ionization Spectrometry?

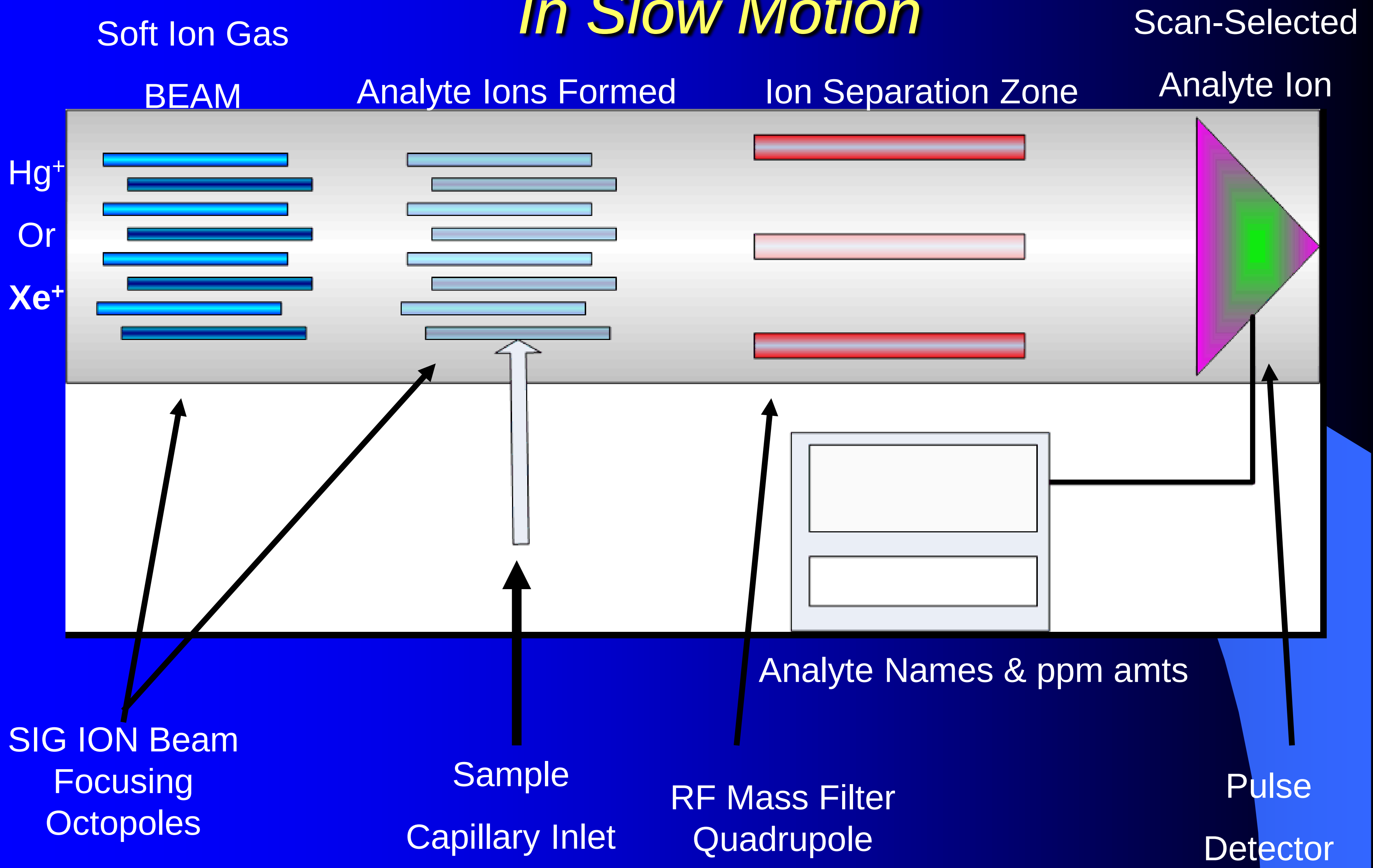
- SIS is a Mass Selective Analyzer:
- CO_2 Sample is ***continuously*** injected into a ***Low Energy Ion Beam*** of Hg^+ or Xe^+ or Kr^+ = soft ionization gas (SIG)
- Sample impurities (analytes) softly fracture into ***<u>only a few</u>*** characteristic <u>ion</u> fragments
  - Fragments are ***size-separated*** by a scanning RF field. Software-selected analyte ions are counted by a pulse detector
  - SIS Display = "***impurity hit list name + ppm level***" – total analysis time = a few seconds
- ***So, Tell me more about how this SIS thing works***

The "Soft Ionization" Process

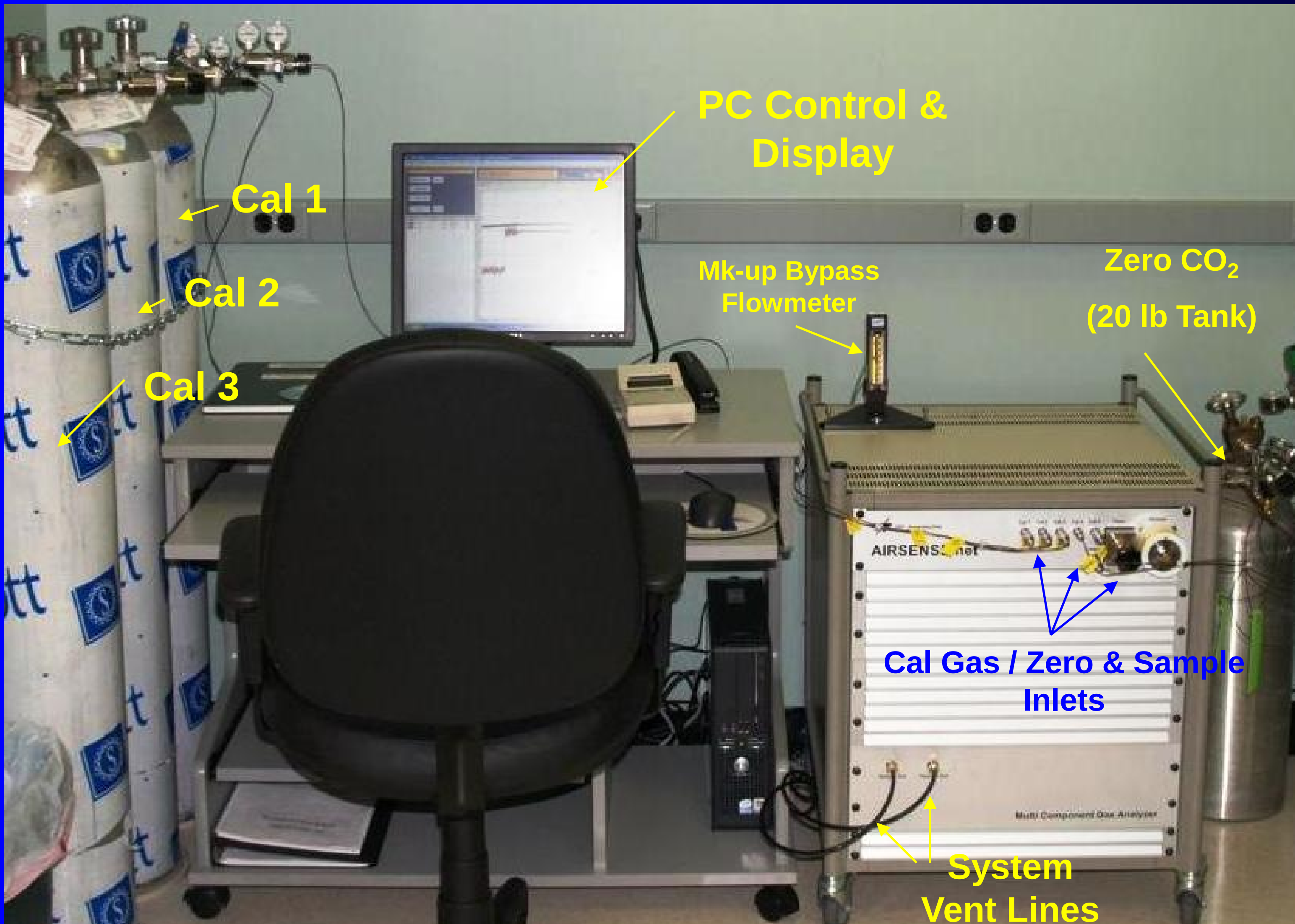


The "Soft Ionization" Process

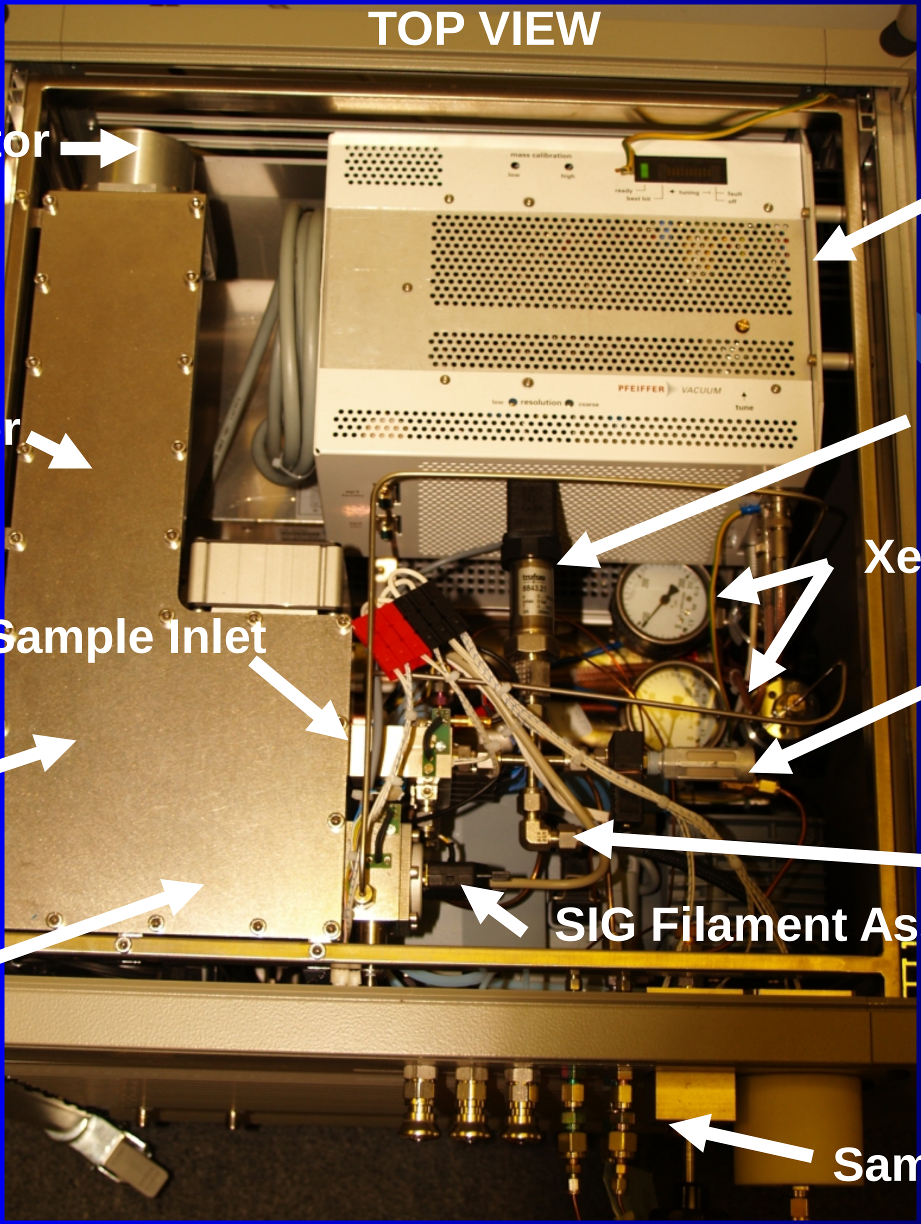
In Slow Motion



SIS Analyzer System



SIS Analyzer – Under-the-Hood



Detector

Mass Separator

Sample Inlet

SIG-Sample Collision Zone

SIG Beam

90º Collimator

RF Filter Control

Inlet Pressure Sensor

Xe & Kr Pressure Gauges

Inlet ↑ Press Make-up

Inlet Pumpdown

SIG Filament Ass’y

Sample / Std / Zero Gas Inlet Ports

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SIS - a "New Application" of an Established Technology

- SIS is a relatively "mature" technology
- Established Applications:
  - Environmental Air Testing
  - Engine Exhaust / Catalyst / Diesel Studies
  - Medical e.g. Disease Diagnosis by Patient Breath Analysis

- **European + Emerging *USA/Canada* CO_2 Supplier QC**

- PET bottle recycling & mfg quality testing*

- Gaseous Headspace Food & Beverage Testing (*Fragrance ID & Brand Profiling*)**

- Other Applications where *many* analytes might exist for only milliseconds & must be *quickly* ID'd & quantified

