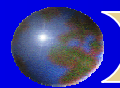


Soft Ionization Spectrometry (SIS):

One Step Closer to a “Magic Box” for Complete Bev-Gas Testing

Presented at the ISBT Quality Conference – Myrtle Beach - 2006



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Background - Review Industrial Sources of CO₂ + 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 Sensory & Toxic Impurities

ISBT Bev-Gas Quality Challenges

- As beverage production grows, *continuous* quality testing becomes v important
- CO₂ Quality Assurance is a complex technical challenge
- All dream of a “Magic Box” that can quickly monitor the *entire ISBT Impurity List*

ISBT CO₂ Purity Guidelines

"The List"

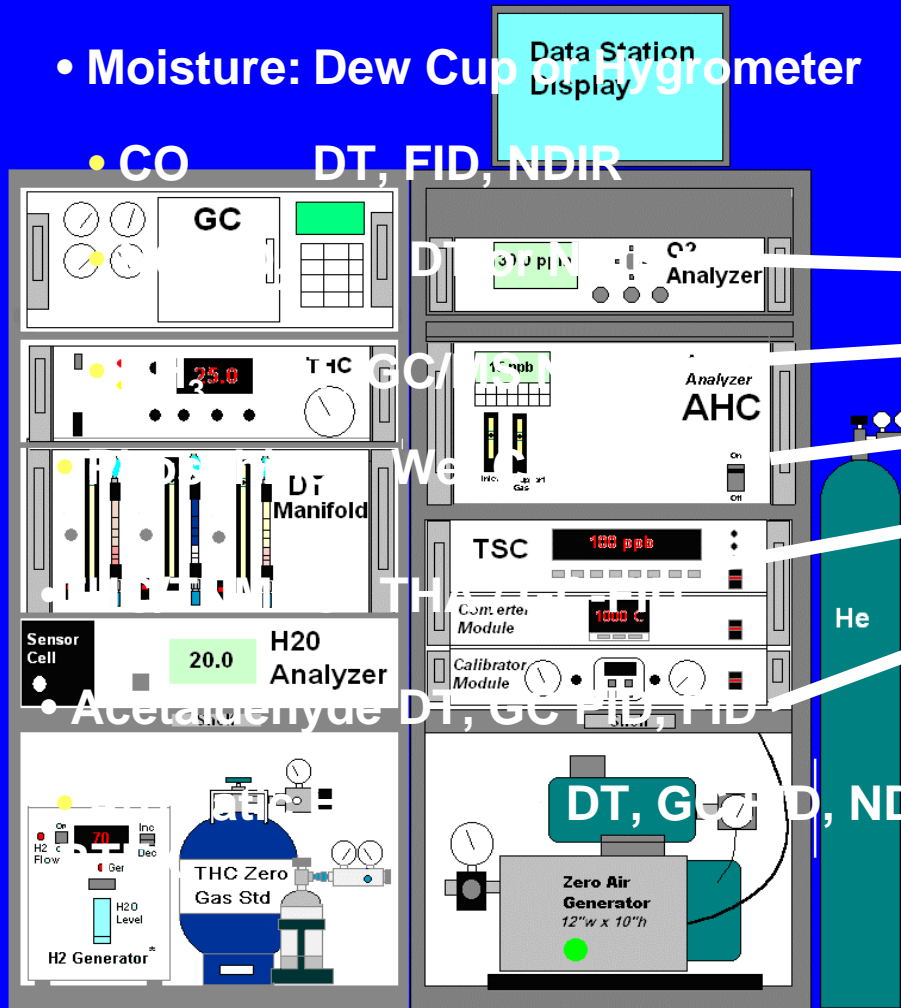
CO₂ Purity	99.9% min	Process
Moisture (H₂O)	20 ppm v/v max	Process
Oxygen (O₂)	30 ppm v/v max	Sensory
Carbon Monoxide (CO)	10 ppm v/v max	Process / Regulatory
Ammonia (NH₃)	2.5 ppm v/v max	Process
NO / NO₂	2.5 ppm v/v (ea) max	Regulatory
Non-Volatile Residue (NVR)	10 ppm x/x max	Sensory
Non-Volatile Organic Residue (NVOR)	5 ppm w/w max	Sensory
Phosphine (PH₃)	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 SO₂	0.1 ppm v/v max	Sensory
Sulfur Dioxide (SO₂)	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 CO₂ Analyzers?

- CO₂ Purity: Zahm/Nagel or GC/MS

- Moisture: Dew Cup or Hygrometer

- CO DT, FID, NDIR



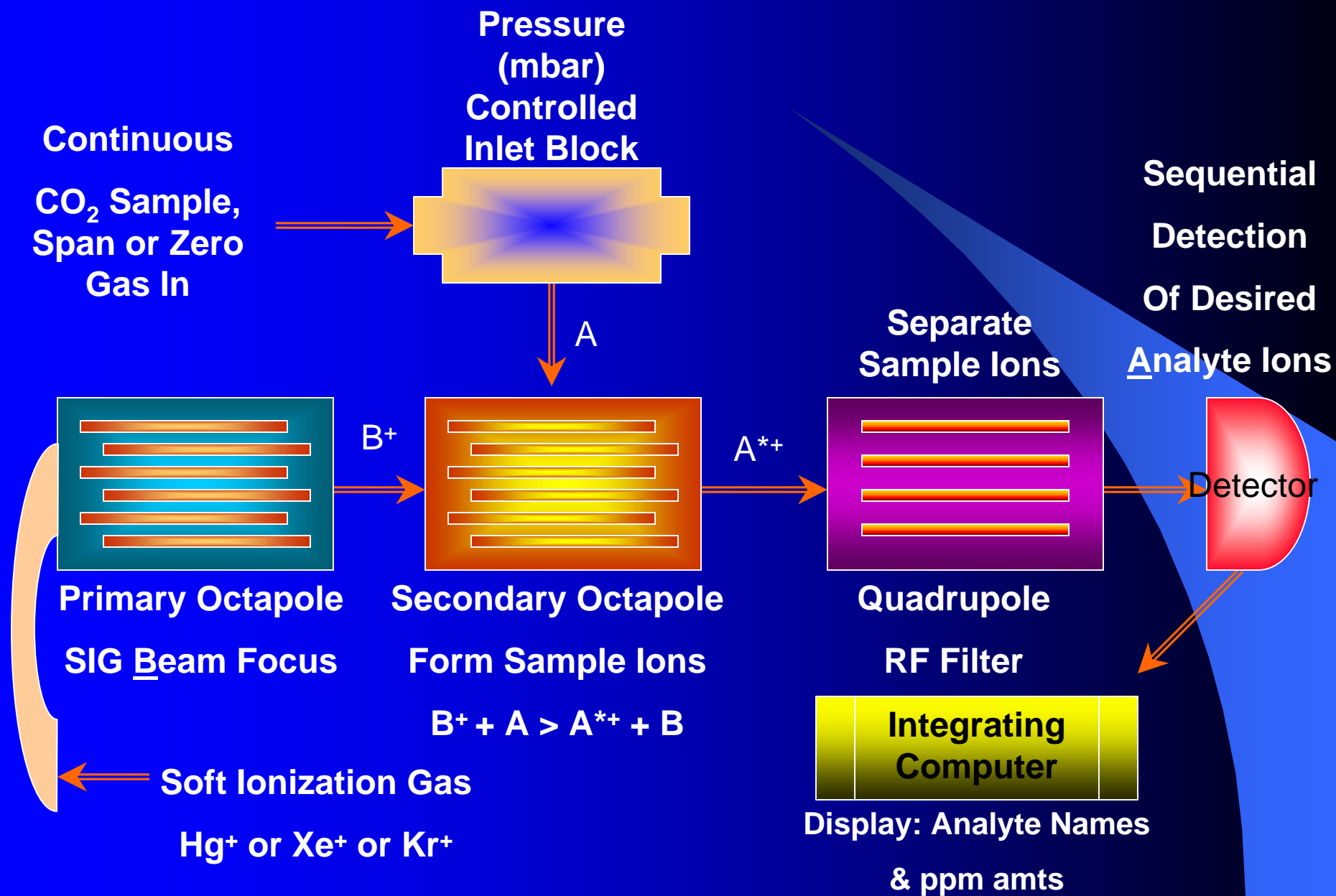
- HCN/VCL DT or Wet Chem

- SO₂ or TRS DT, SCD, CLD

What Is Soft Ionization Spectrometry?

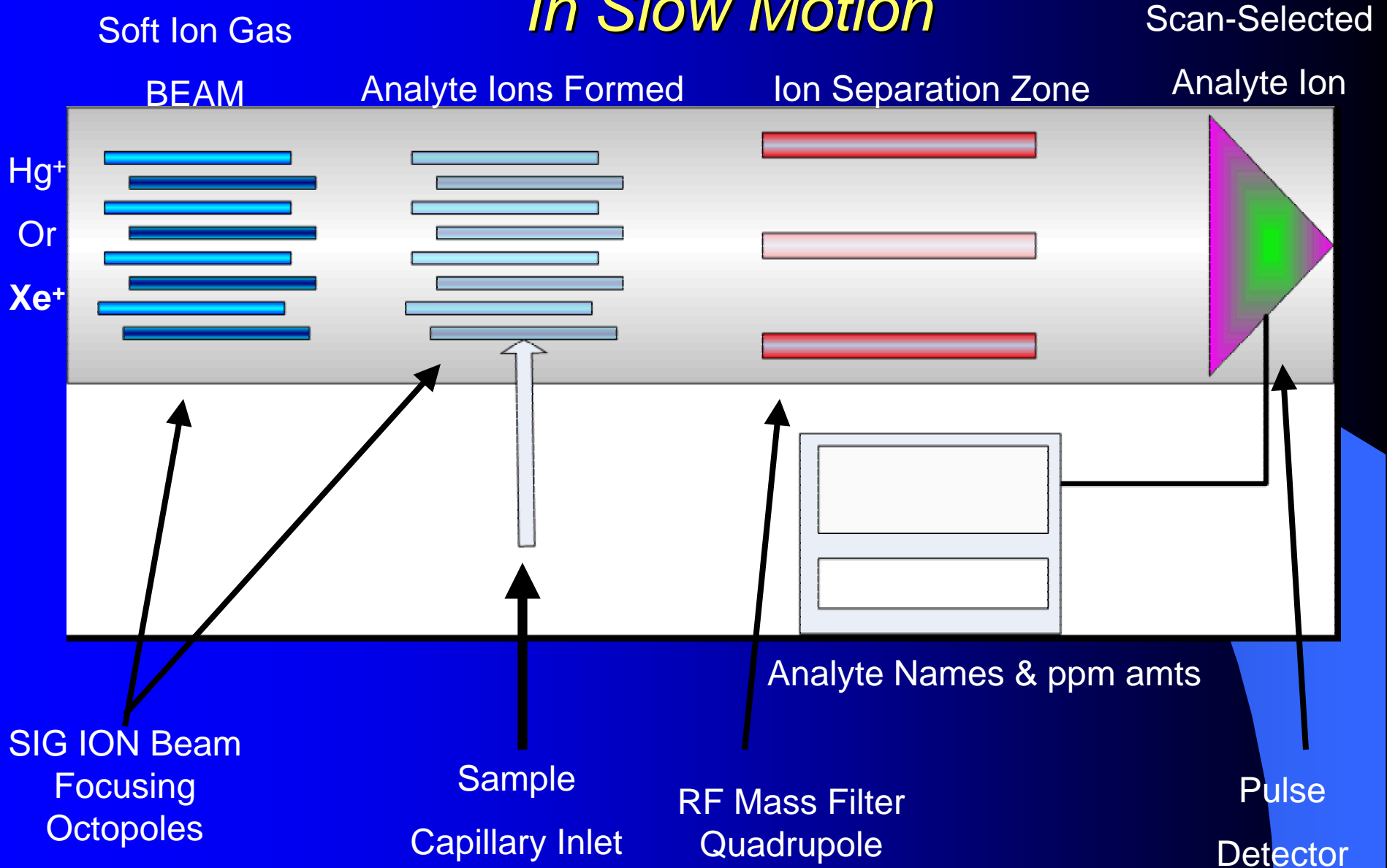
- SIS is a Mass Selective Analyzer:
- CO₂ Sample is **continuously** injected into a **Low Energy Ion Beam** of Hg⁺ or Xe⁺ or Kr⁺ = soft ionization gas (SIG)
- Sample impurities (analytes) softly fracture into **only a few** characteristic ion fragments
 - Fragments are **size-separated** by a scanning 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 + Std Prep/Support Equipment

