What Puts the "O" in NVOR?

Nicole James, Mark Taylor, Asif Rahman, Victoria Castronova, & Don Pachuta, Ph.D.

Questions to be Answered

- Do ***you*** know what the *"O"s* can be in NVOR?

- Do you know ***how*** it can affect your CO_2 quality?

- What steps may be needed to further improve fountain beverage CO_2 quality?

For the purpose of this paper,
"NVOR" **will be referenced as** ***"O"***

I. Background & Definitions

Non-Volatile Residue (NVR):

- Grand total of suspended & dissolved solid particulate matter (ex. rust, metallic corrosion products, dirt, adsorbent bed fines (ex. charcoal, silica gel), filter fibers, transfer material wear particles…….

PLUS

- All forms of Organic semi-volatiles & non-volatiles (oils, greases, plastic & elastomeric leachates)

Non-Volatile Organic Residue (NVOR):

- All forms of Organic semi-volatiles & non-volatiles (oils, greases, plastic & elastomeric leachates)

General "O" Properties:

- Low Vapor Pressure (approx. decane C10+ in MW)
- Soluble or Suspended Organic Impurities in Liquid phase CO_2
- Solubility in extracting solvents (ex. hexane, $MeCl_2$)

I. Background & Definitions

Potential Quality Effects of “O”:

- Sensory Issues (various) – possible toxicity **= “O” dependent**

ISBT Bev-Grade Limit:

- Non-Volatile Organic Residue (NVOR) = **5 ppm w/w max**

(USFCC Food Grade NVR = **10 ppm max**, No NVOR limit defined)

Recommended Analytical Method:

- ISBT Method 8.0: “Total Non-Volatile (NVR) and Non-Volatile Organic Residue (NVOR) by Gravimetry

Useful References:

ISBT 2010 ‘Bulk CO_2 Quality Guidelines & Analytical Methods Reference”. **ISBT** 2006 “Fountain CO_2 Quality Guideline” **CGA G-6.11**-2008 “**Concentration of Impurities in Bulk Carbon Dioxide Storage Tanks at Customer Sites**. **EIGA** “Minimum Specifications for Food Gas Applications: IGC Doc 126/11/E . **EIGA** “Carbon Dioxide Source Qualification Quality Standards & Verification” IGC Doc 70/08/E. Many others also.

Liquid CO_2 Solvency Factor

O=C=O

- **Linear Molecule – non-polar but!**
- Liquid CO_2 - a great & unique solvent – similar to solvent strength properties of hexane
- Solvency includes many oils, elastomeric plasticizing agents & common organic impurities from feed gases
- Dissolves large relatively non-polar molecules (oils) as well as small non-polar – semi-polar oxygenated molecules
- LCO_2 (supercritical) used as a "green" commercial cleaner for many metal parts, semi-conductor industry, medical equipment, decaffeination of coffee, many others solvent applications.

This is why a Liquid phase CO_2 sample is recommended for ISBT analysis of most potential impurities.

II. Potential Sources of "O"

Overview

Compressor Oils

Elastomeric Hoses & Tubing

O-Rings & elastomeric parts

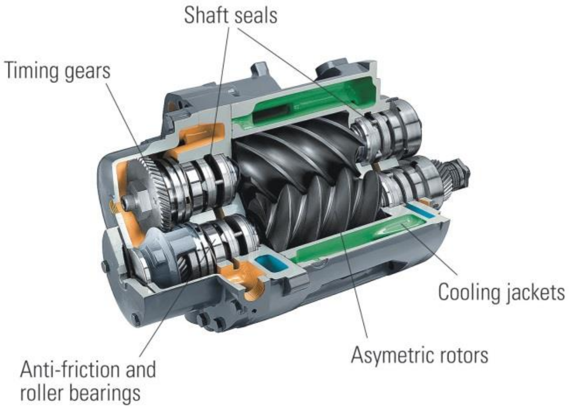
Piping & Hardware Assembly Aids

Feed Gas Bio-Oil Residues

Compressor Related Oil Sources

Compressor Types: Used to compress CO_2 gas before refrigerated liquefaction or trans-fill of LCO_2 into transport vessels

- Rotary Screw Oil-Injected: (common)
- Reciprocating (some "oil-less")
- Rotary Sliding Vane
- Centrifugal - Axial Flow



Mechanism of Oil contamination – intimate oil – gas / liquid CO_2 contact

Calculations of potential trace "O" in produced LCO_2 illustrated later

Compressor Oils

Lubricant contamination via weepage, wear & thermo-oxidative breakdown – ex. from oil-injecting compressors.

Even some "Oil-less" compressors have some oil, ex. crankcase oil –but isolated.

- **Petroleum Based – Highly Refined Mineral "White" Oils (paraffinic hydrocarbons - Food Grade)**

- **Synthetic Oils (Polyalphaolefin [PAO] = paraffinic hydrocarbon) - Food Grade**

3 Food Grade Classes

Food Grade is Mandatory

H1: Lubricants used in Food Grade processing environments where there is a possibility of incidental food contact.

H2: Used on equipment & machine parts where there is no possibility of contact.