**** AND Beyond???***

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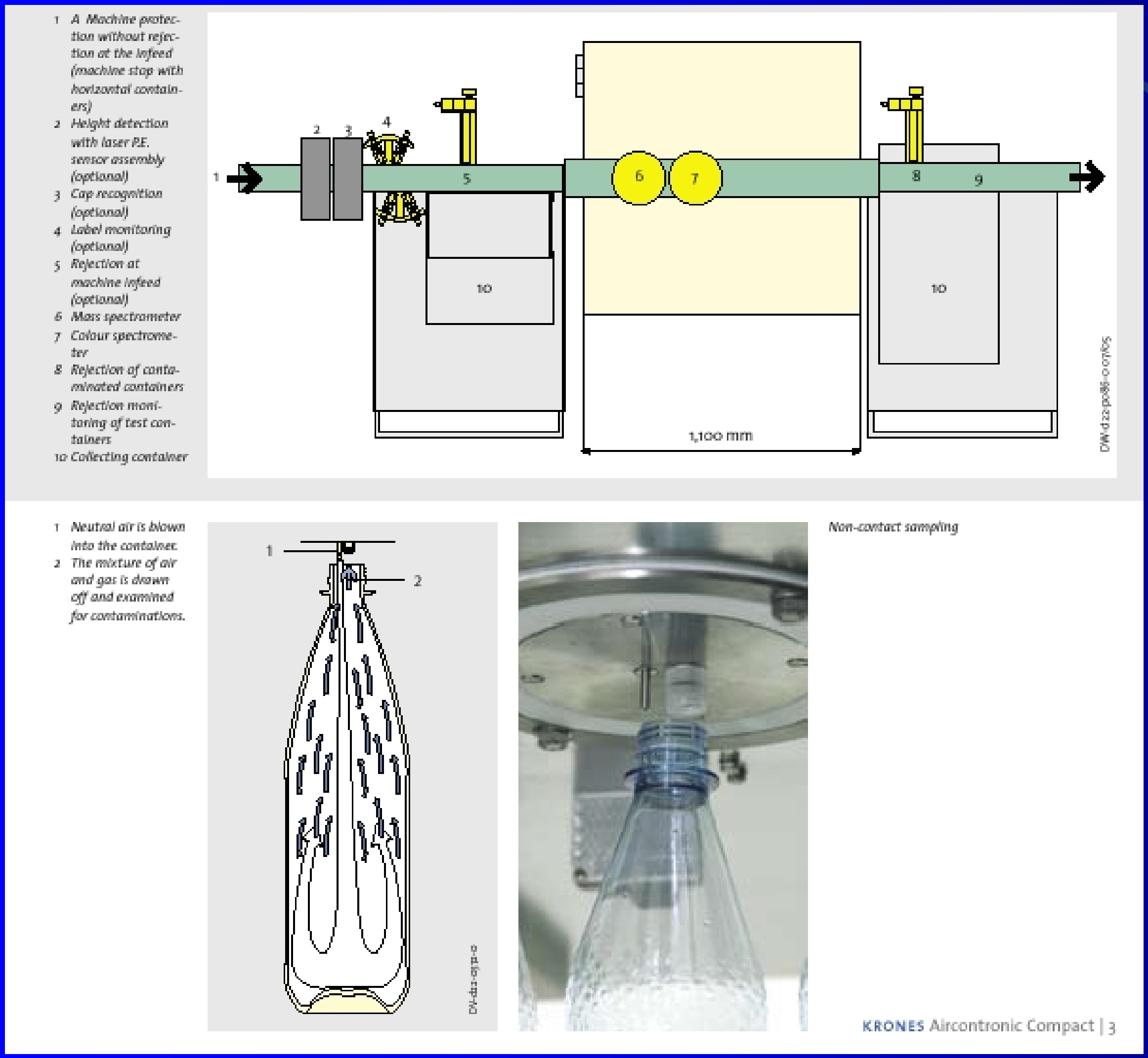
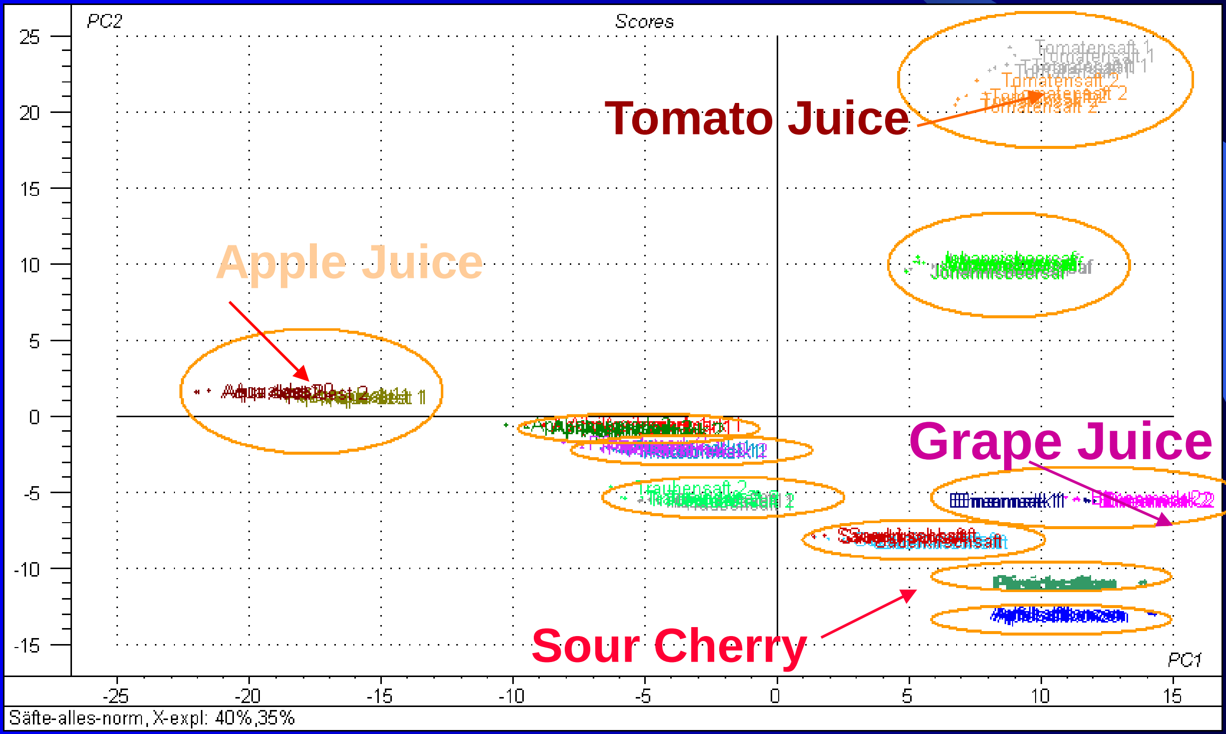
PET Bottle Recycling-High Speed QC Testing*



*AND Beyond – for another day

Fragrance *Mass Moment* ID Profile*

= Apple juice, peach juice, pear juice, grape juice, apricot juice, tomato juice, sour cherry juice, currant juice, water



**AND Beyond – for another day*

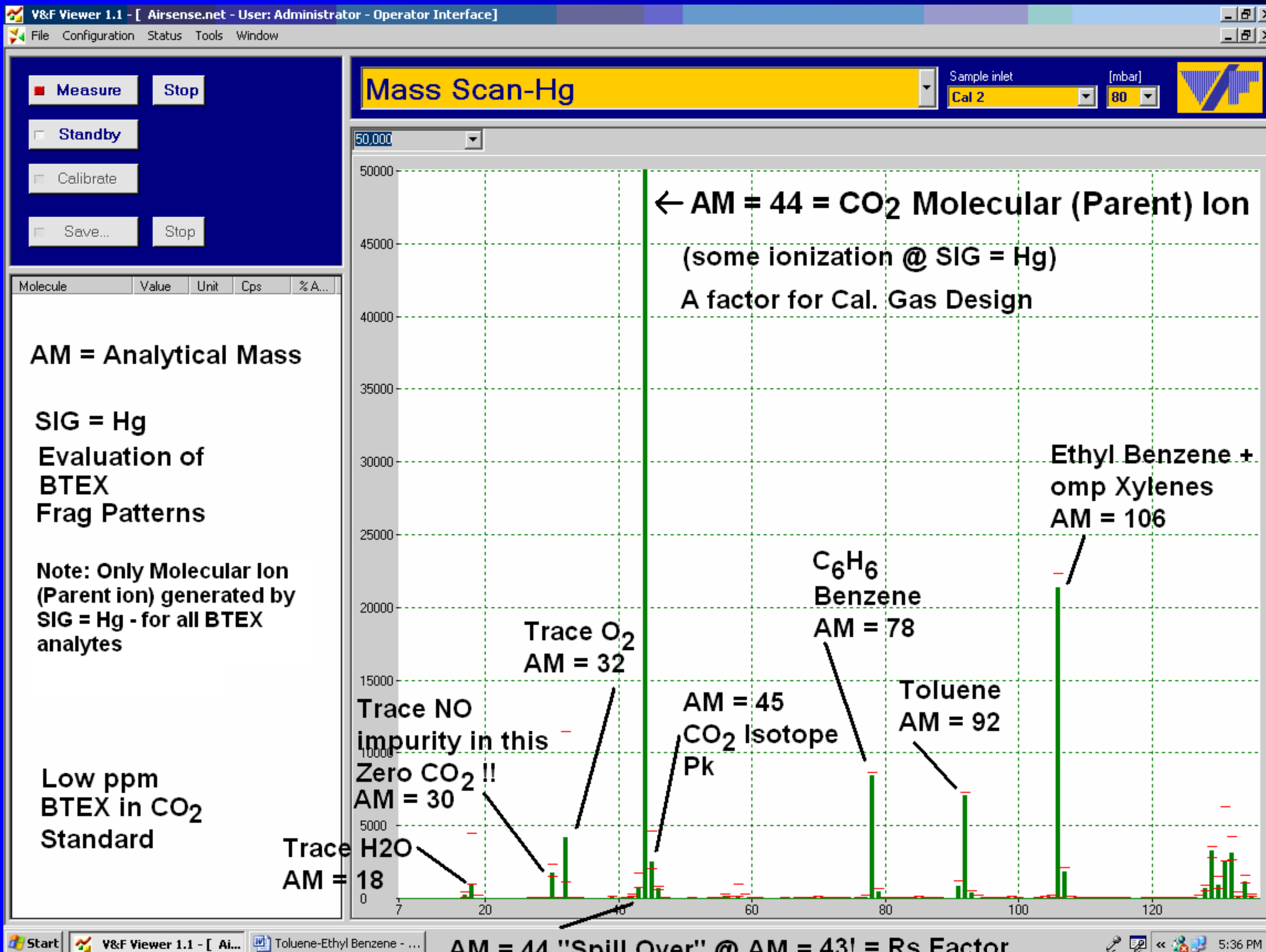
So, How might SIS work in the "*Real World*" of Bev-Gas Testing?

Our R&D Objectives & Current Focus

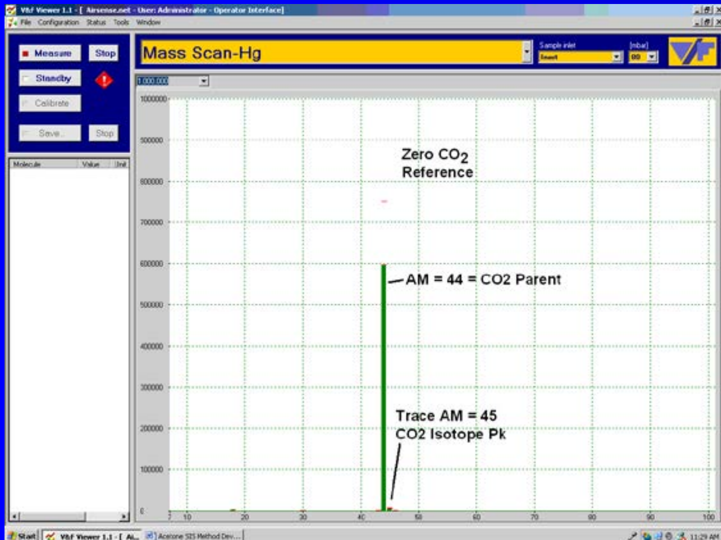
- Develop SIS Methods (SIG, AM, Scan, Count) for key ISBT-listed CO_2 impurities
- Evaluate: LDR / Sensitivity / Precision / Accuracy & DL *vs* ISBT Method Guidelines
- *Identify potential interferences* + their influence + develop corrective actions
- Evaluate: Analysis - Calibration Strategy + SIS Ops & Maintenance Requirements

SIG & AM Selection Process

Sometimes its “easy”



SIG & AM Selection Process – The "Frag Factor"



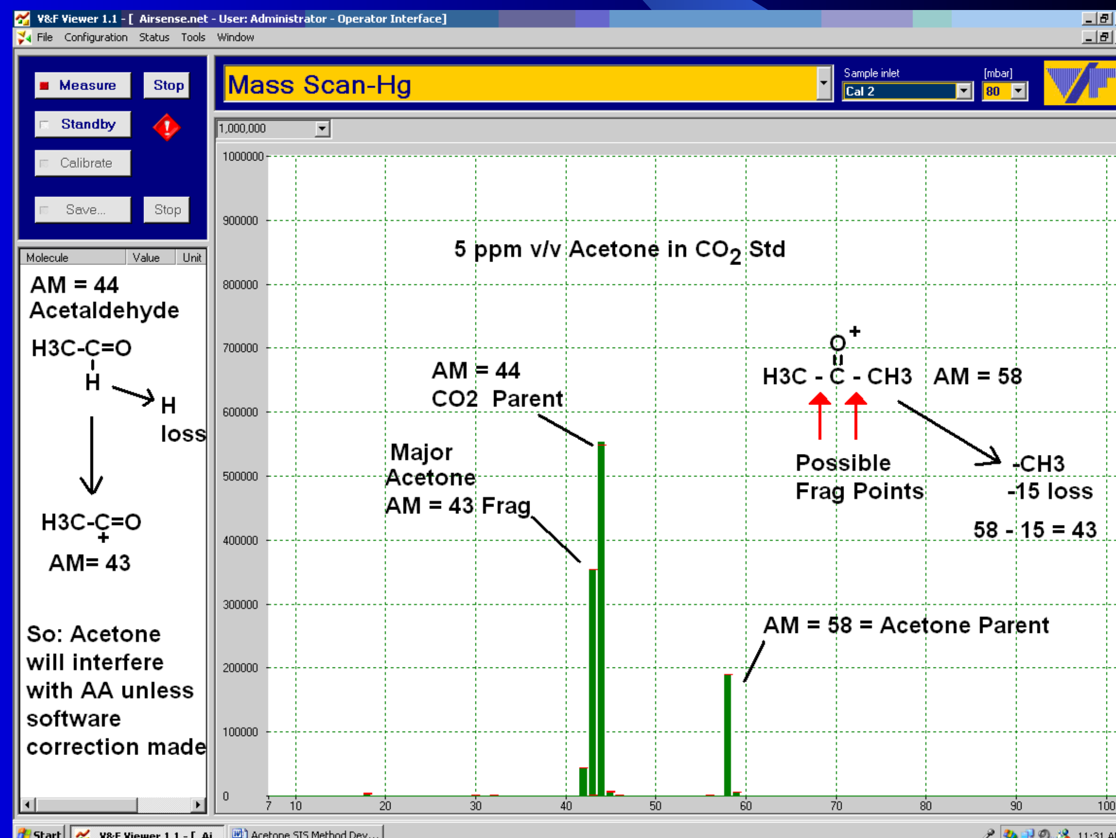
(Sometimes its not-so-easy)