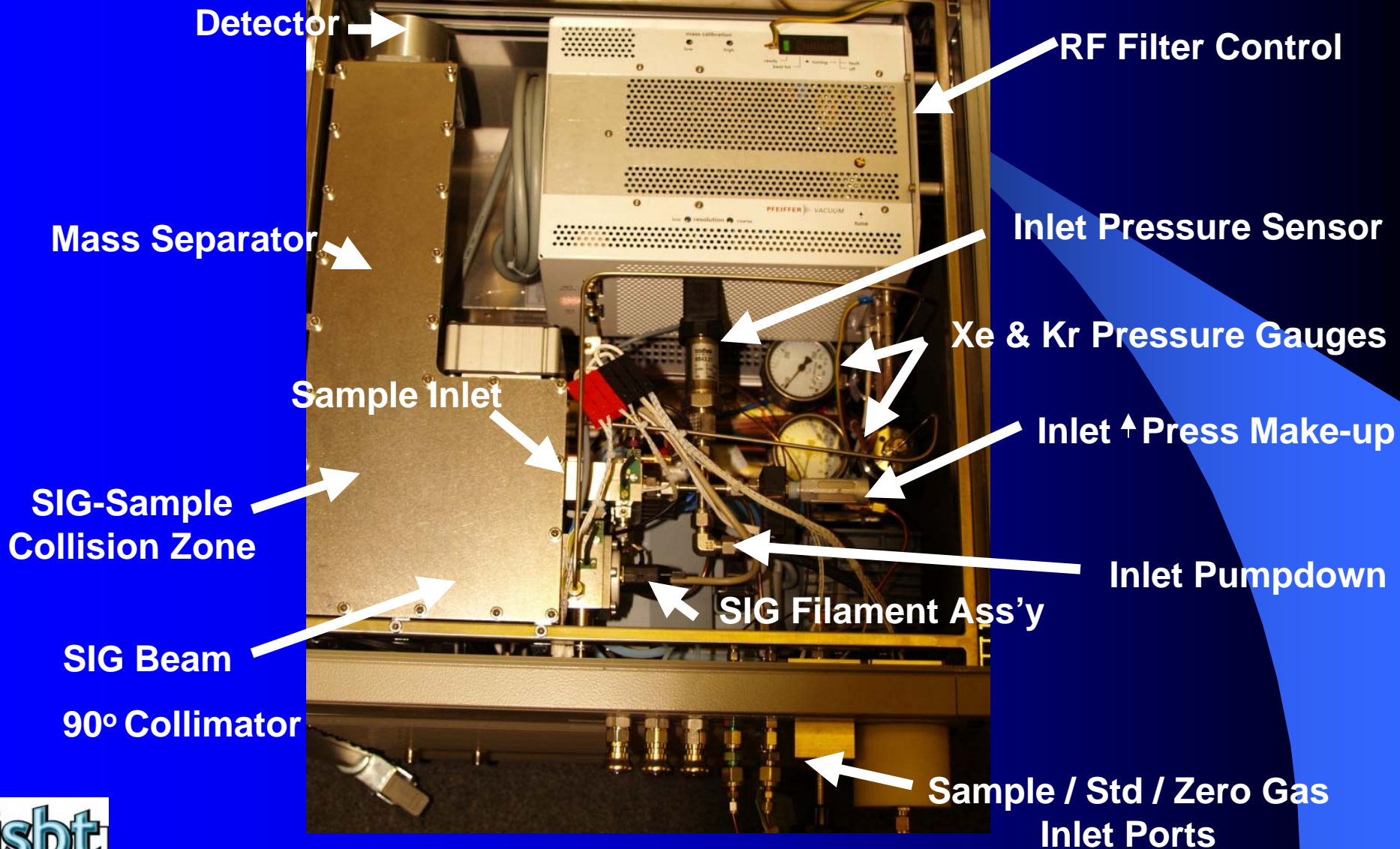
Our Evaluation System



Zero
CO₂
Stds

SIS Analyzer – Under-the-Hood

TOP VIEW



SIS - a “New Application” of an Established Technology

- SIS is a relatively “mature” technology
- Traditional Applications:
 - Environmental Air Testing
 - Combustion Kinetics / Catalyst Testing

Applications where *many* analytes exist for only milliseconds & must be *quickly* quantified

- Recent: European CO₂ supplier QC + PET bottle recycling / testing

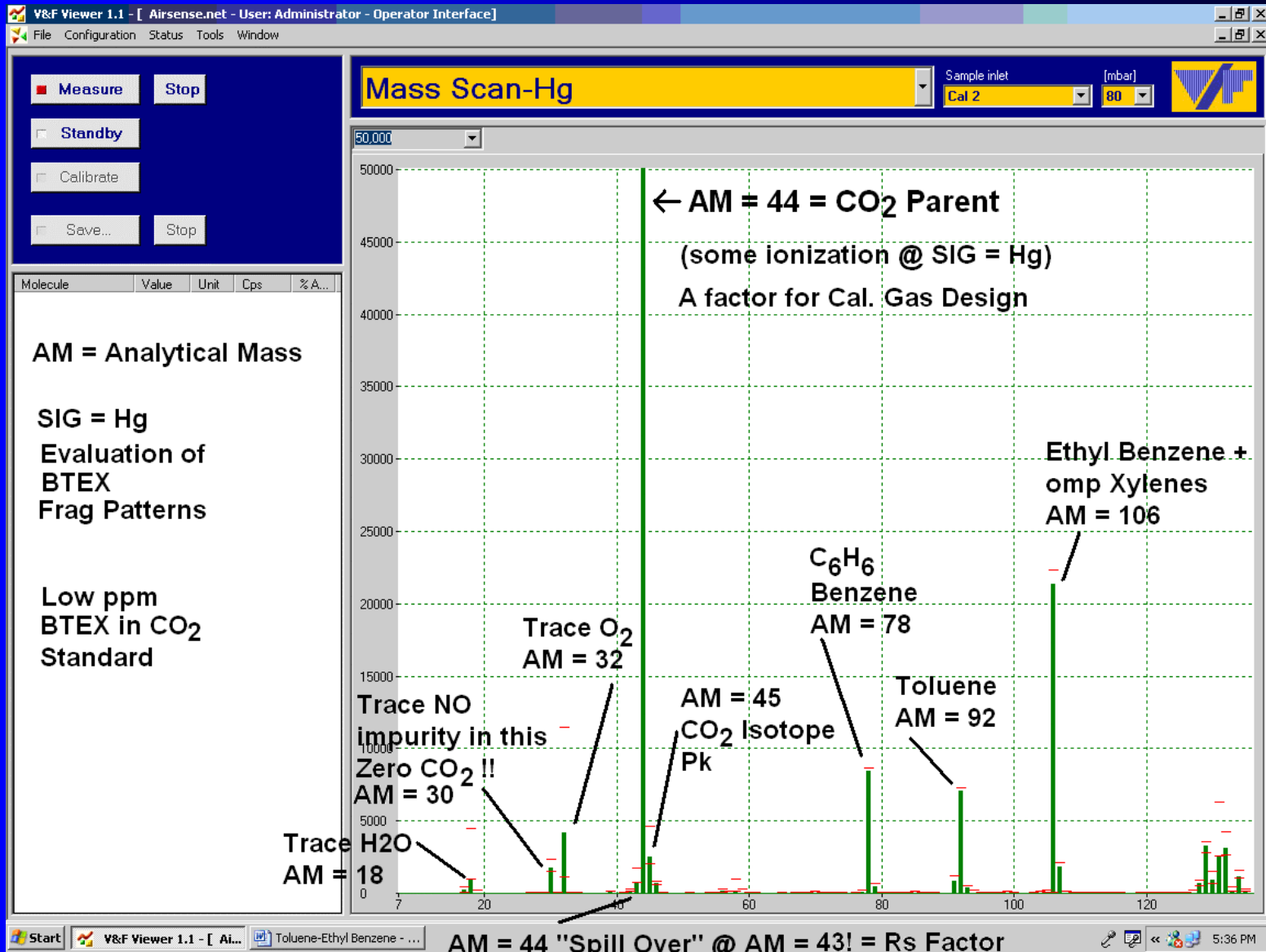
So, How might SIS work in the “*Real World*” of Bev-Gas Testing?

Our R&D Objectives

- Develop SIS Methods (SIG, AM, Scan, Count) for key ISBT-listed CO₂ 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

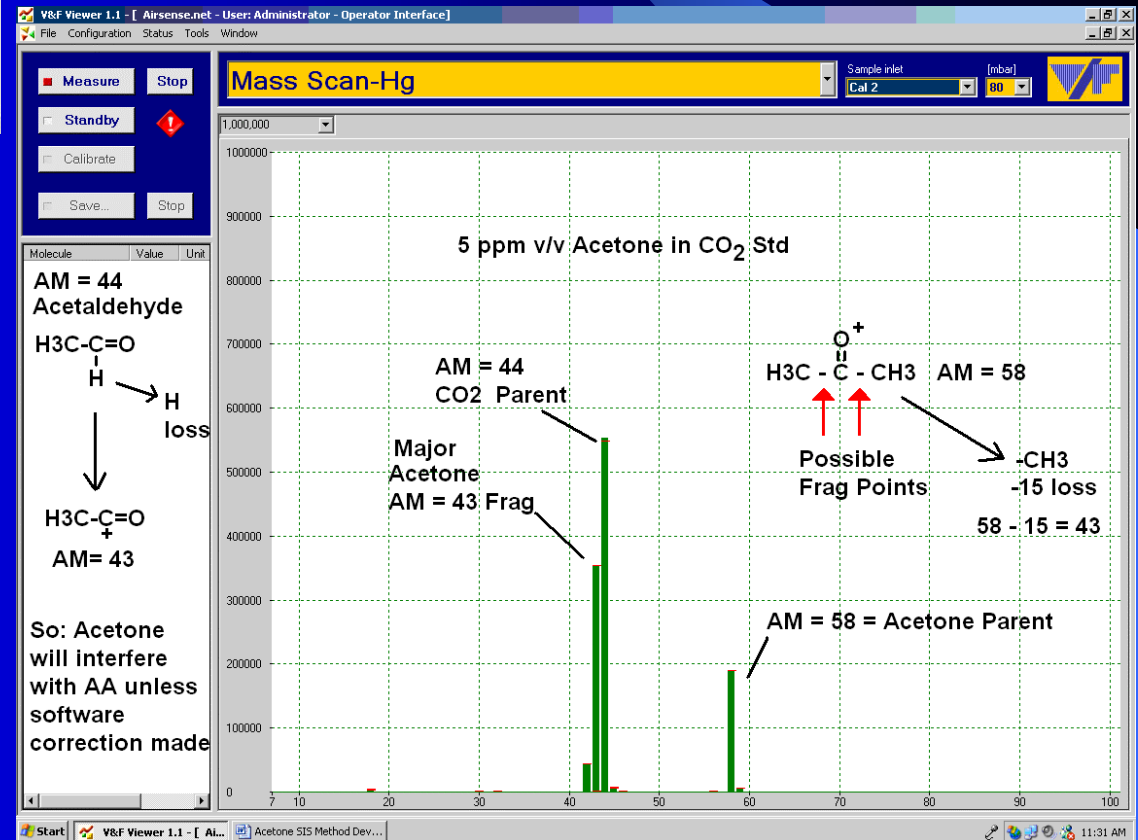
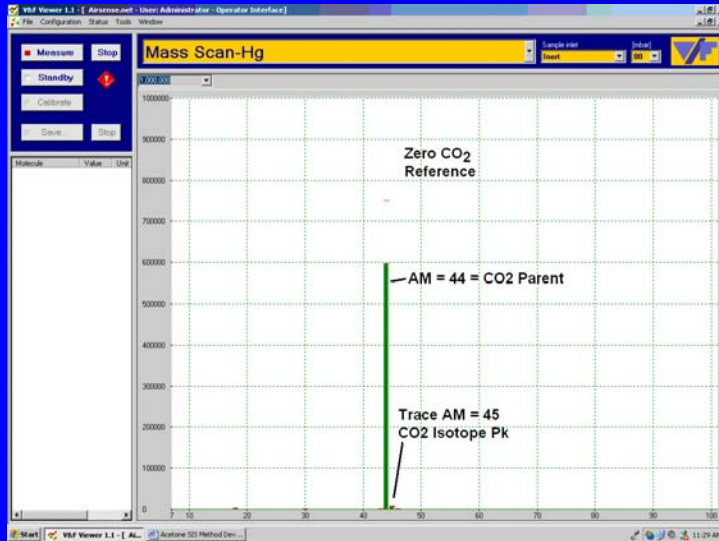
SIG & AM Selection Process

Sometimes its "easy"



SIG & AM Selection Process – The “Frag Factor”

(Sometimes its not-so-easy)

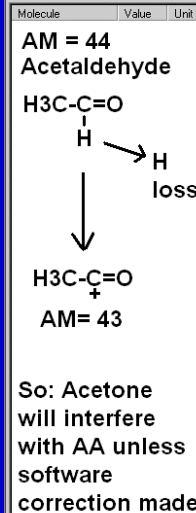


Basic SIG & AM Studies

Needed to ID potential Interferences for design of

Appropriate Software & Calibration Routine

Corrective Measures



SIS - Aromatic Hydrocarbon (AHC) Data

(ISBT CO₂ Limit = 20 ppb v/v as Benzene + report all other target AHC's)

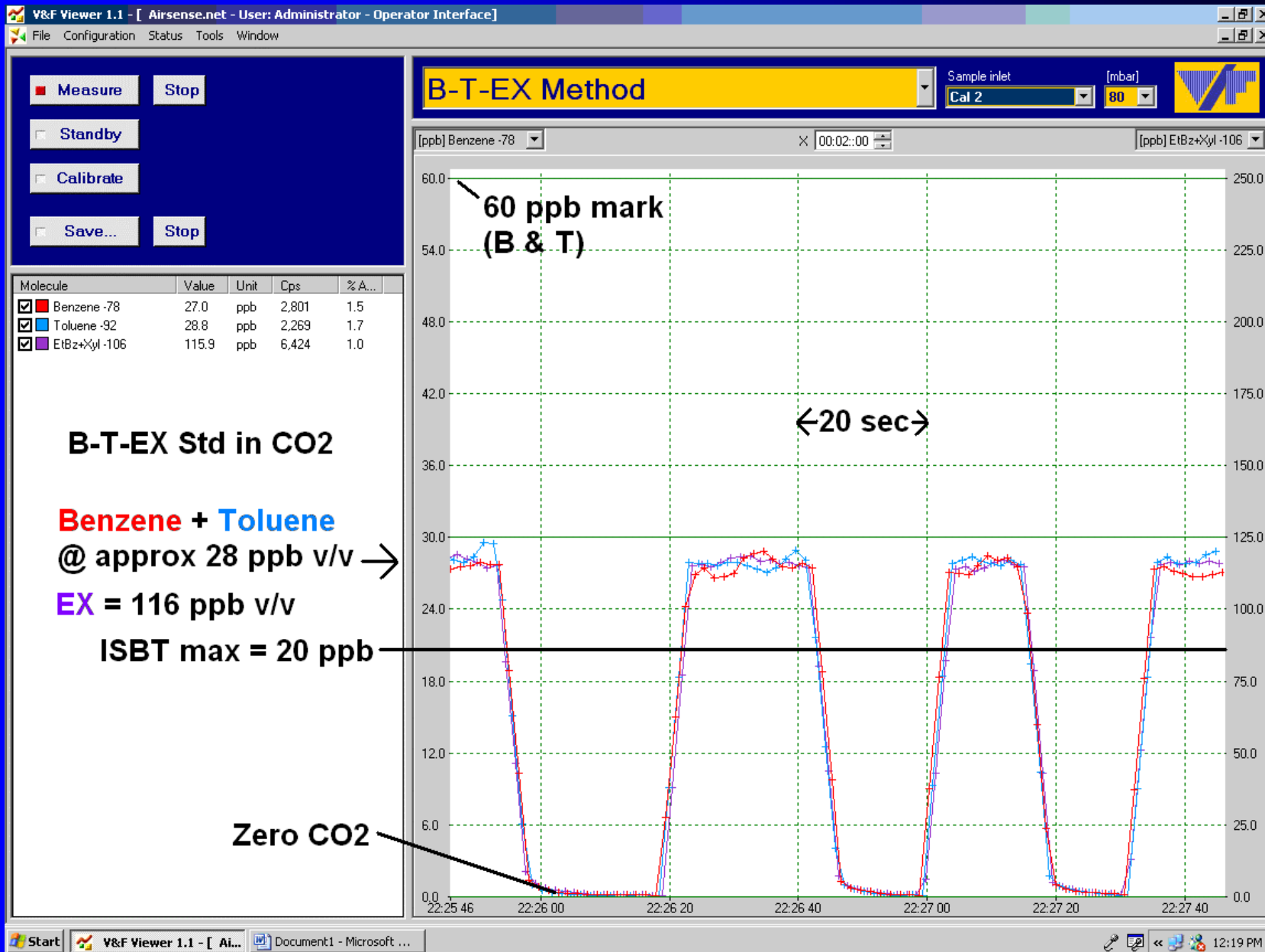
Our Results

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 CO₂ @ 28 ppb v/v level



SIS Data: B-T-EX in CO₂ @ 15 ppb v/v level



V&F Viewer 1.1 - [Airsense.net - User: Administrator - Operator Interface]

File Configuration Status Tools Window

Measure Stop

Standby

Calibrate

Save... Stop

B-T-EX Method | Sample inlet: Cal 2 | [mbar] 80

[ppb] Benzene -78 | X 00:02:01 | [ppb] EtBz+Xyl -106

60 ppb scale mark
B & T

6 ppb

ISBT 20 ppb AHC Limit

Benzene + Toluene @ 15 ppb v/v
EX @ 61 ppb v/v

Zero CO2 0.0 ppb v/v

Molecule	Value	Unit	Cps	% A...
<input checked="" type="checkbox"/> Benzene -78	14.6	ppb	1,520	2.1
<input checked="" type="checkbox"/> Toluene -92	14.6	ppb	1,157	2.4
<input checked="" type="checkbox"/> EtBz+Xyl -106	60.5	ppb	3,369	1.4