Basic SIG & AM Studies

Needed to ID potential Interferences for design of

Appropriate Software & Calibration Routine

Corrective Measures



SIS - Aromatic Hydrocarbon (AHC) Data

(ISBT CO_2 Limit = 20 ppb v/v as Benzene + report all other target AHC's)

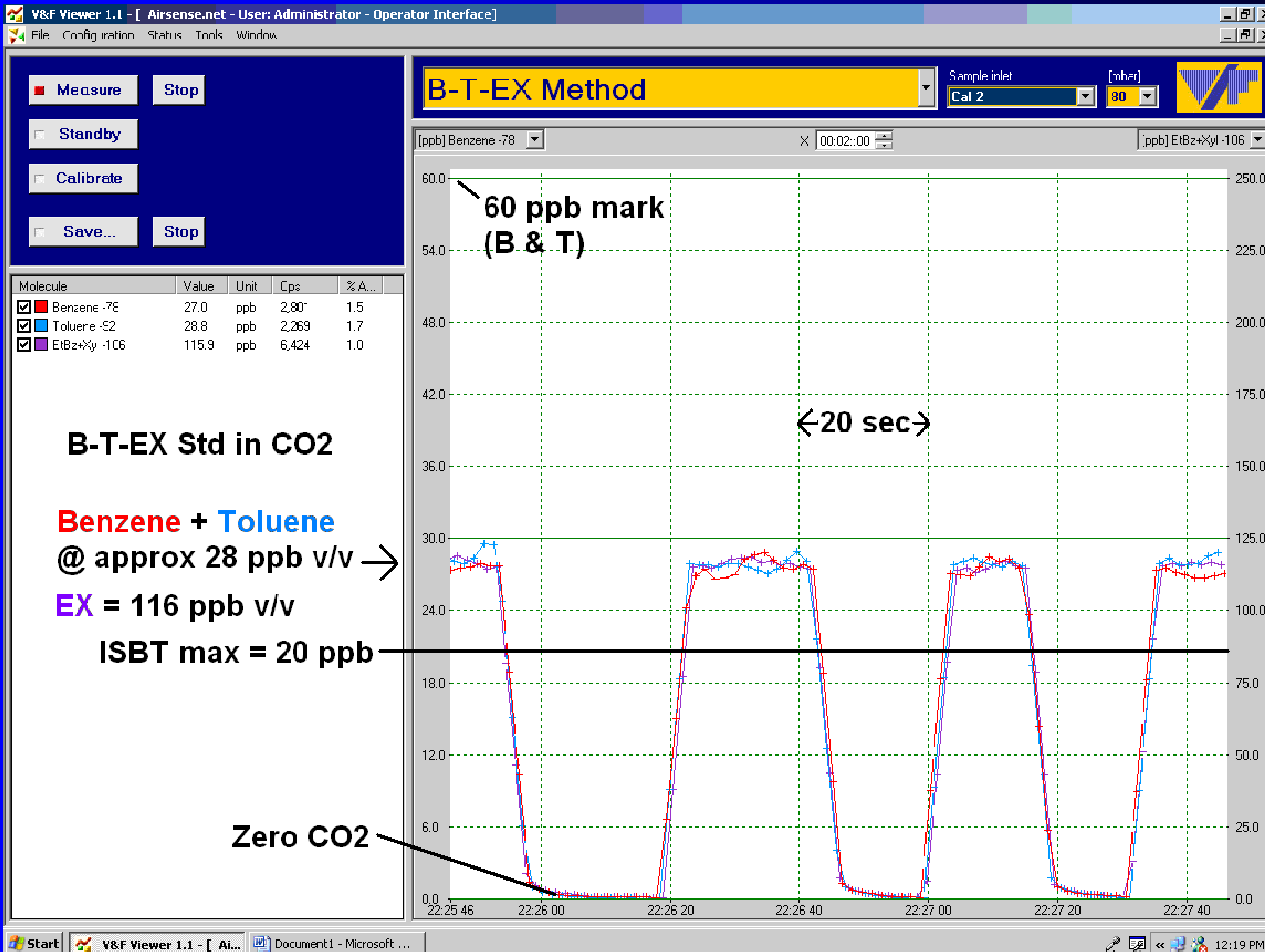
Our Results

AHC	SIG	AM	LDR ppb v/v	DL ppb v/v	Interference (s)
Benzene	Hg	78	LT 0 - 1000+	LT 1	None found-to-date
Toluene	Hg	92	LT 0 - 1000+	LT 1	None found-to-date
Ethyl Benzene + o,m,p Xylenes	Hg	106	1 -1000+	LT 5	None found-to-date Note: EBz + Xylenes measured as Total

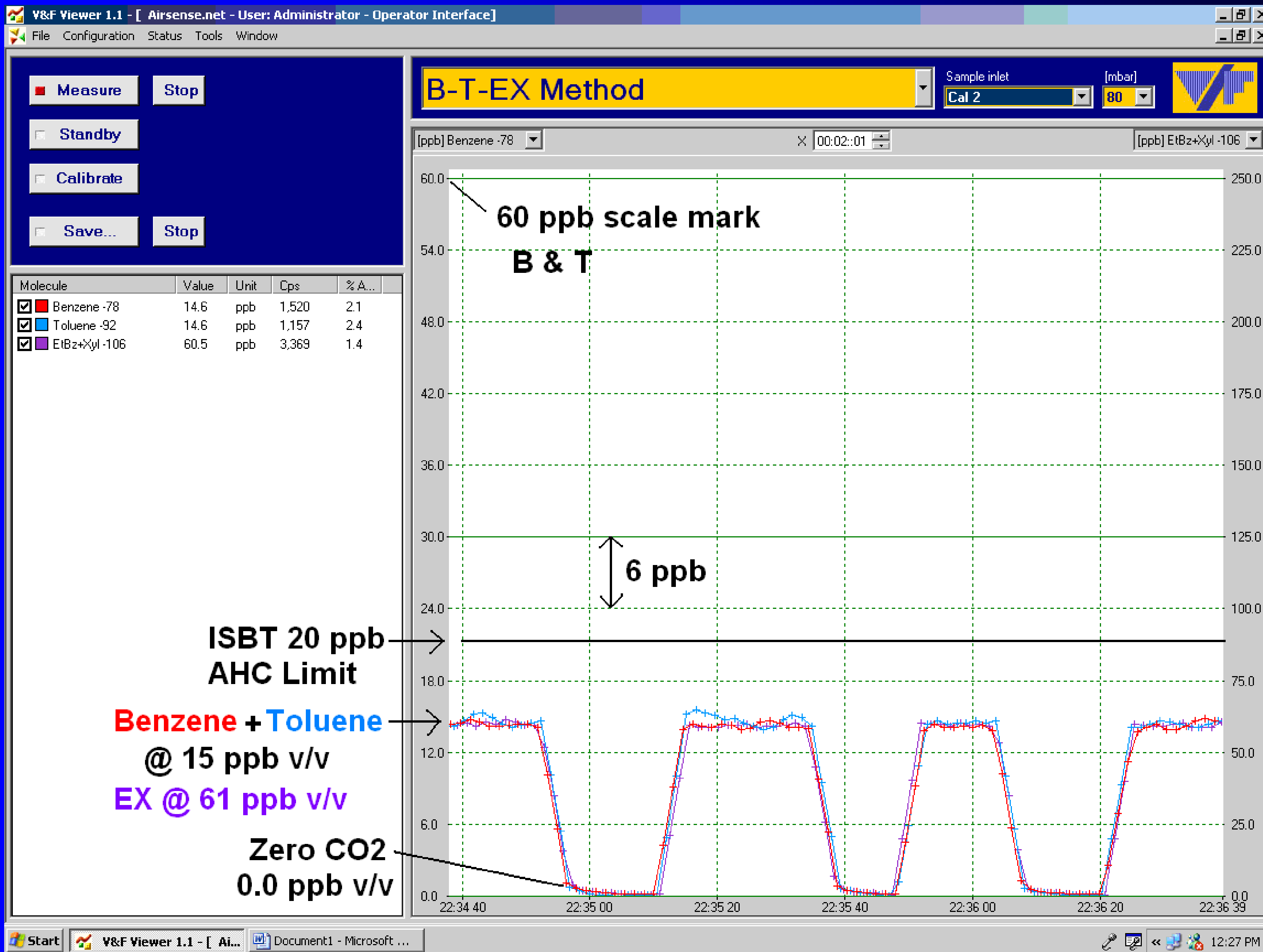
Speciation Information B-T-EX

Use of Benzene Cal Gas for Indirect Cal of TEX works v. well

SIS Data: B-T-EX in CO_2 @ 28 ppb v/v level



SIS Data: B-T-EX in CO_2 @ 15 ppb v/v level



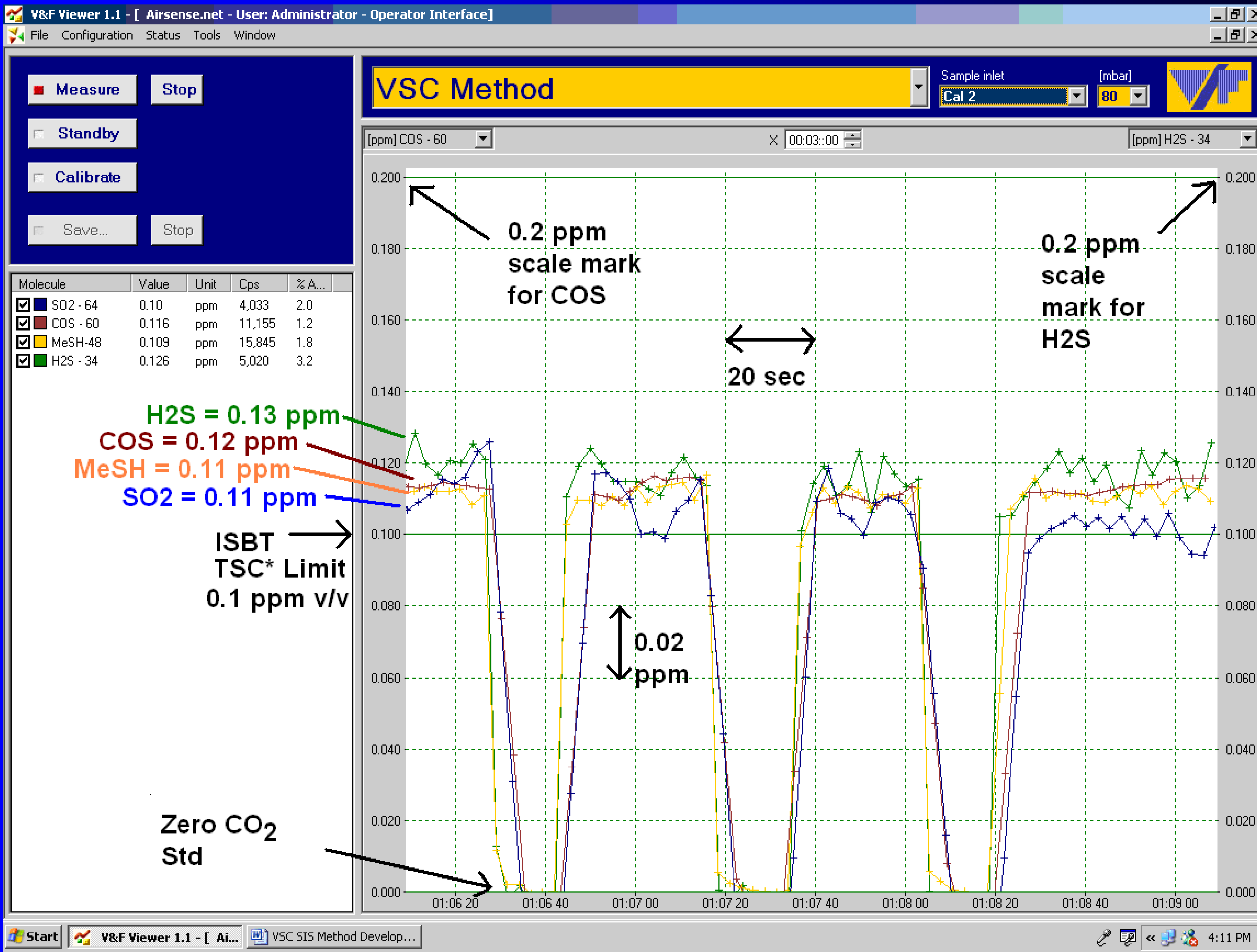
SIS - Volatile Sulfur Compounds (VSC) Data

ISBT Limit = 0.1 ppm v/v as TSC* = sum of VSC target impurities excluding SO_2, SO_2 = 1 ppm v/v max

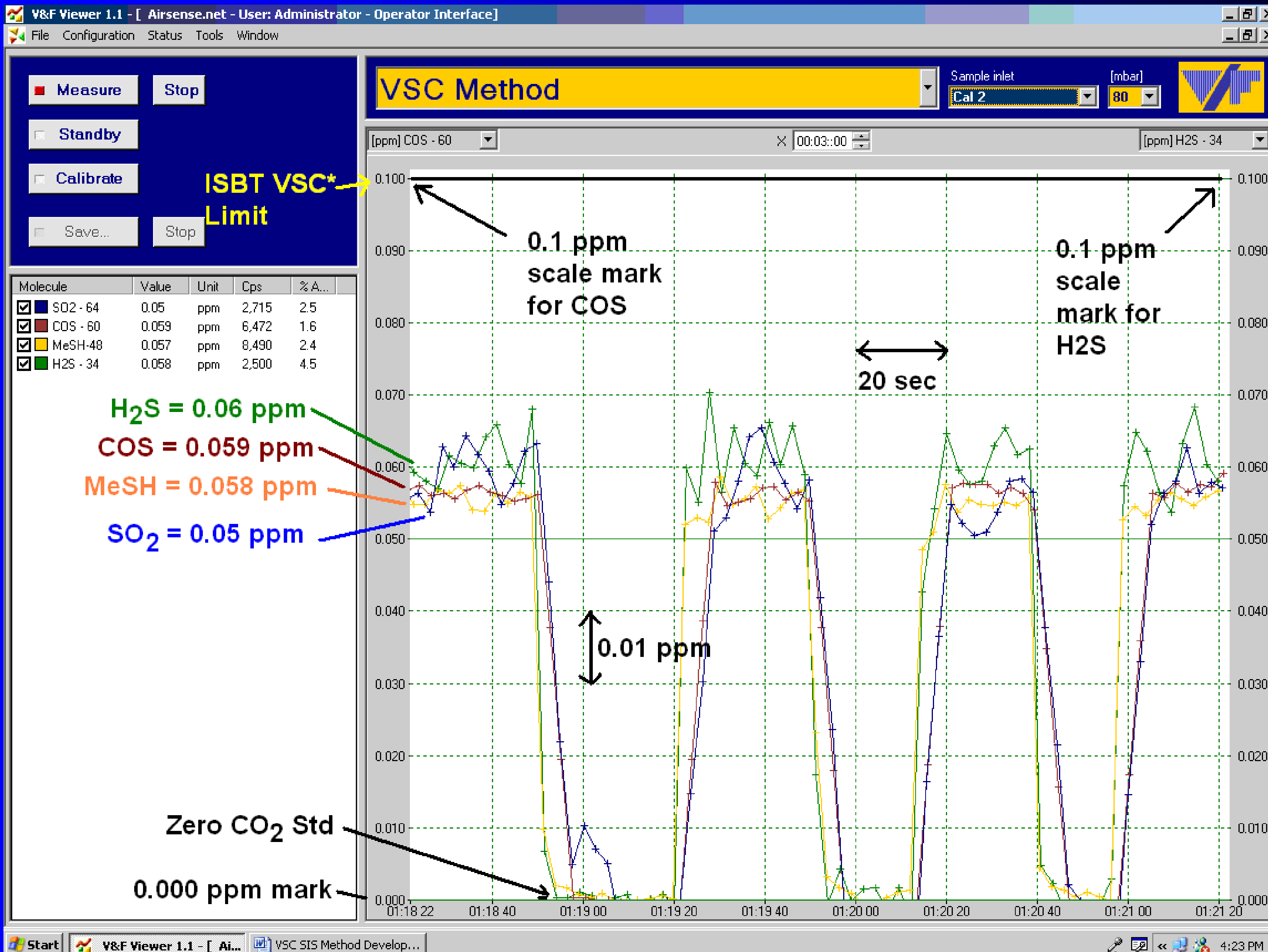
Useful Speciation information achieved

VSC	SIG	AM	LDR ppb v/v	DL ppb v/v	Interference (s)
H_2S	Hg	34	0 – 1000+	LT 5	PH_3 @ AM = 34 (Note: PH_3 = Rare)
COS	Xe	60	0 – 1000+	LT 5	None found-to-date
SO_2	Xe	64	0 – 1000+	5	None found-to-date
MeSH	Hg	48	0 – 1000+	LT 5	None found-to-date
CS_2	Hg	76	0 – 1000+	LT 5	None found-to-date
DMS + EtSH	Hg	62	0 – 1000+	LT 5	Vinyl Chloride (VCL) AM = 62, correct using AM = 64 isotope (Note: VCL = rare) Note: Measures Total DMS + EtSH

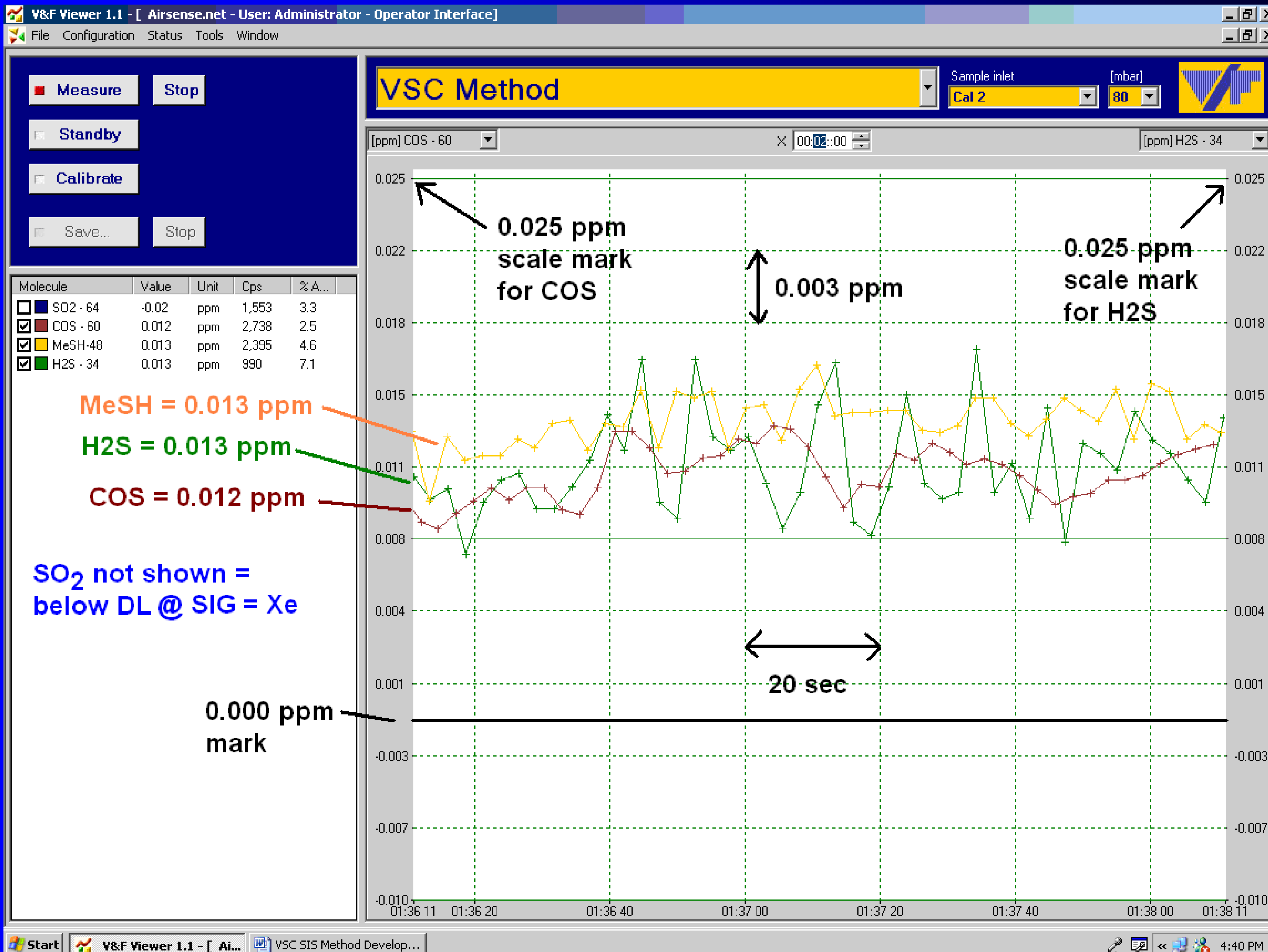
SIS Data: VSC in CO_2 @ 110 ppb v/v level



SIS Data: VSC in CO_2 @ 60 ppb v/v level



SIS Data: VSC in CO_2 @ 13 ppb v/v level



SIS - Volatile Oxygenated Compounds (VOX) Data

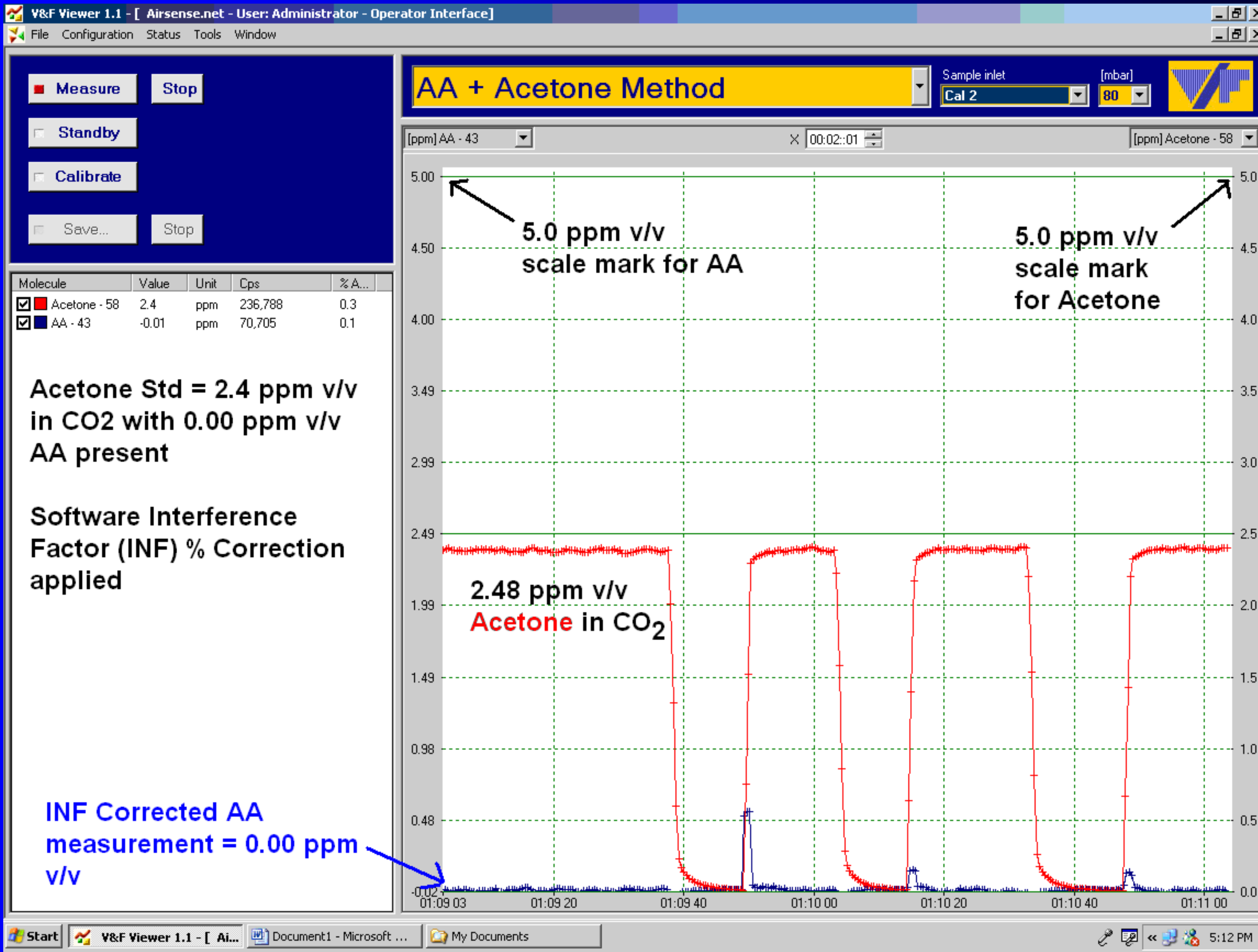
ISBT Limit = 0.2 ppm v/v as Acetaldehyde (AA) + Speciation information needed for THC/TNMHC calcs etc.

VOX	SIG	AM FR = Frag	LDR ppm v/v	DL ppm v/v	Interference (s)
AA	Hg	43^{fr}	0 - 5+	LT 0.05	Acetone = Major INT, i-PA = INT, i-Butanes = INT, n-Butane= minor INT
DME	Hg	46	0 - 5+	LT 0.05	No effect on AA, NO_2 = INT
MeOH	Xe	31^{fr}	0 - 5+	LT 0.05	No effect on AA, EtOH / nPA = INT
EtOH	Hg	45^{fr}	0 – 5+	LT 0.05	No effect on AA, DME = minor INT
N-Butanol	Hg	56^{fr}	0 - 5+	LT 0.05	No effect on AA
Acetone	Hg	58	0 - 5+	LT 0.05	Major AA effect, Butanes = INT
EtOAc	Hg	70^{fr}	0 - 5+	LT 0.05	No effect on AA

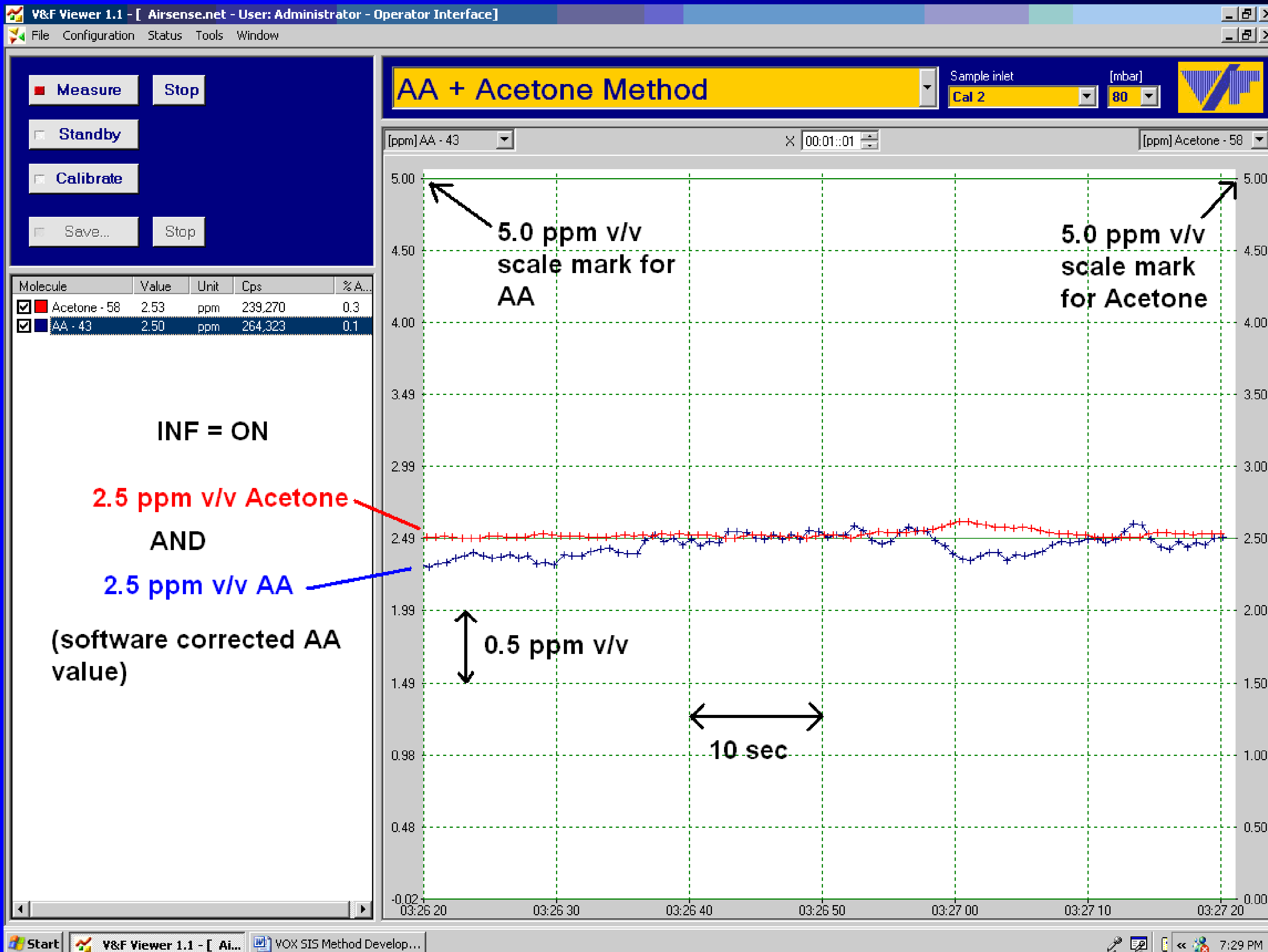
Other VOX impurities studied to date: n / i -Propanols, i -Butanols, Ethylene Oxide