12:27 PM

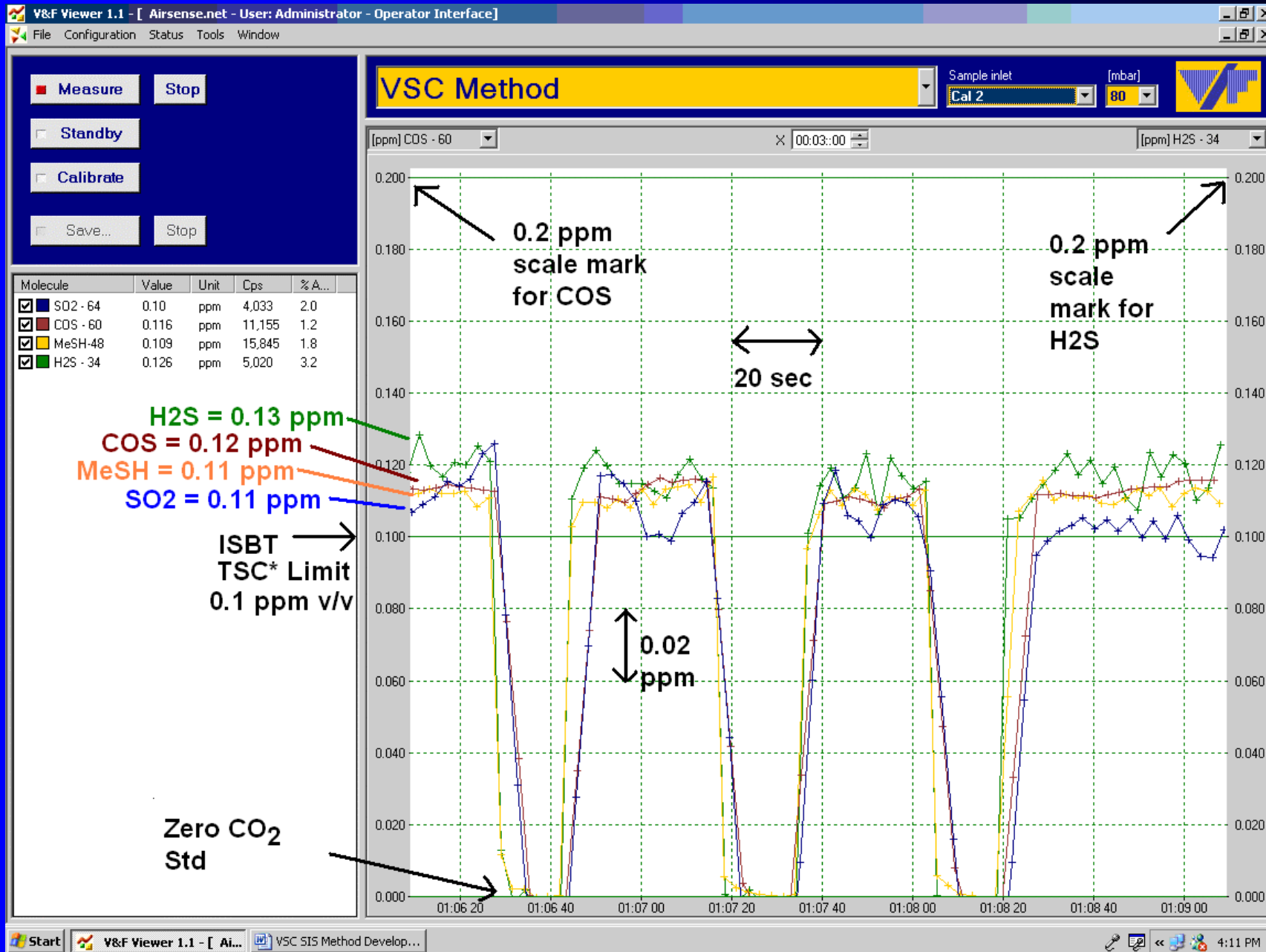
SIS - Volatile Sulfur Compounds (VSC) Data

ISBT Limit = 0.1 ppm v/v as TSC* = sum of VSC target impurities excluding SO₂, SO₂ = 1 ppm v/v max

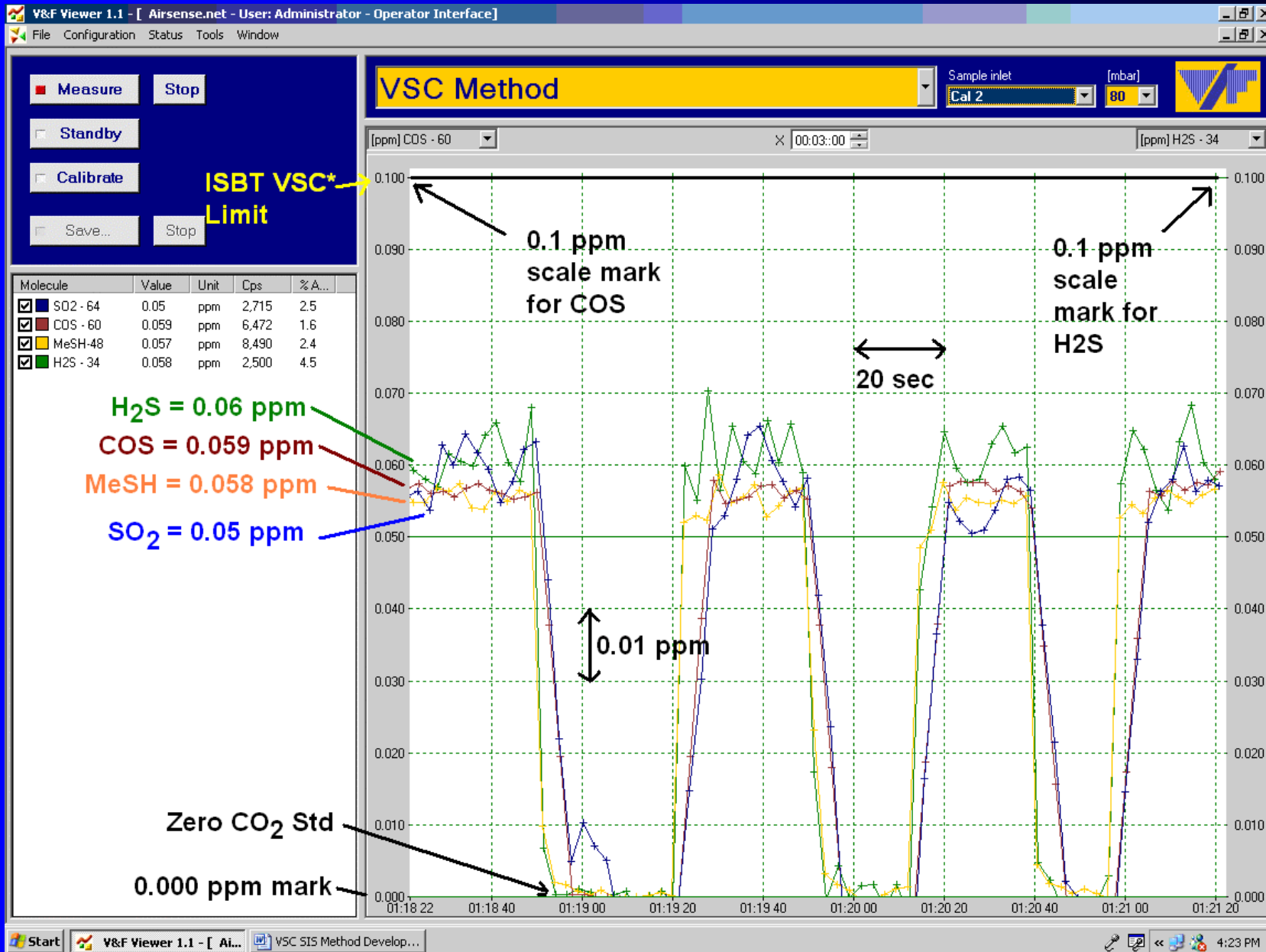
Useful Speciation information achieved

VSC	SIG	AM	LDR ppb v/v	DL ppb v/v	Interference (s)
H ₂ S	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

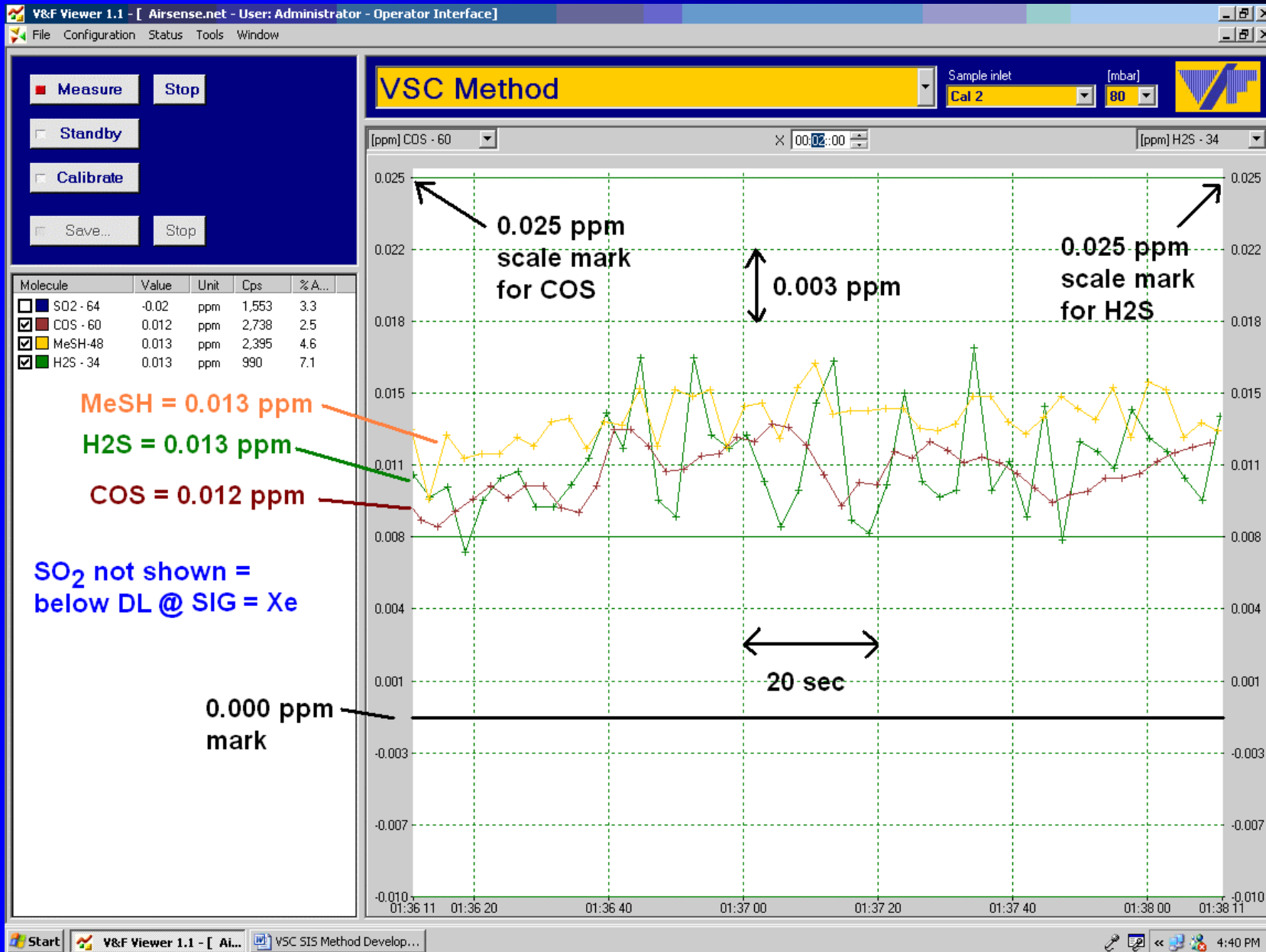
SIS Data: VSC in CO₂ @ 110 ppb v/v level



SIS Data: VSC in CO₂ @ 60 ppb v/v level



SIS Data: VSC in CO₂ @ 13 ppb v/v level



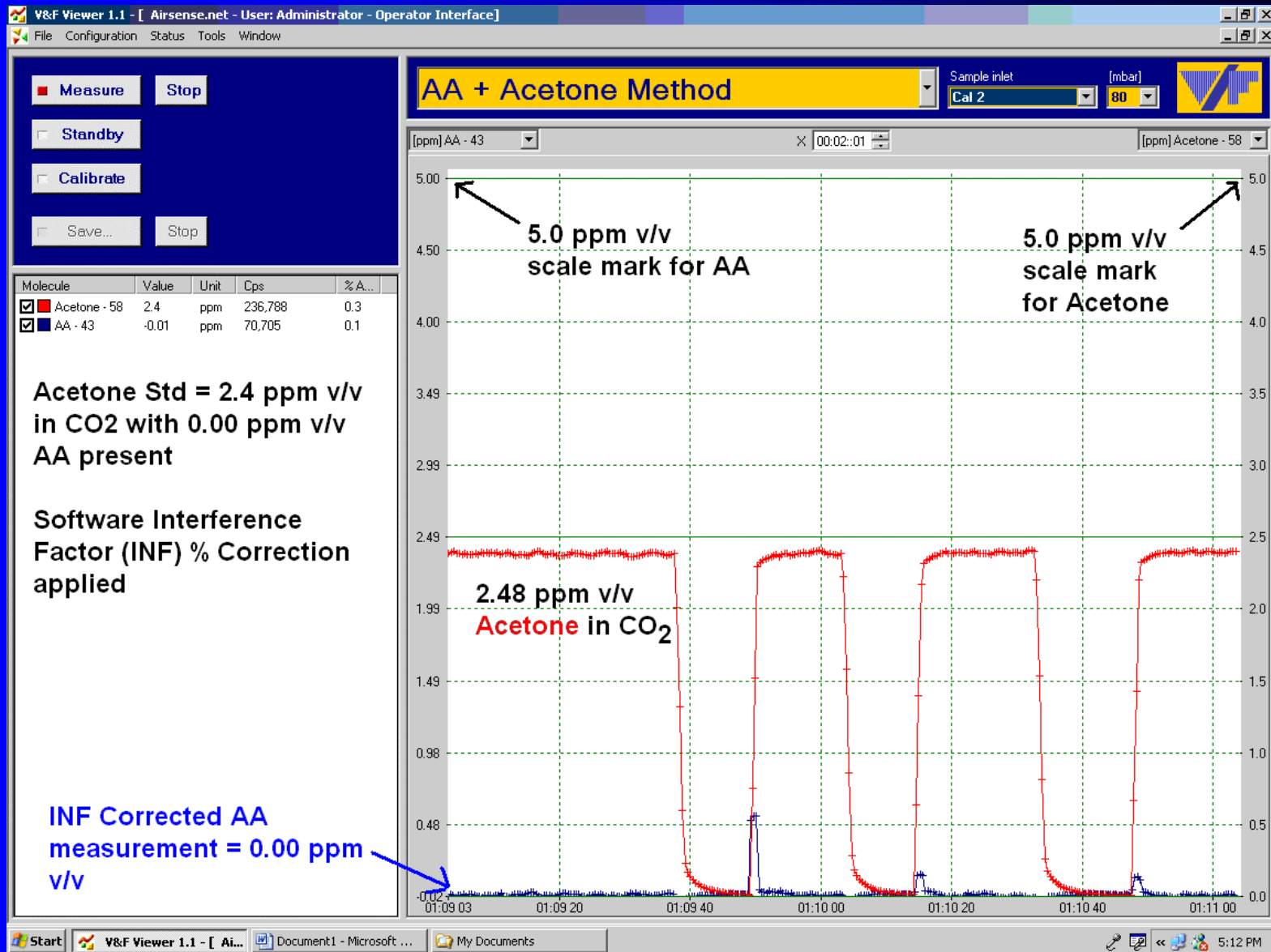
SIS - Volatile Oxygenated Compounds (VOX) Data

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

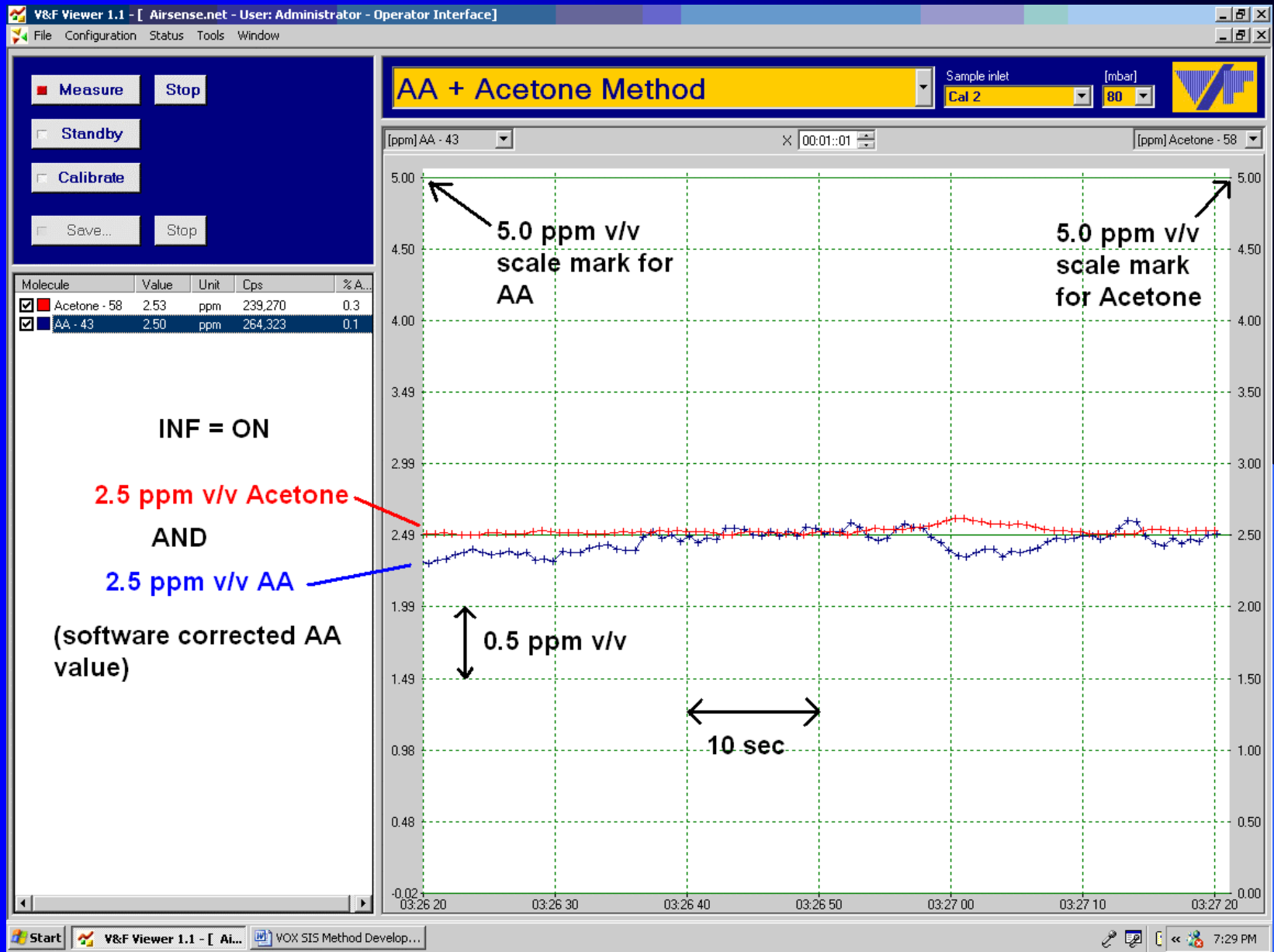
VOX	SIG	AM FR = Frag	LDR ppm v/v	DL ppm v/v	Interference (s)
AA	Hg	43 ^{fr}	0 - 5+	LT 0.1	Acetone = Major INT, i-PA = INT, i-Butanes = INT, n-Butane = minor INT
DME	Hg	46	0 - 5+	LT 0.1	No effect on AA, NO ₂ = INT
MeOH	Xe	31 ^{fr}	0 - 5+	LT 0.1	No effect on AA, EtOH / nPA = INT
EtOH	Hg	45 ^{fr}	0 - 5+	LT 0.1	No effect on AA, DME = minor INT
N-Butanol	Hg	56 ^{fr}	0 - 5+	LT 0.1	No effect on AA
Acetone	Hg	58	0 - 5+	LT 0.1	Major AA effect, Butanes = INT
EtOAc	Hg	70 ^{fr}	0 - 5+	LT 0.1	No effect on AA

SIS Data: VOX in CO₂ @ 2.5 ppm v/v Acetone / 0.00 AA – INF Corrected

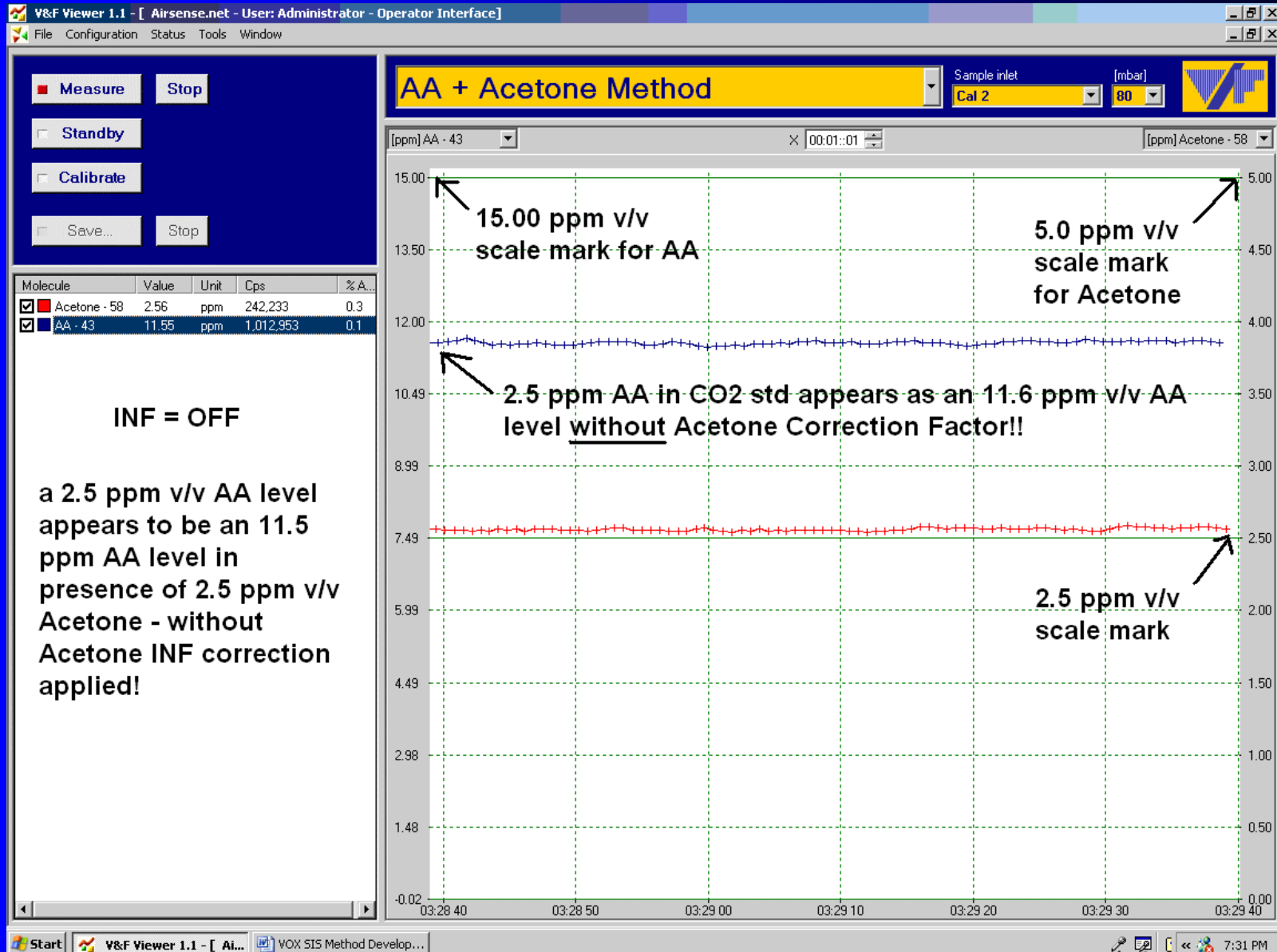
Key to Success is having accurate Interference Correction Data