SIS Data: VOX in CO_2 @ 2.5 ppm v/v Acetone / 0.00 AA – INF Corrected

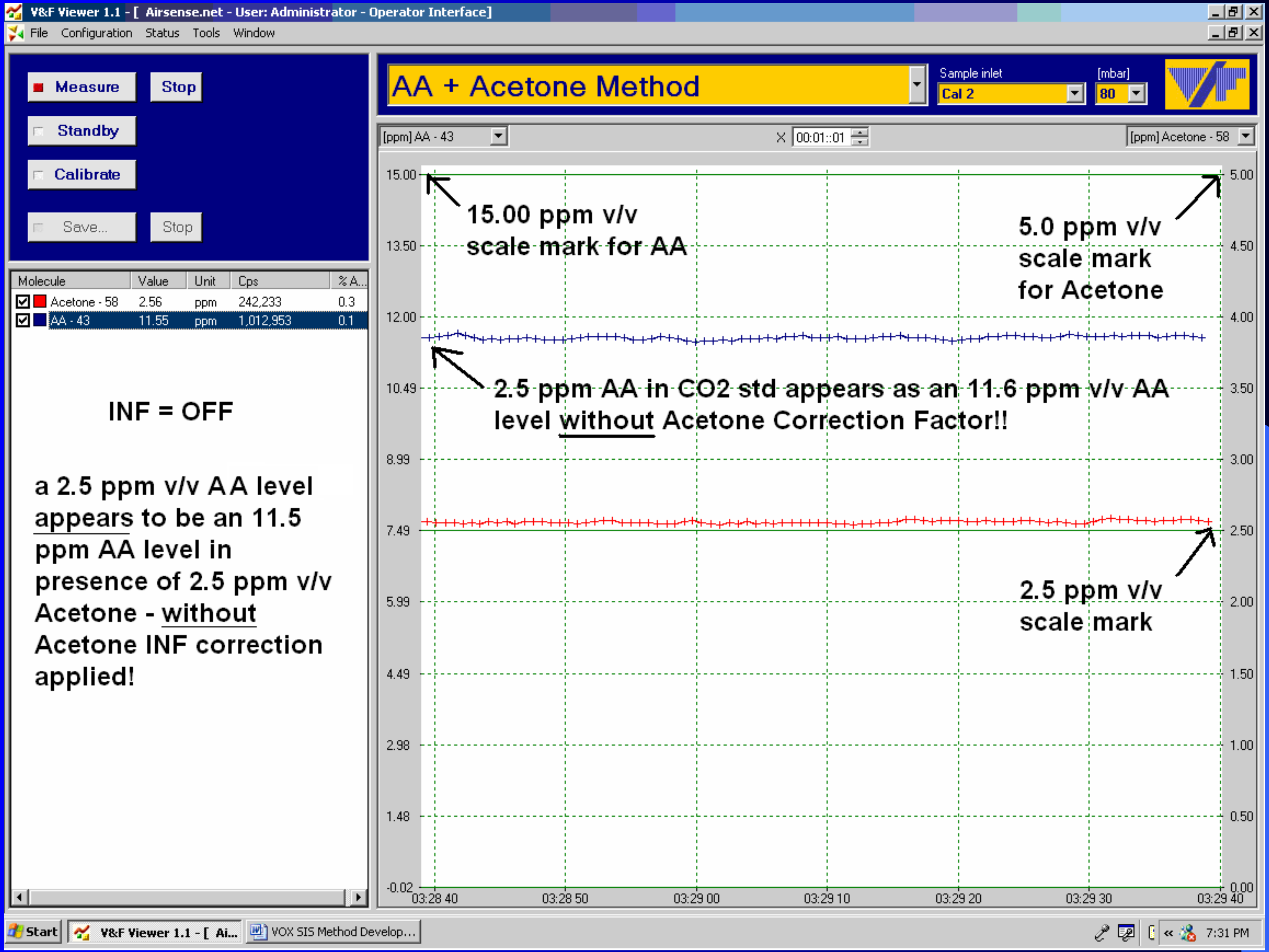
Key to Success is having accurate Interference Correction Data



SIS Data: VOX in CO_2 @ 2.5 ppm v/v Acetone + AA – INF Corrected



SIS Data: VOX in CO_2 @ 2.5 ppm v/v Acetone/AA if NO INF Correction



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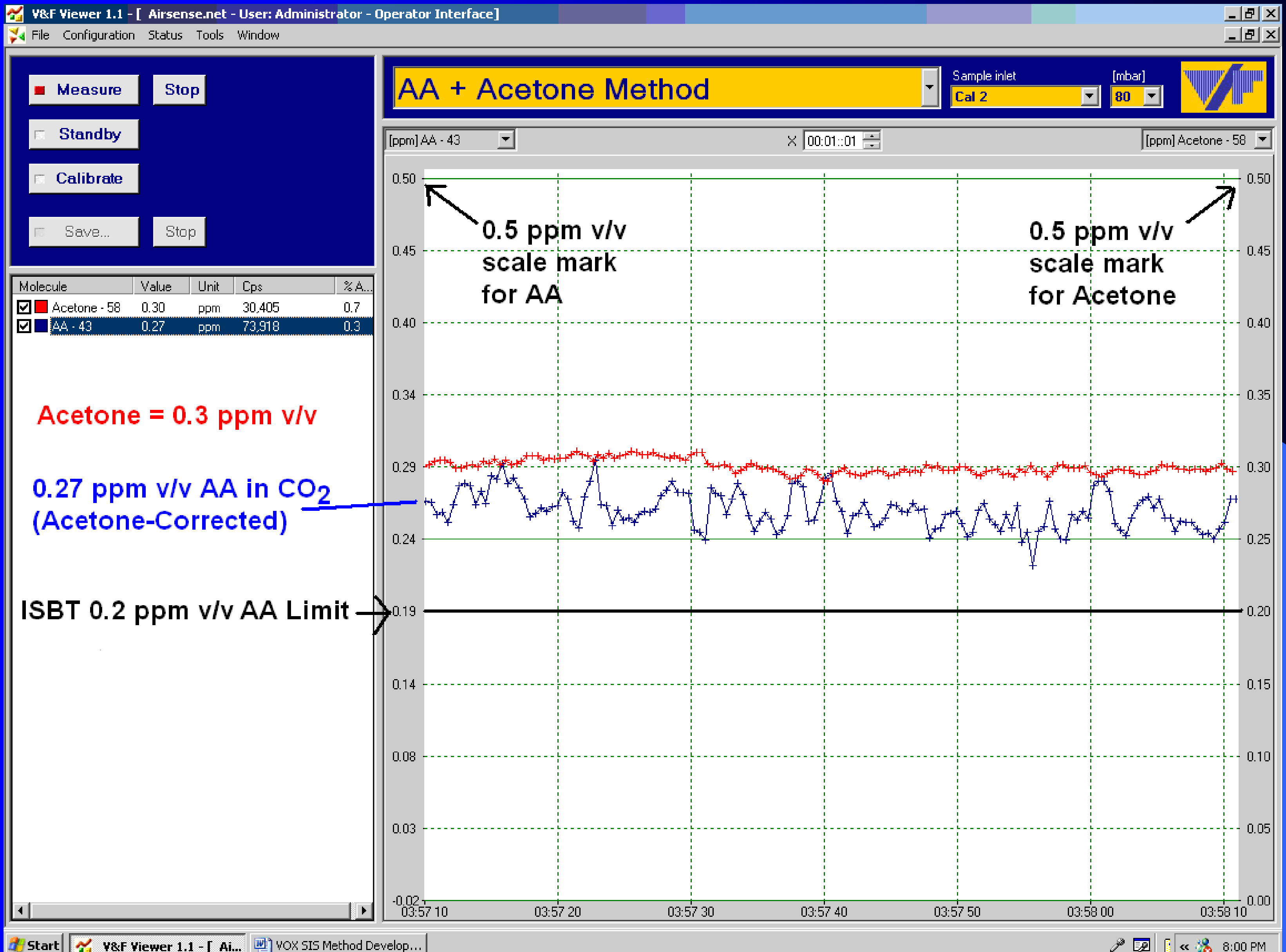
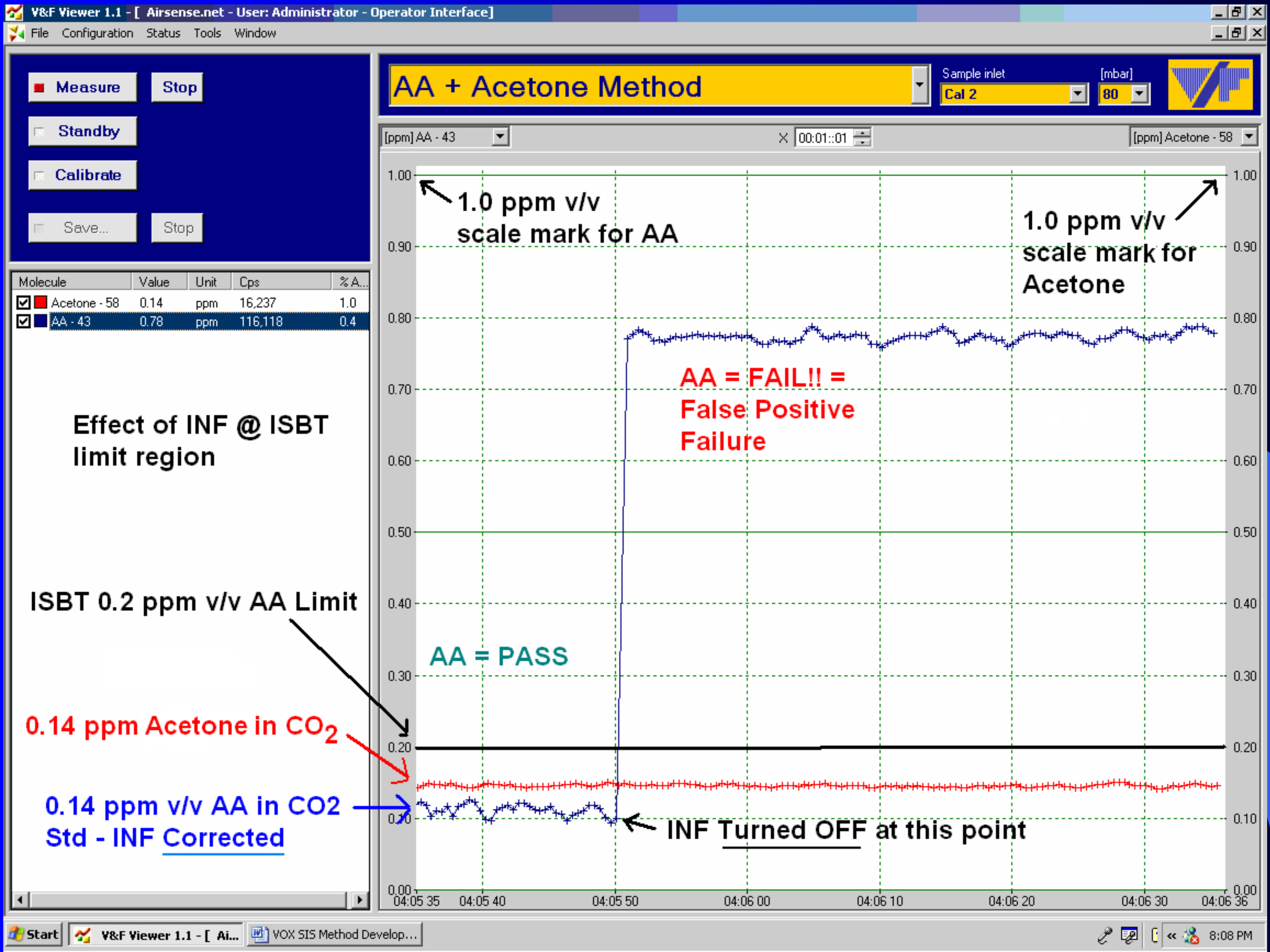
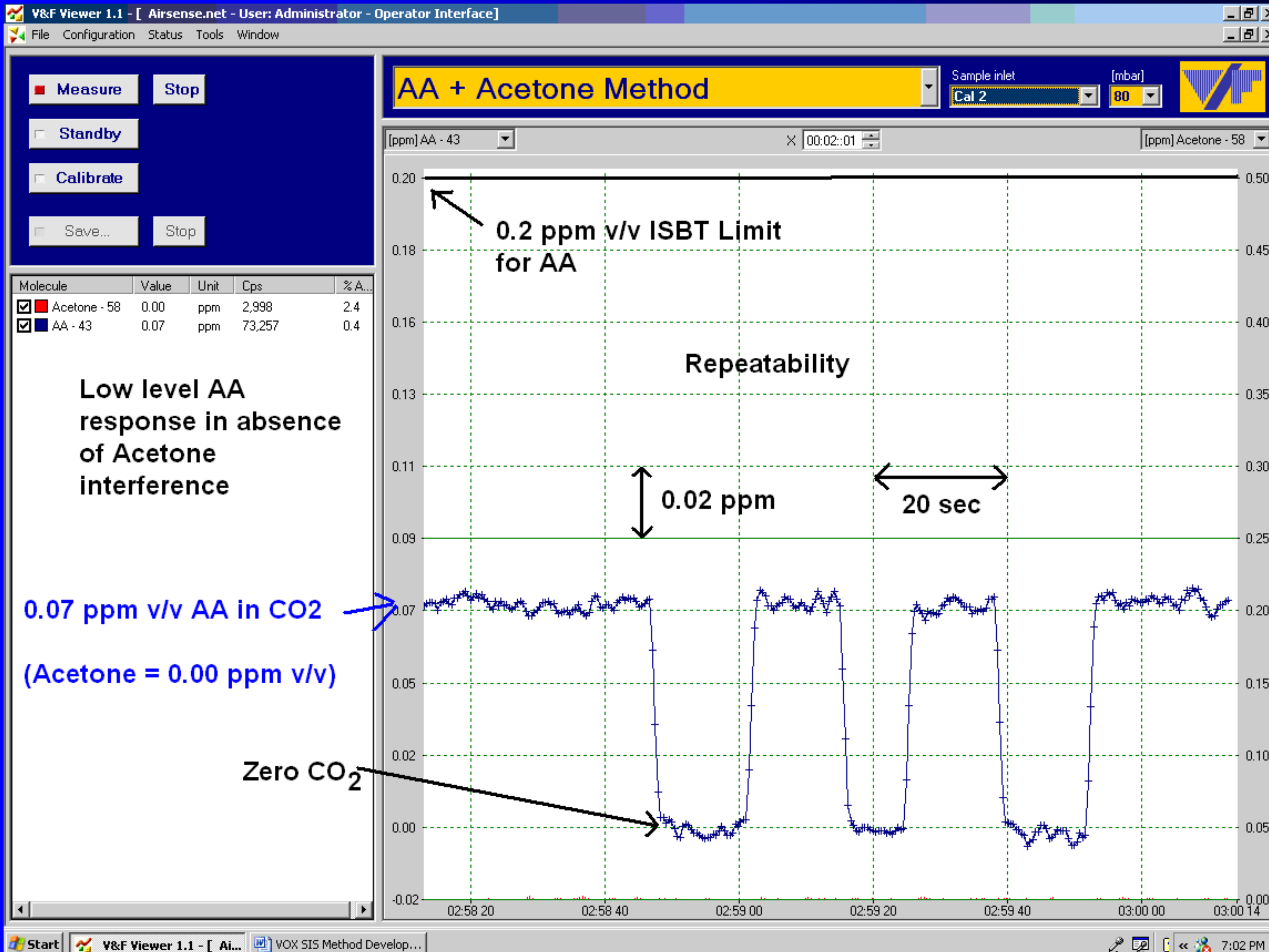
SIS Data: VOX in CO_2 @ 0.27 ppm v/v AA + Acetone INT Correction



SIS Data: VOX in CO_2 @ 0.1 ppm v/v AA + Acetone INF ON/OFF



SIS Data: VOX in CO_2 @ 0.07 ppm v/v AA – if No Acetone present



SIS - Volatile Hydrocarbons (VHC) Data

ISBT Limit = 50 ppm v/v THC as Methane including 20 ppm v/v max as Total Non-Methane HC's

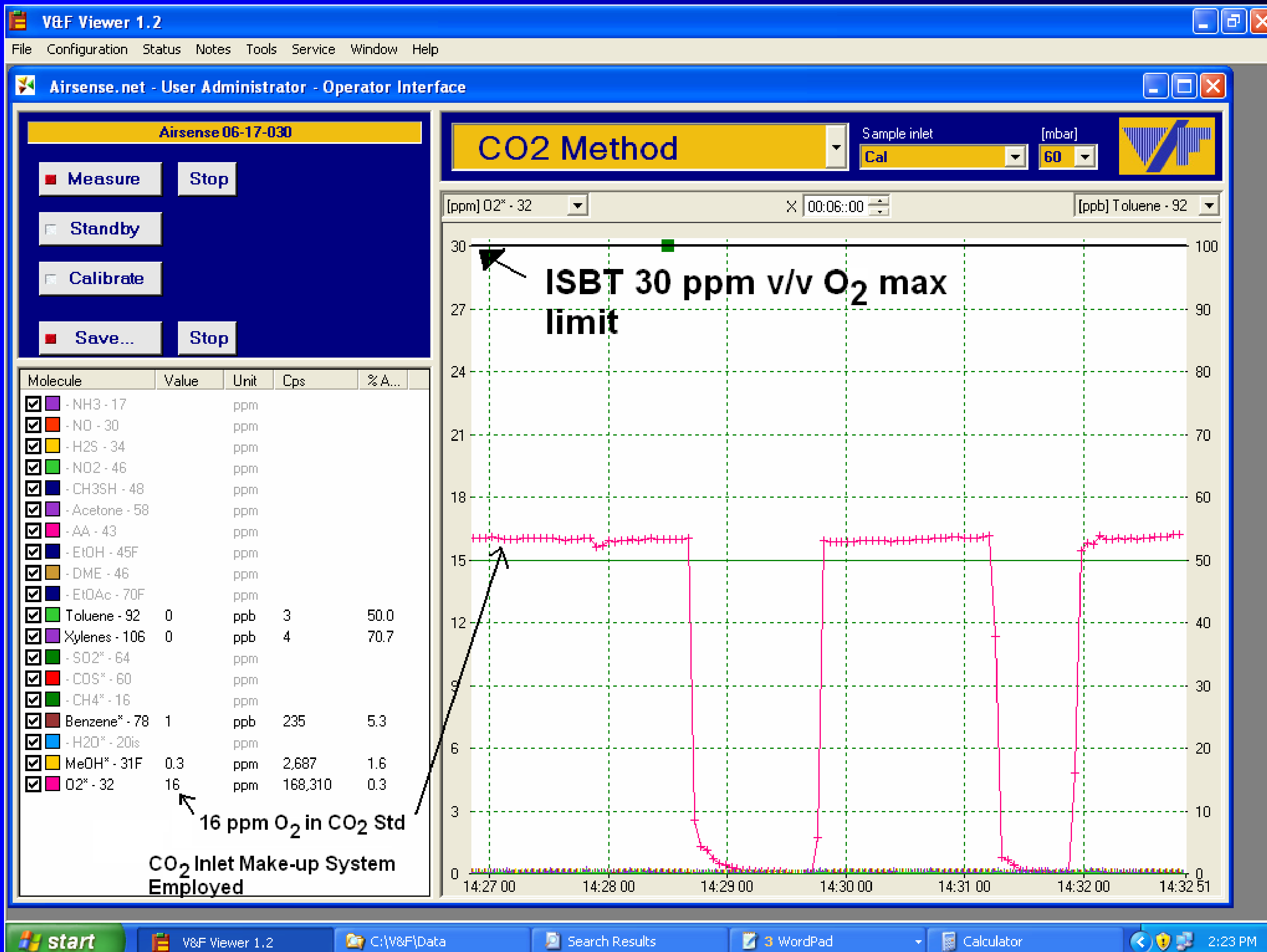
VHC	SIG	AM fr= Frag	LDR ppm v/v	DL ppm v/v	Interference (s)
CH_4	Xe	16	0 – 100+	LT 0.5	None found-to-date
Ethane	Xe	30	0 – 20+	LT 0.05	NO = INT (AM = 30)
Propane	Xe	29fr	0 – 10+	LT 0.05	Ethane = Minor INT, ETO = INT @ Frag = 29, n-Butane = Minor INT
N-Butane	Hg	58	0 - 5+	LT 0.05	Minor INT for AA
N-Pentane[1]	Hg	42fr	0 - 5+	LT 0.05	ID @ AM = 72 Parent

Note 1: n-Pentane C-C-C-C-C → C-C-C (AM=42) +

Other VHC's not studied-to-date

SIS Data: O_2 in CO_2 @ 16 ppm v/v (CO_2 MK-UP System Employed)

Use of CO_2-based Cal Gas Stds is recommended for all Analytes



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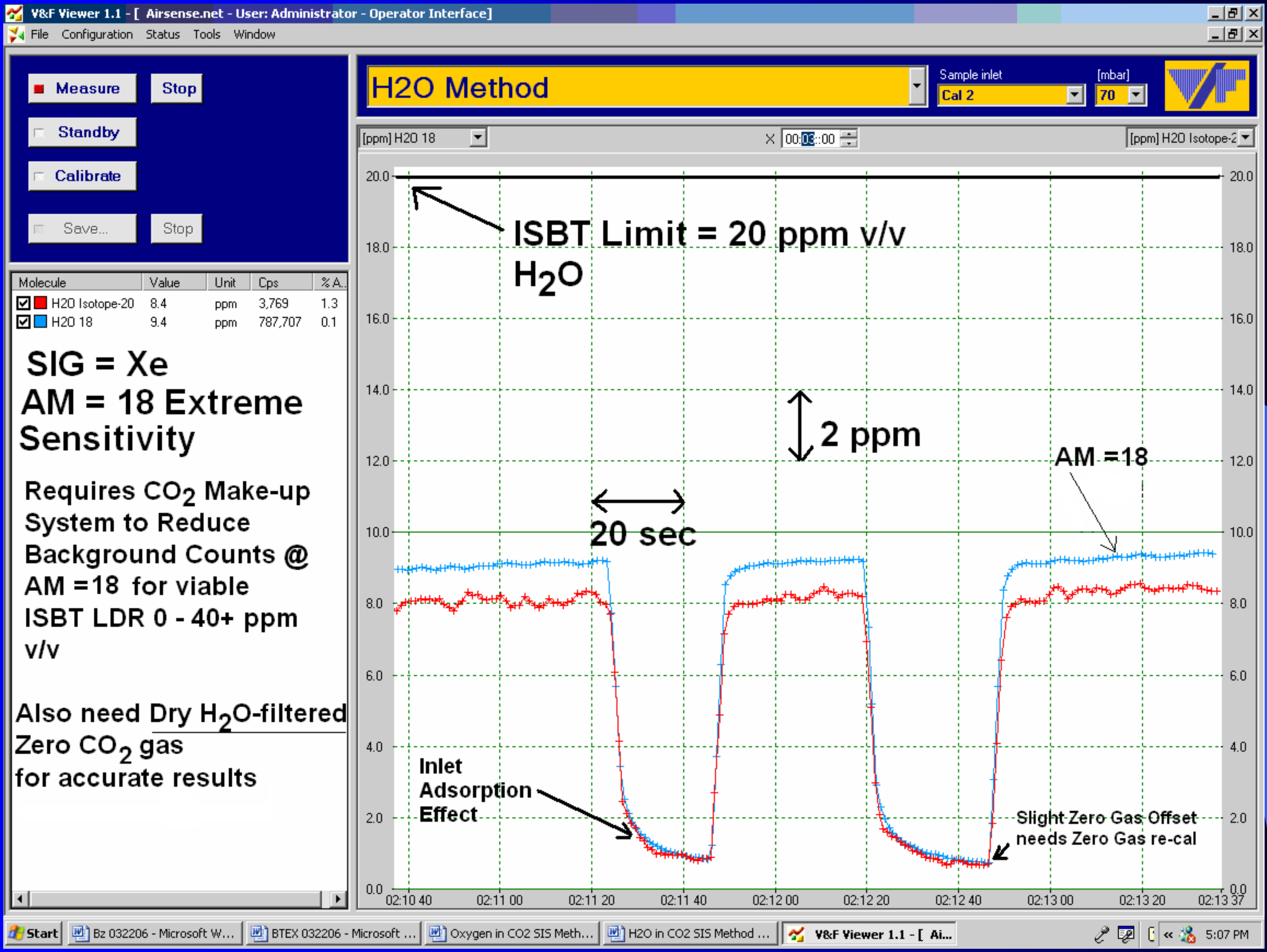
SIS Data: H_2O in CO_2 @ 8 ppm v/v Level

Use of Indirect H_2O Cal Method @ SIG = Xe is viable option



SIS – Data for Other ISBT Listed CO_2 Impurities

Impurity	SIG	AM FR = Frag IS = Isotope	LDR ppm v/v	DL ppm v/v	Interference (s)
O_2	Xe	32	0 – 40+	LT 1	None found-to-date
H_2O	Xe	18	0 – 30+	LT 1	None found to-date
NO	Hg	30	0 - 5+	LT 0.05	None found-to-date
NO_2	Hg	46	0 - 5+	LT 0.05	DME = INT AM = 46
NH_3	Hg	17	0 - 5+	LT 0.05	None found-to-date
HCN	Xe	27	0 - 5+	LT 0.1	VCl = INT HCN Lower DL @ SIG = Xe + Kr
VCl	Hg	64^{is}	0 - 5+	LT 0.05	Use VCl Isotope AM = 64

Note 1: PH_3 study not completed SIG = Hg, AM = 34

Note 2: CO work was not successful for this ISBT application

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SIS Applicability to ISBT CO_2 List