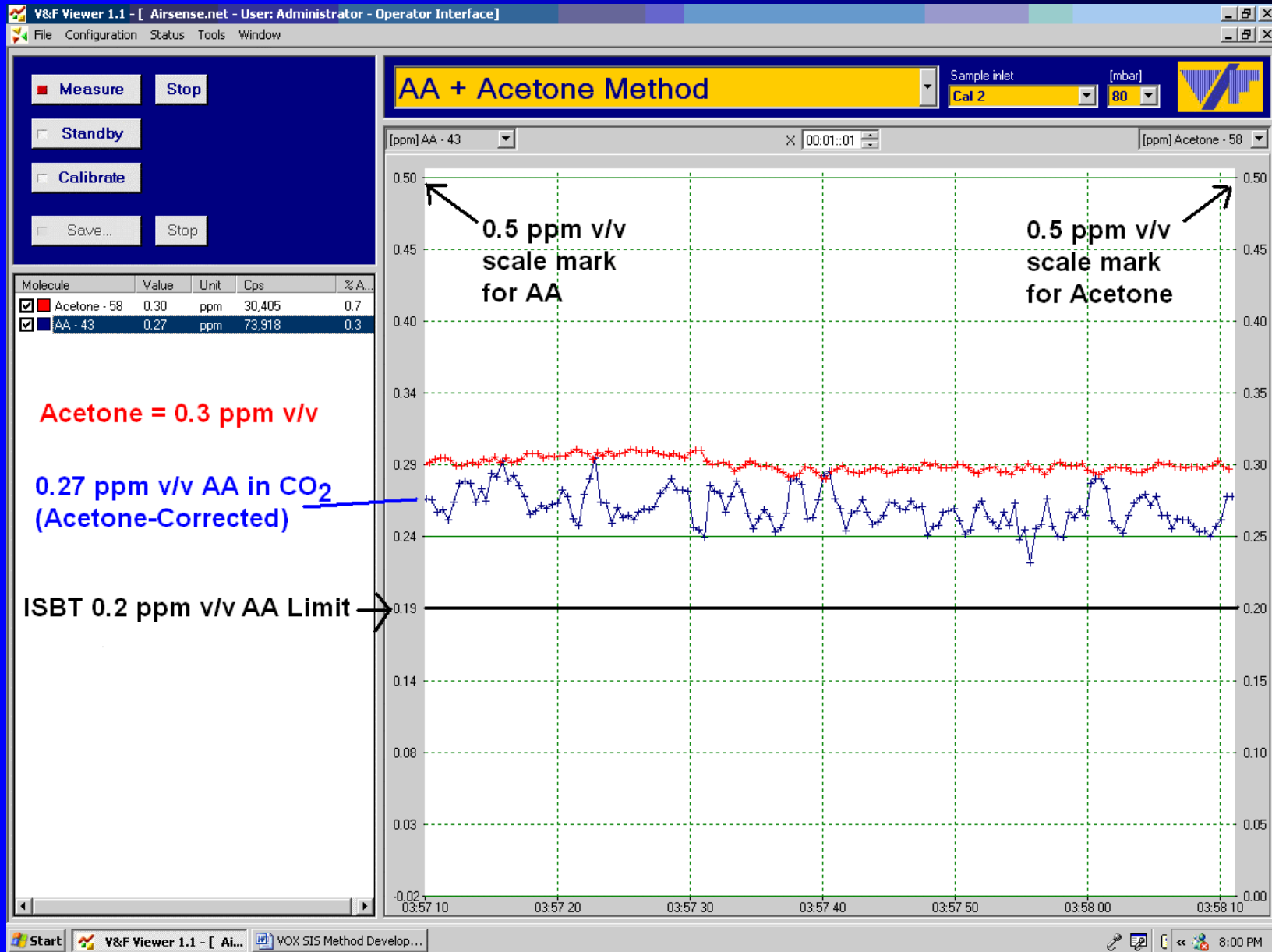
SIS Data: VOX in CO₂ @ 2.5 ppm v/v Acetone + AA – INF Corrected



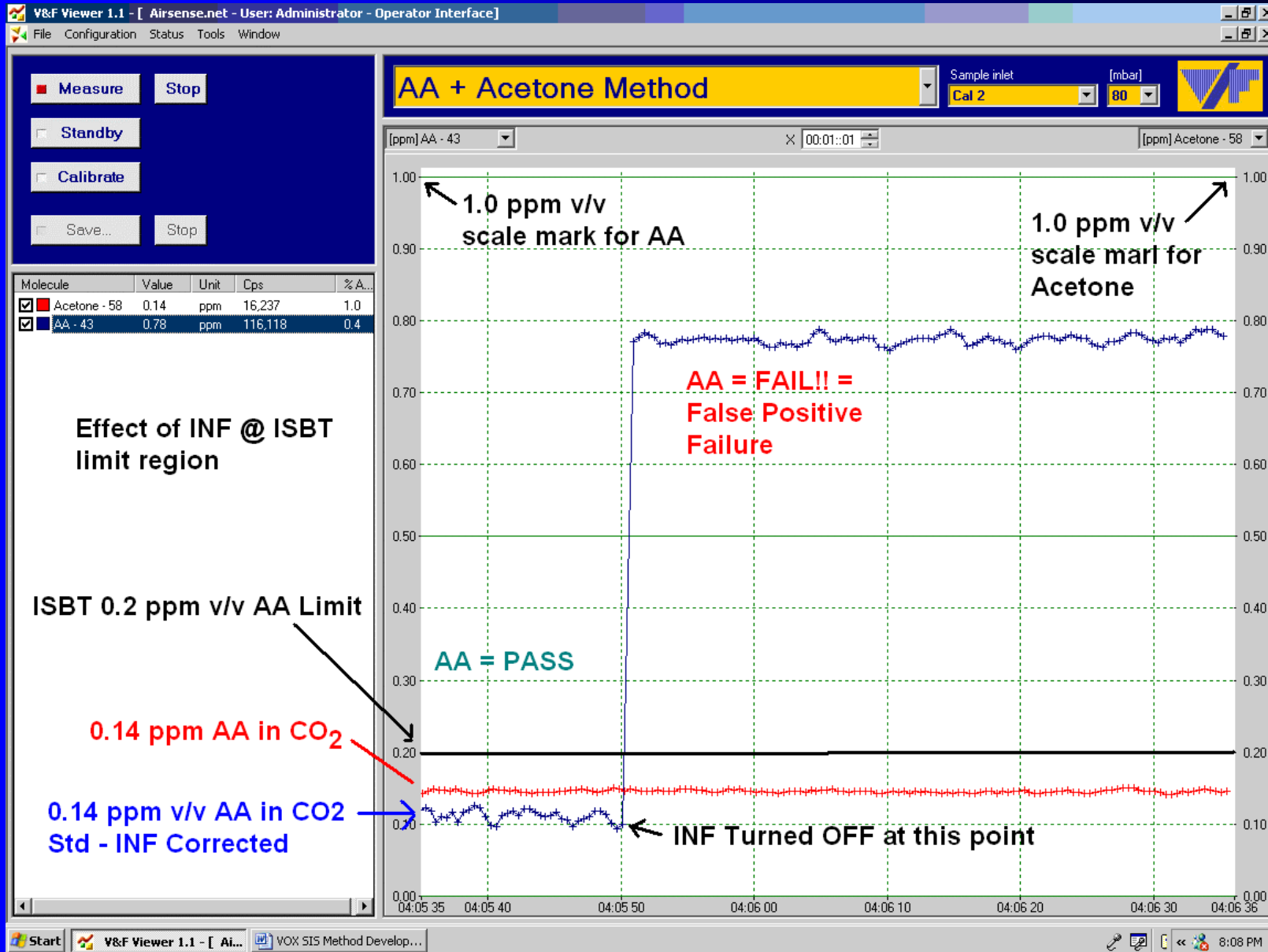
SIS Data: VOX in CO₂ @ 2.5 ppm v/v Acetone/AA if NO INF Correction



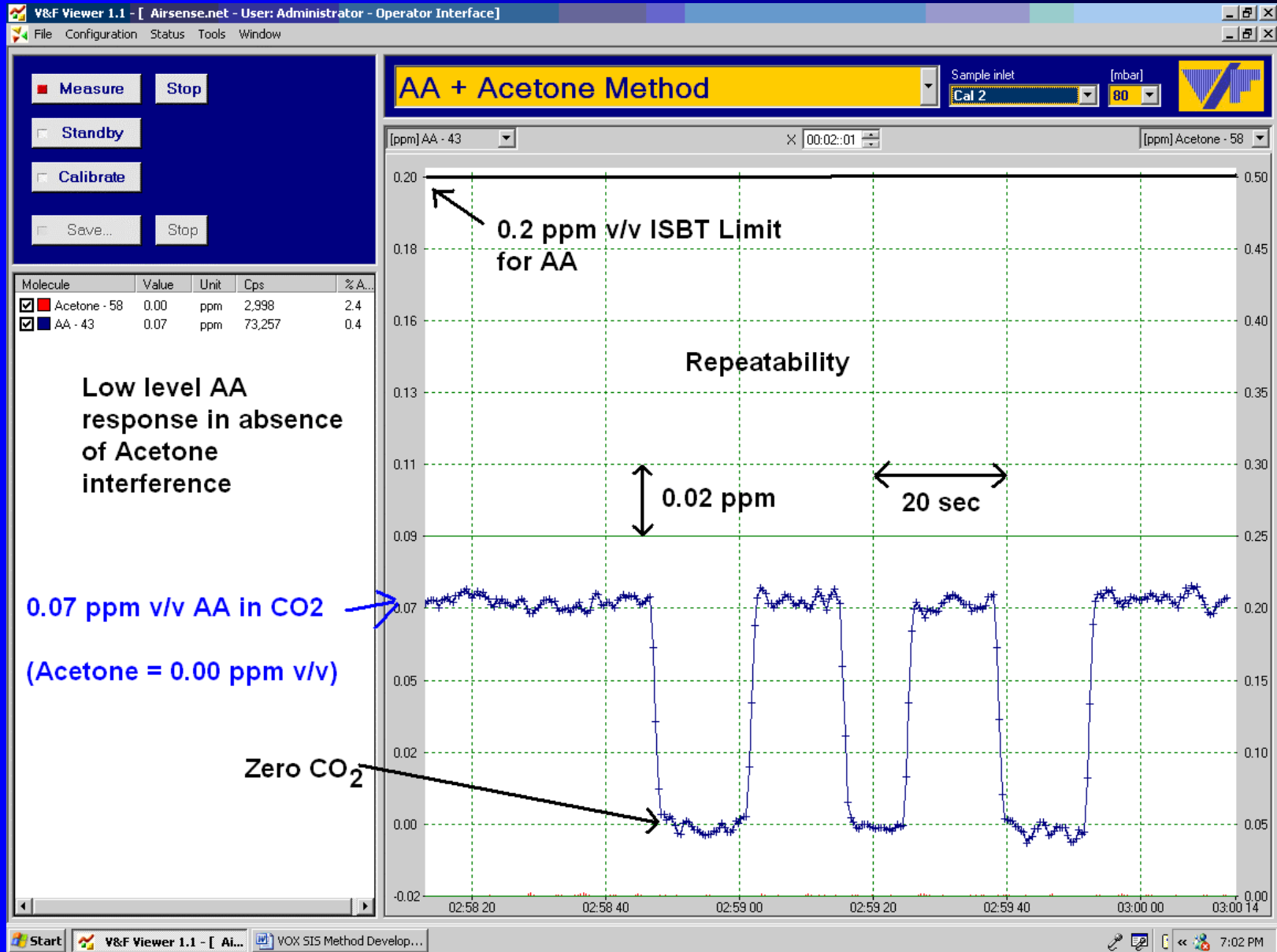
SIS Data: VOX in CO₂ @ 0.27 ppm v/v AA + Acetone INT Correction



SIS Data: VOX in CO₂ @ 0.1 ppm v/v AA + Acetone INF ON/OFF



SIS Data: VOX in CO₂ @ 0.07 ppm v/v AA – if No Acetone present



SIS - Volatile Hydrocarbons (VHC) Data

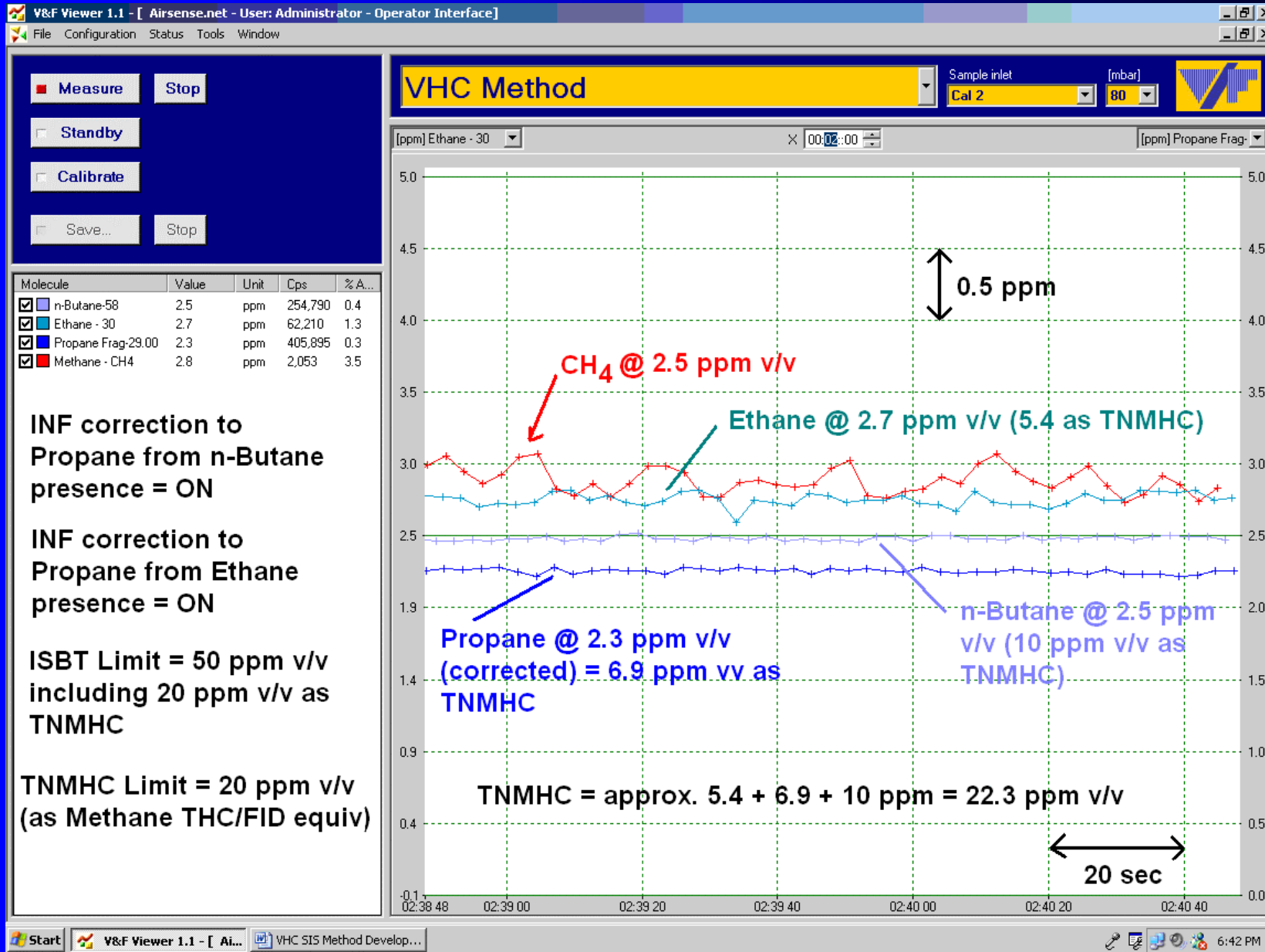
ISBT Limit = 50 ppm v/v THC as Methane including 20 ppm v/v max as Total Non-Methane HC's

VHC	SIG	AM fr= Frag	LDR ppm v/v	DL ppm v/v	Interference (s)
CH₄	Xe	16	0 – 100+	LT 0.5	None found-to-date
Ethane	Xe	30	0 – 20+	LT 0.1	NO = INT (AM = 30)
Propane	Xe	29^{fr}	0 – 10+	LT 0.1	Ethane = Minor INT, ETO = INT @ Frag = 29, n-Butane = Minor INT
N-Butane	Hg	58	0 - 5+	LT 0.1	Minor INT for AA,
N-Pentane¹	Hg	42^{fr}	0 - 5+	LT 0.1	ID @ AM = 72 Parent

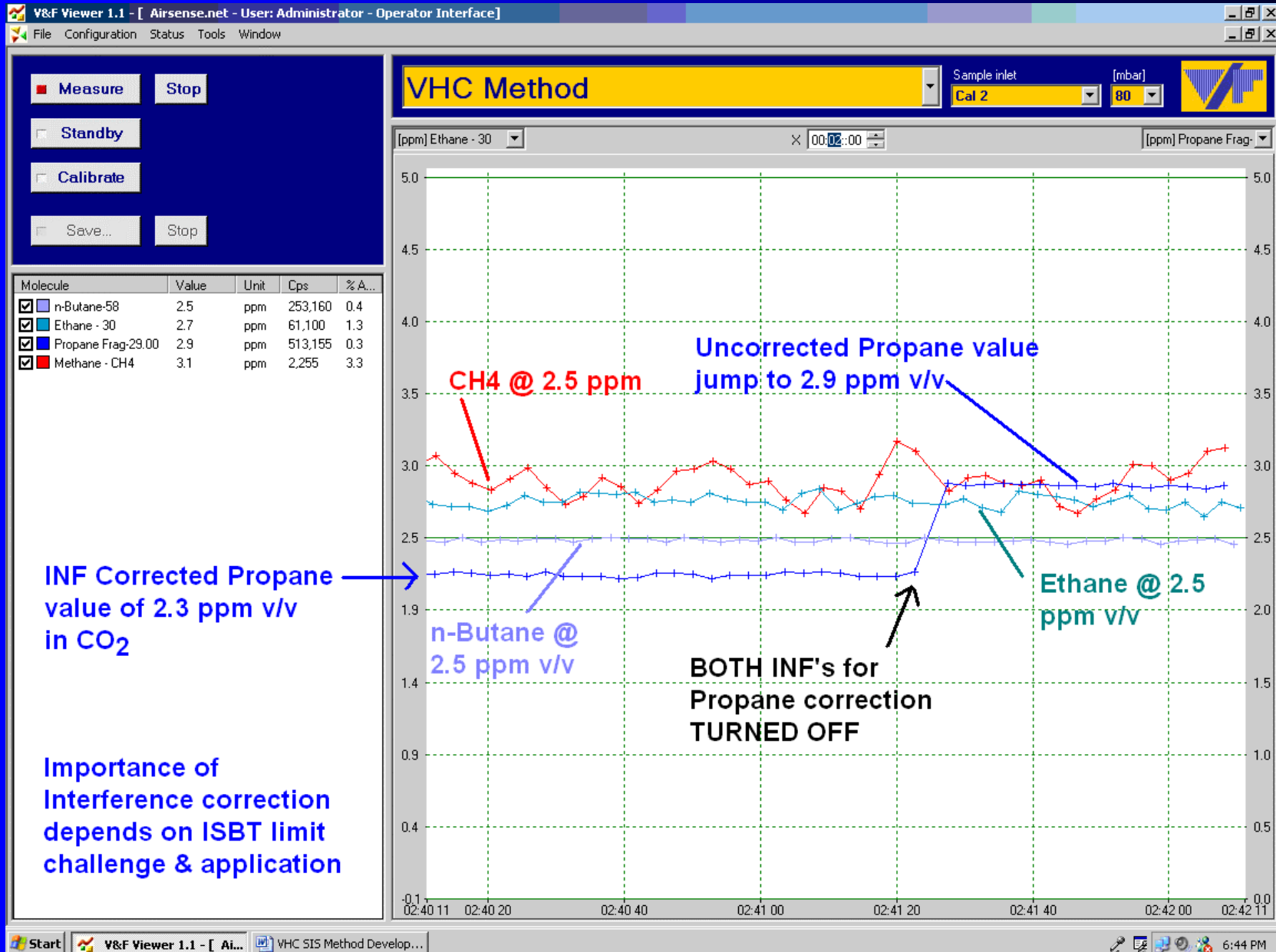
Note 1: n-Pentane $C-C-C-C-C \rightarrow C-C-C$ (AM=42)
+