ISBT LISTED IMPURITY	SIS Measurable?	Comments
CO_2 Purity	NO (but positive CO_2 ID)	Can't do N_2, H_2, Ar
Moisture (H_2O)	**YES** (use CO_2 Make-up Gas)	Can go sub-ppm range
Oxygen (O_2)	**YES** (use CO_2 Make-up Gas)	Requires O_2 in CO_2 Stds
Carbon Monoxide (CO)	NO	Poor Sensitivity issues
Ammonia (NH_3)	**YES**	Needs passivated inlet
NO / NO_2	**YES** (+ speciation)	Some minor INF's (not common)
Non-Volatile Residue (NVR)	NO	Can't do particulates / non volatiles
Non-Volatile Organic Residue (NVOR)	NO (but C6+ = Yes)	Can't do V. Hi MW oils/grease
Phosphine (PH_3)	**YES** (+ H_2S) PH_3= RARE	Can't distinguish from H_2S
Total Volatile Hydrocarbons (THC) & TNMHC	THC = **YES** TNMHC = **YES**	Get CH_4 + Algorithm Sum of all TNMHC's vs THA-FID signal
Acetaldehyde (AA)	**YES** (+ VOX speciation)	Needs corrections for INF's
Aromatic Hydrocarbons (AHC)	**YES** (B-T-EX)	V good precision / low DL's no known INF's
Total Sulfur Content (TSC*) less SO_2	**YES** (+ speciation)	Algorithm Sum of VSC's
Sulfur Dioxide (SO_2)	**YES**	Easily Speciated from COS
HCN	**YES**	V. Low DL no common INF
Vinyl Chloride	**YES**	V Low DL

SUMMARY

SIS Performance vs Traditional Bev-Gas Analyzers

- **Speed**: Advantage vs many analyzer systems (e.g. LT 1 min vs 10-20 min for full ISBT analyte list)
- **Footprint:** Good vs common analyzer rack systems
- **Versatility**: Flexible list of monitored impurities vs most traditional Analyzers
- **Speciation Capability**: Less than GC but advantages vs single analyte analyzers. Minimizes DT use.
- **Measurement Quality**: LDR / Precision / DL: equivalent or superior to traditional analyzers
- **Freedom from Interferences**: Mixed – Application dependent: For AHC - is superior to many systems. Awareness of interferences is key to success (e.g. AA). Proper SIG / AM selection, Sequencing + Software-correction routines are effective in most cases.
- **Calibration**: Indirect Calibration = advantage. Recommend CO_2 based Cal gas – a disadvantage
- **Support**: Does not require He, N_2, H_2, Zero Air or expert/skilled operators
- **Maintenance**: Need for periodic SIG gas replacement + SIG Filament changes

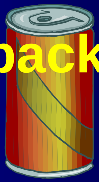
Where do we go from Here?

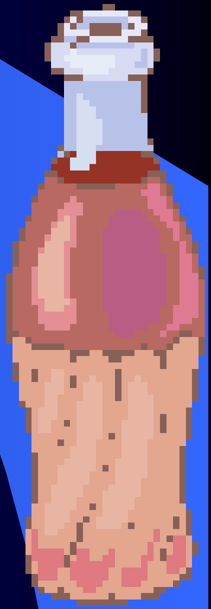
R&D – New **CO_2 SIS Methods Development *Feedgas* + *in-Process Gas* (e.g. Before/After Filter Beds = instant bed breakthrough warning) + *<u>Captured</u>* Recycle Gas use!**

-Trace O_2 in Bev-Grade N_2 (*NEW* ISBT N_2 Guidelines coming)

- Impurities in PET bottles, preforms & resins (e.g. AA levels)

SIS-based **Methods for trace aromatics in new / aged packaged beverages (shelf-life / stability testing)**





-AND Beyond??

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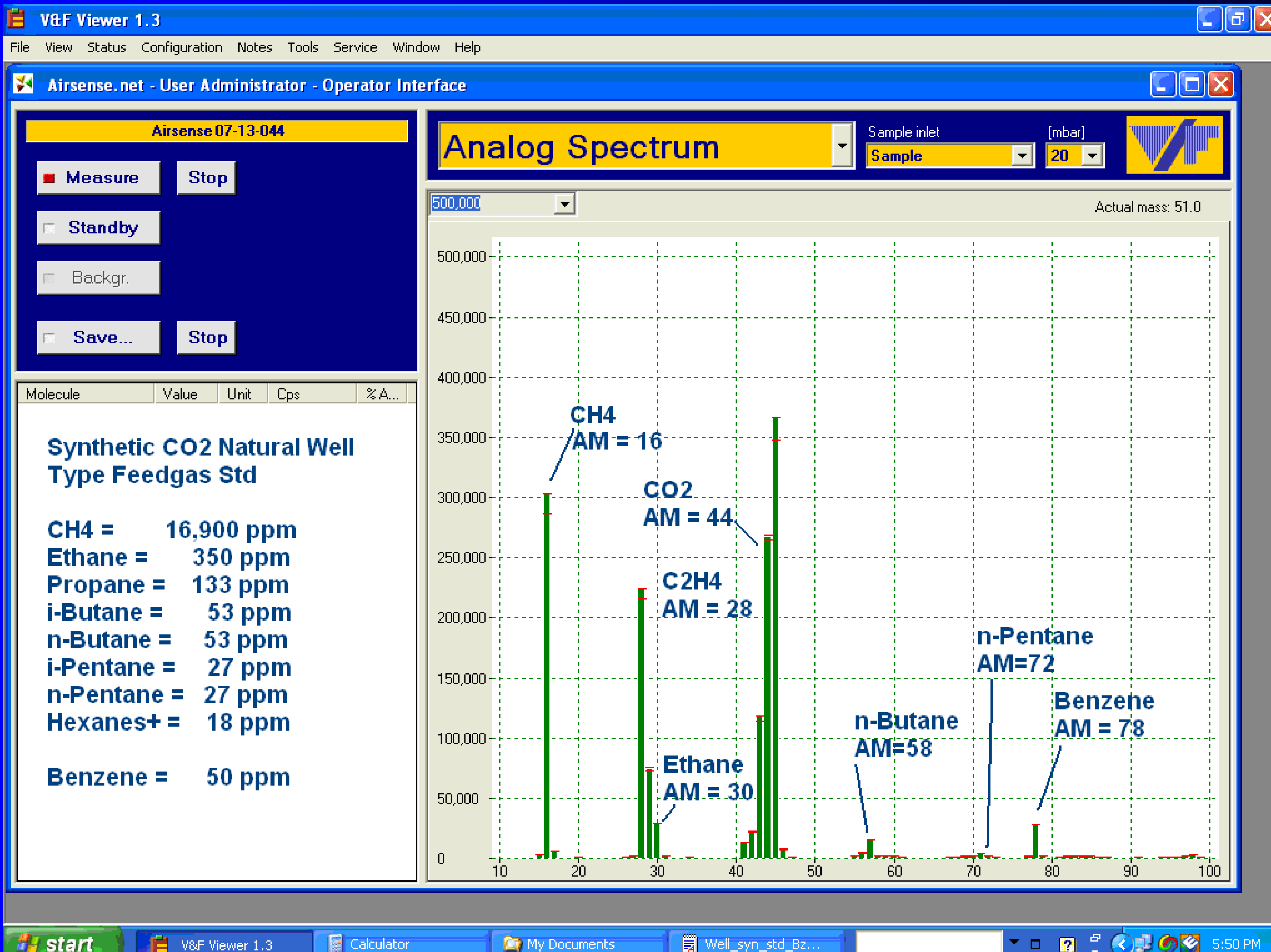
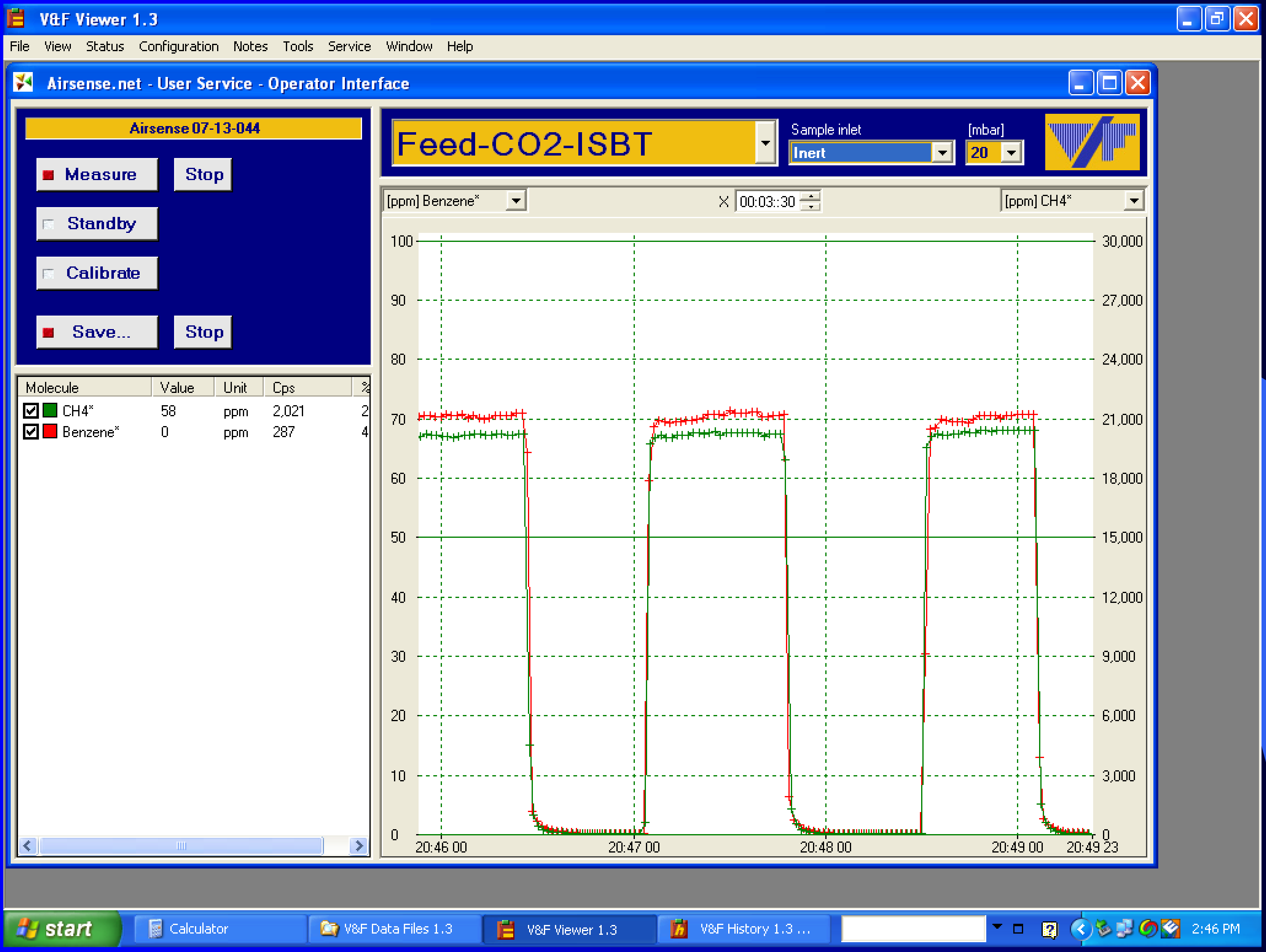
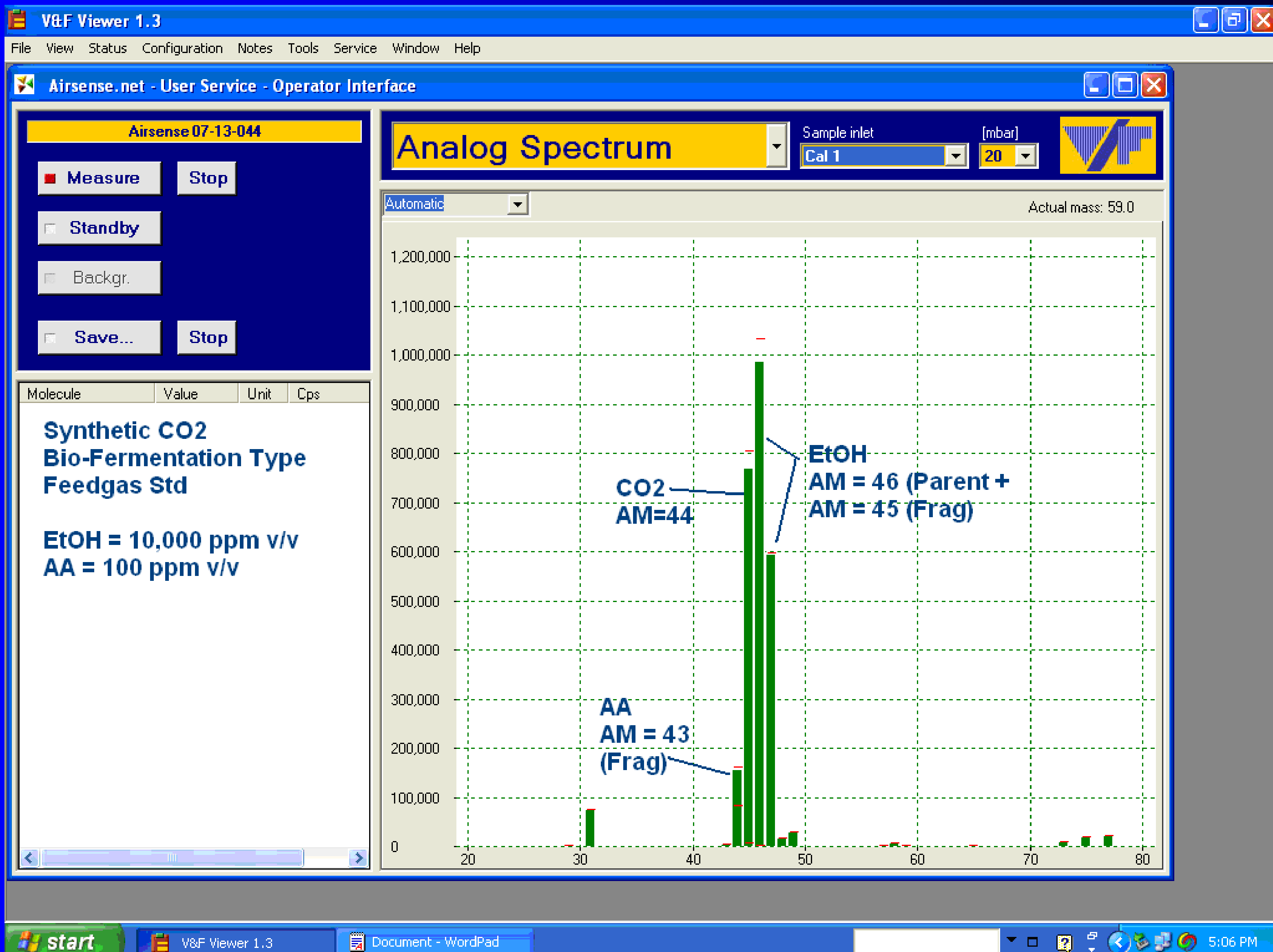
CO_2 Feedgas Method R&D - NatWells



CO_2 Feedgas Method R&D – NatWells Method Optimization In-Progress



CO_2 Feedgas Method R&D - BioFerm



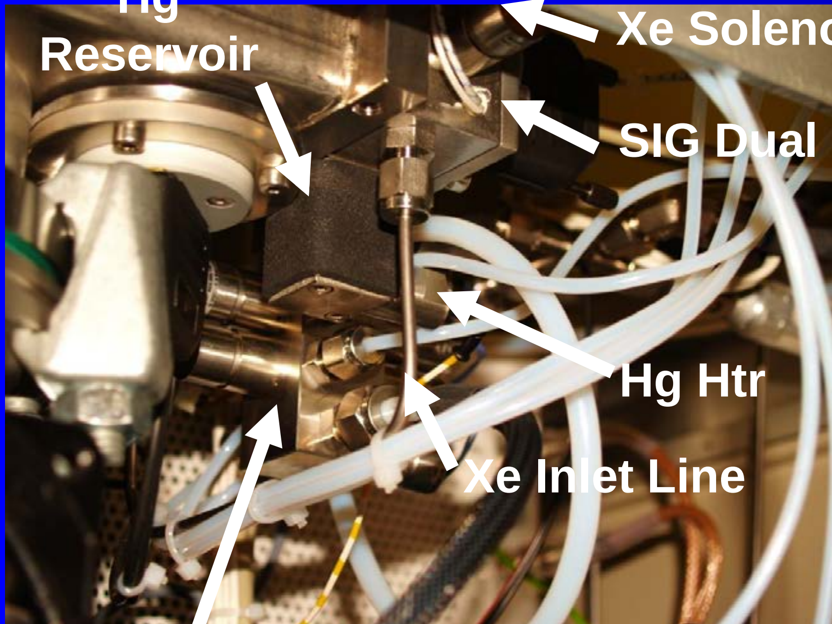
Acknowledgements

Our Special Thanks to:

Mr. Rodney Resch & Mr. Walter Woodland – ***V&F*** Instruments

Questions??

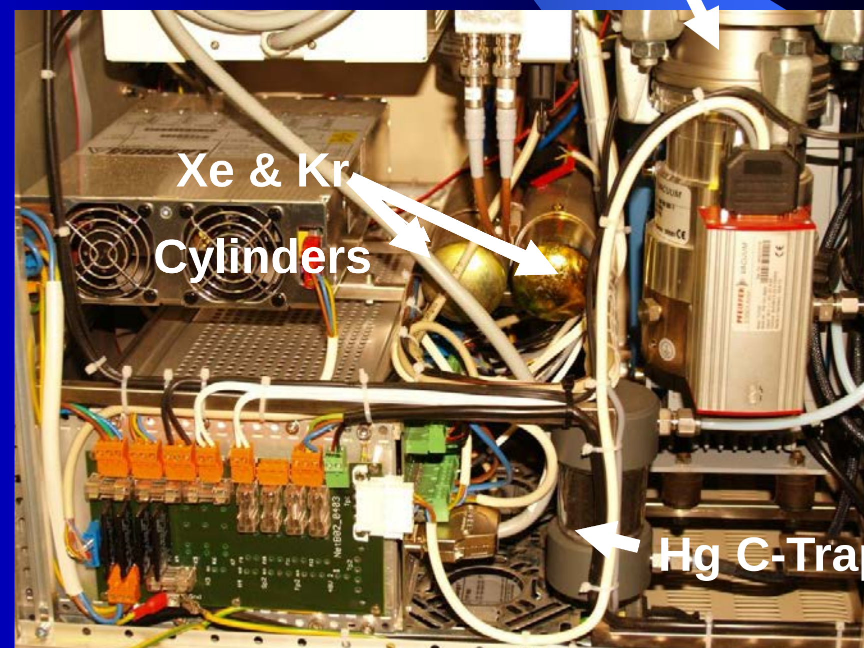
SIS Analyzer – Under-the-Hood



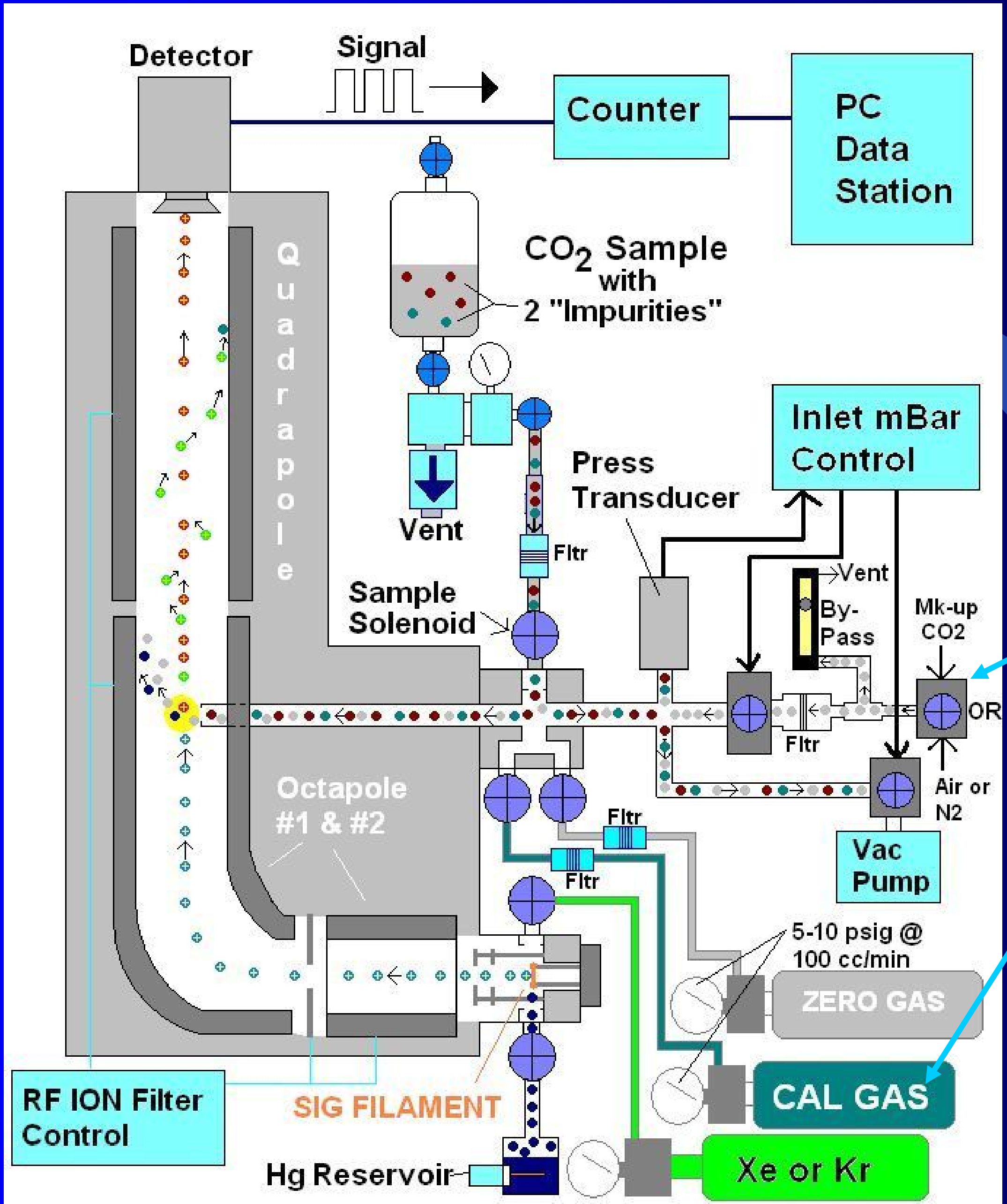
Sample / Span Gas / Zero

Gas Inlet Manifold & Solenoids

Left Side View →



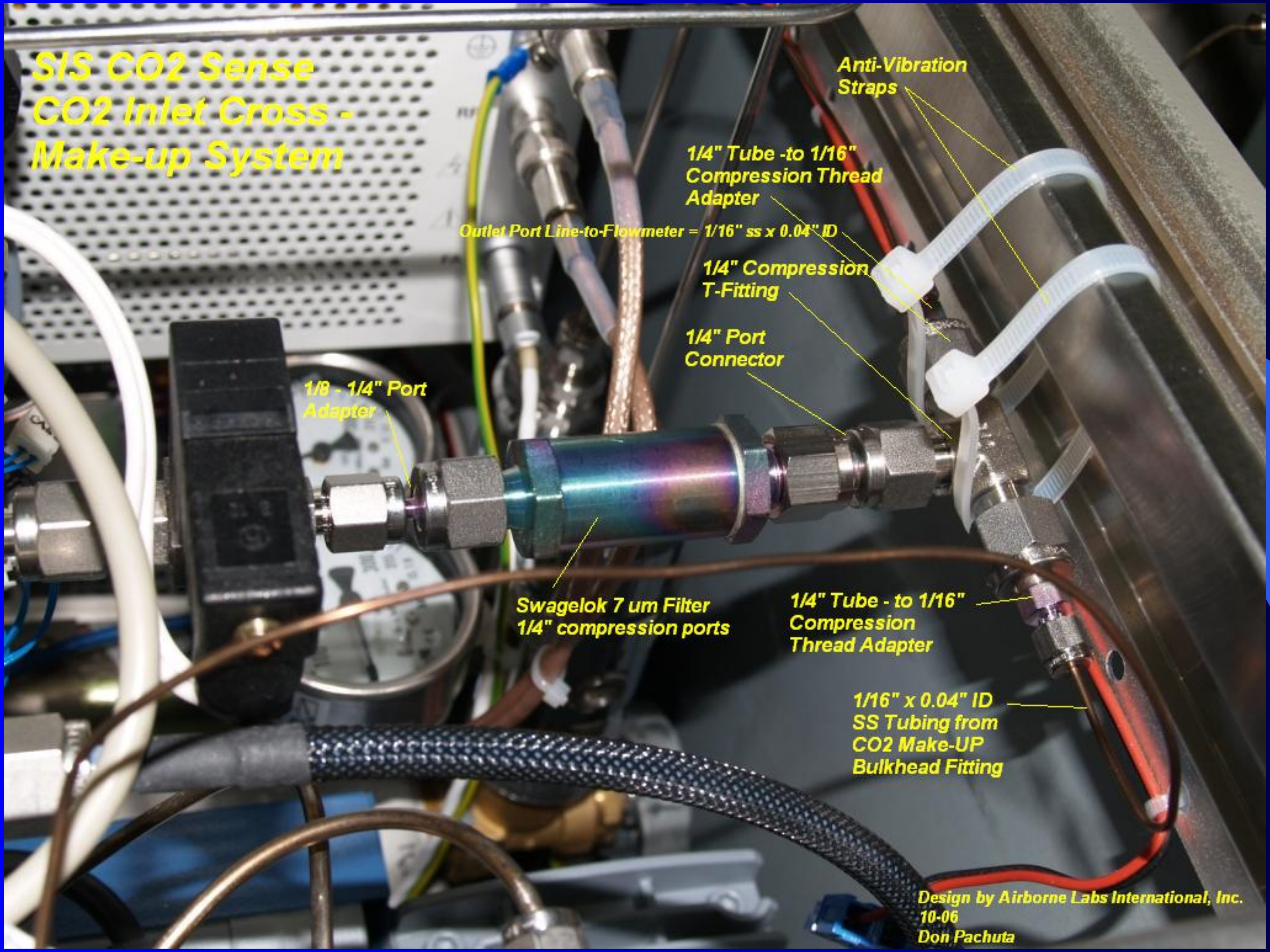
The "Soft Ionization" Process – *NEW* CO_2 System



***New* Inlet Pressure Make-Up System Developed**

3 Optimized ISBT Cal Gas Stds in CO_2 Developed

New CO_2 Make-up System



Required for accurate trace O_2 + H_2O SIS measurements

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NEW - ISBT List SIS Calibration Strategy *(3 Combo Cal Std Cylinders – CO_2 Balance Gas + Certified – 3-stage filtered CO_2 Zero Gas Std)*

SIS Cal Std #1: ***Benzene – COS – AA – CH_4***

SIS Cal Std #2: ***Acetone – DME – DMS – O_2***

SIS Cal Std #3 Option 1: ***CO – Ethane – MeOH – NO_2***

or

SIS Cal Std #3 Option 2: ***CO – n-Pentane – EtOH – NO_2***

Certified Zero Gas – *ISBT-List* Tested 20 lb Tank of High Purity CO_2 + 3-bank Filtered (H_20 – Charcoal – O_2 scrubber cartridges)

List of key Cal Std analytes selected -- based on *SIG Gas* + *AM's* used + *interference correction* routines used & ability to act as *accurate surrogate stds* for <u>other</u> ISBT List target analytes (e.g. H_2S, SO_2 , NO, TEX, H_2O, HCN, etc)

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NEW THC / TNMHC / TCS*+ TOVO Algorithms

Required for SIS data correlation to existing (historical) THC (FID), GC and TSC Analyzer Data + ISBT / Bottler Impurity Guideline Limits

- ***THC (FID) Equivalence*: R_{fi}'s of all common THC (FID) active impurities (e.g. C2-C5 VHC's + VOX + VSC targets *established & algorithm written* – to convert *SIS* data into THC(FID) "equivalence as CH_4" values + *TNMHC calculated* (THC – CH_4).**
- ***TSC* Equivalence: SIS* Algorithms written to properly calculate *TSC** value (based on ISBT Method 14.0) of all *SIS speciated* VSC targets – less SO_2.**
- ***TOVO (Total "Other" Volatile Oxygenates) Equivalence*:**
- **SIS Algorithm written to calc TOVO from *SIS speciated* VOX data.**