Other VHC's not studied-to-date

SIS Data: VHC in CO₂ @ 2.5 ppm v/v Level - 2 Propane INF's ON

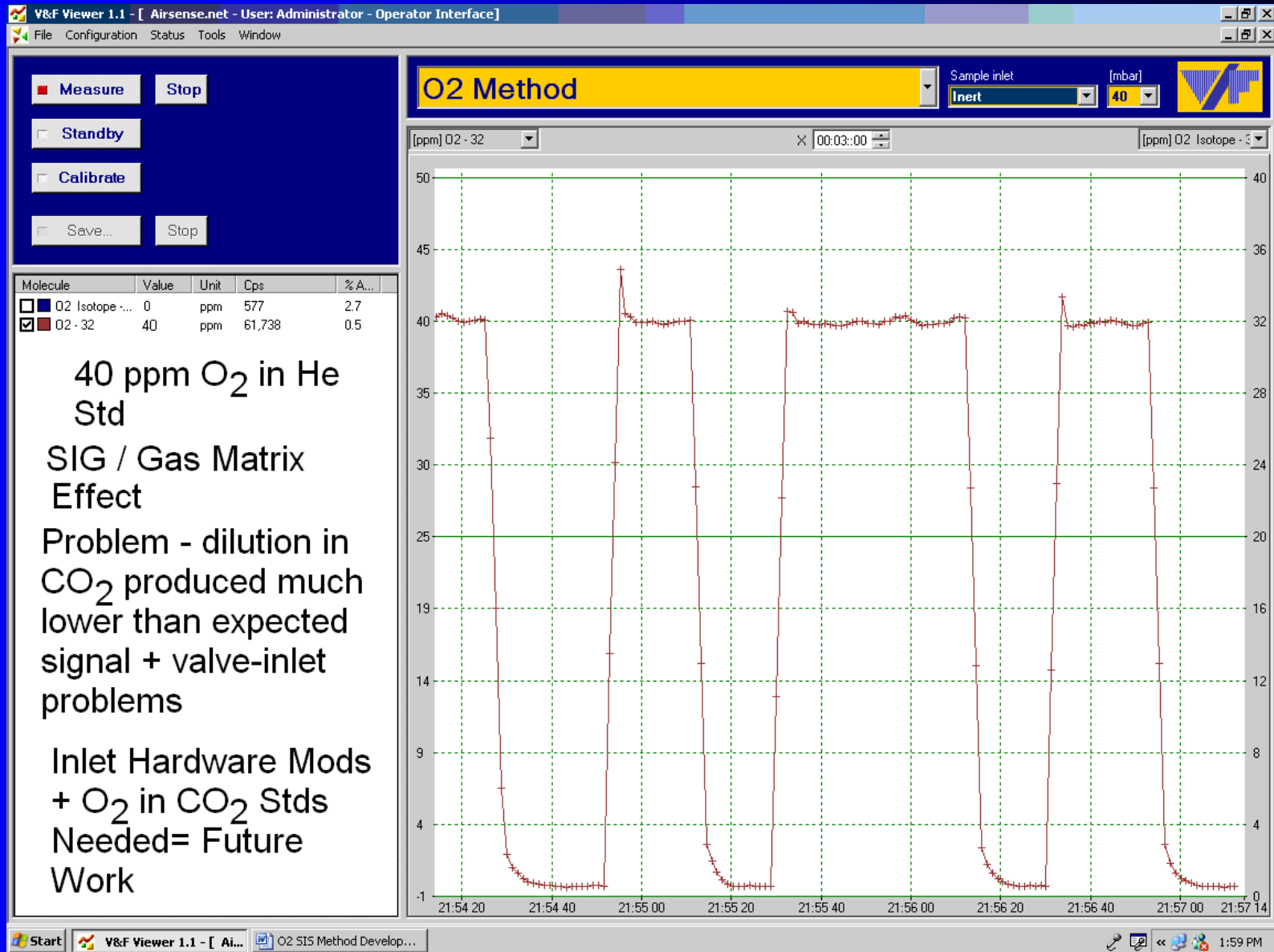


SIS Data: VHC in CO₂ @ 2.5 ppm v/v Level - 2 Propane INF's ON/OFF



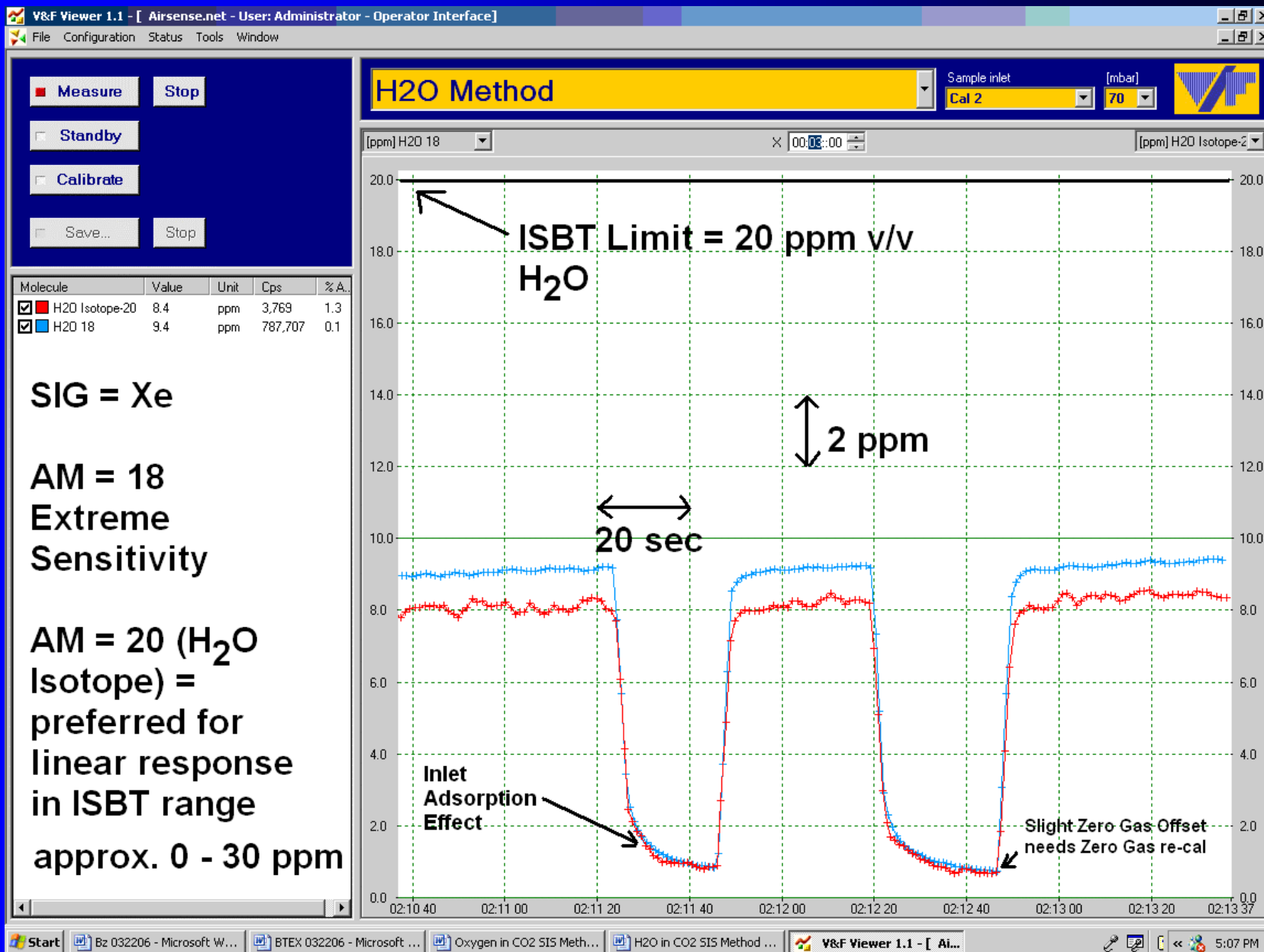
SIS Data: O₂ in He/CO₂ @ 40 ppm v/v = Effect of Cal Gas Matrix!

Use of CO₂-based Cal Gas Stds is recommended for all Analytes



SIS Data: H₂O in CO₂ @ 8 ppm v/v Level

Use of Indirect H₂O Cal Method @ SIG = Xe is viable option



SIS – Data for Other ISBT Listed CO₂ Impurities

Impurity	SIG	AM FR = Frag IS = Isotope	LDR ppm v/v	DL ppm v/v	Interference (s)
NO	Hg	30	0 - 5+	LT 0.05	None found-to-date
NO₂	Hg	46	0 - 5+	LT 0.05	DME = INT AM = 46
NH₃	Hg	17	0 - 5+	LT 0.05	None found-to-date
HCN	Xe	27	0 - 5+	LT 0.1	VCI = INT HCN Lower DL @ SIG = Xe + Kr
VCI	Hg	64^{is}	0 - 5+	LT 0.05	Use VCI Isotope AM = 64

Note 1: PH₃ study not completed SIG = Hg, AM = 34

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

SIS Applicability to ISBT CO₂ List

<u>ISBT LISTED IMPURITY</u>	<u>SIS Measurable?</u>	<u>Comments</u>
CO ₂ Purity	NO (but positive CO ₂ ID)	Can't do N ₂ , H ₂ , Ar
Moisture (H ₂ O)	YES	Can go sub-ppm range
Oxygen (O ₂)	Maybe (hardware mods)	Needs 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 ₂ S) PH ₃ = RARE	Can't distinguish from H ₂ S
Total Volatile Hydrocarbons (THC) & TNMHC	THC = YES TNMHC = YES	Get CH ₄ + need 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)	Need 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 CO₂ based Cal gas – a disadvantage
- **Support**: Does not require He, N₂, H₂, Zero Air or expert/skilled operators
- **Maintenance**: Need for periodic SIG gas replacement + SIG Filament changes

Acknowledgements

Mr. Rodney Resch & Mr. Walter
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Airborne Labs International