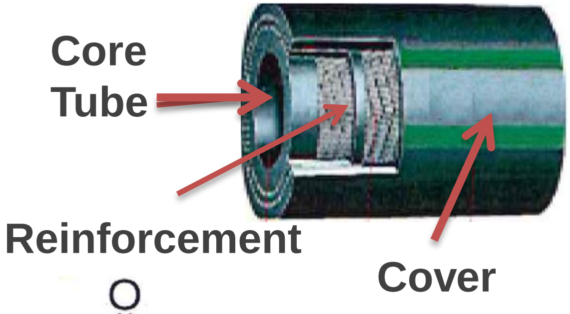
H3: Typically edible oils used to prevent rust on hooks, trolleys & other such equipment.

Elastomeric & Metal Hoses, Tubing, O-Rings

Flexible, High Pressure, Jacketed, Elastomeric Transfer Hoses (LCO_2 “compatibility” class required + “Food” Grade)

DIMS = 20 – 100 ft x 0.5 - 2” ID

- Metal Hoses also used (no elastomers, no “O”) – but are heavier & more prone to icing



- *Plasticizers: phthalates, diesters, mold release agents & other additives leached by LCO_2 solvency*

- *Phthalates being replaced with lower toxicity agents – **but LCO_2 Solubility?***

Plasticizers present @ rel <u>high % levels</u> in some hose & tubing formulations (≤ 30%)

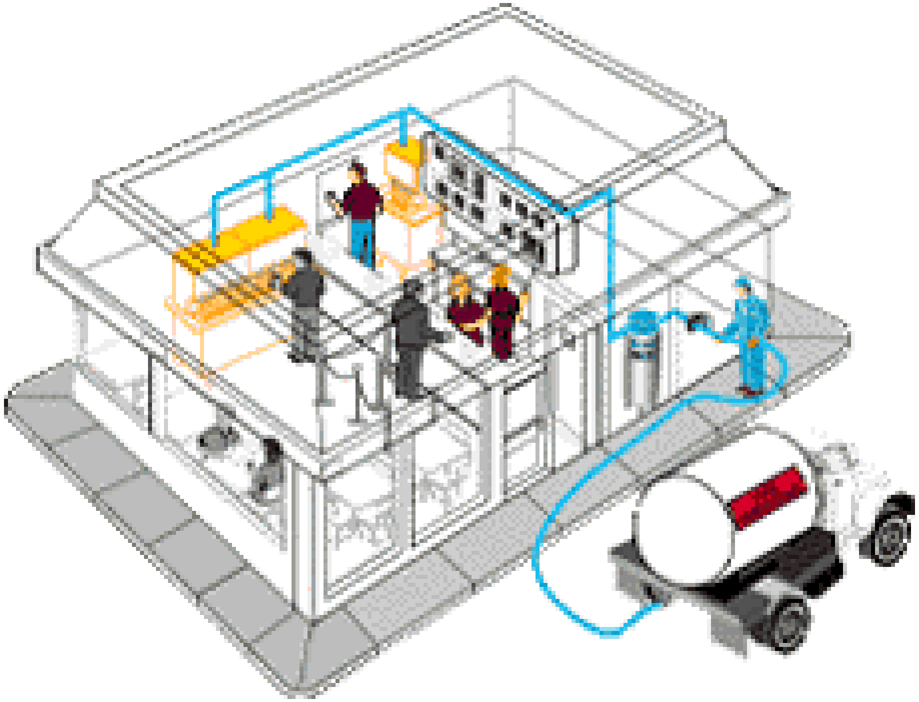
Incompatible hydraulic rubber hoses with C-steel sleeves should not be used – (Buna-N not compatible, see Praxair CO_2 Compatibility Charts?)

III. Known Causes of <u>High</u> “O”

- Use of **non-LCO_2 compatible** hoses, O-Rings or seals
- **New Hose /** polymeric transfer lines installed (Hoses typically replaced ≈ 1X / yr due to outer cover wear)
- **Existing** CO_2 plants after major hardware maintenance
- **New** CO_2 plant plumbing, tanks / hardware that need purging
- Compressor ageing or **seal failure** (increased weepage)
- Use of sample cylinders with an **excessive** amount of valve stem grease applied (sampling artifact)
- Improper **sampling** procedures (artifact errors)

III. Known Causes of High "O"

- **Infrequent** or **no** scheduled MBT LCO_2 charge drainage schedules or periodic in-service CO_2 purity screening checks – in fountain / bar outlets due to **many years** of constant **vapor withdrawal (distillation)**



What to do if you ever have an "O" issue?

Q: *If a high NVOR in your LCO_2 is measured*

A: First find out if it is "real" or a possible Sampling or Analysis Artifact = Red Herring = False Positive.

Q: *How do you do that?*

A: First, re-sample & look for result consistency.

If **inconsistent** – then most likely a sampling or analysis artifact was involved.

If **consistent** – it is probably "for real" so know the possible "O" sources in your process or from your supplier.

If "real", some additional detective work involving qualitative "O" analysis & Scientific Process of Elimination is typically required.

V. Analytical Methods

Basic Methods	Advanced Methods

Basic Methods

- ISBT Method 8.0
  - Procedure A
  - Procedure B
- Snow Cone Screening
- “O” Mist Detector Tube
- Field Microscopes

Advanced Methods

- FTIR Spectrometry
- Gas Chromatography
- Transesterification – GC
- Liquid Chromatography
- Elemental Analysis

Basic Analytical Methods

ISBT Method 8.0 Procedure A

Step 1: Snow generation

Basic Analytical Methods

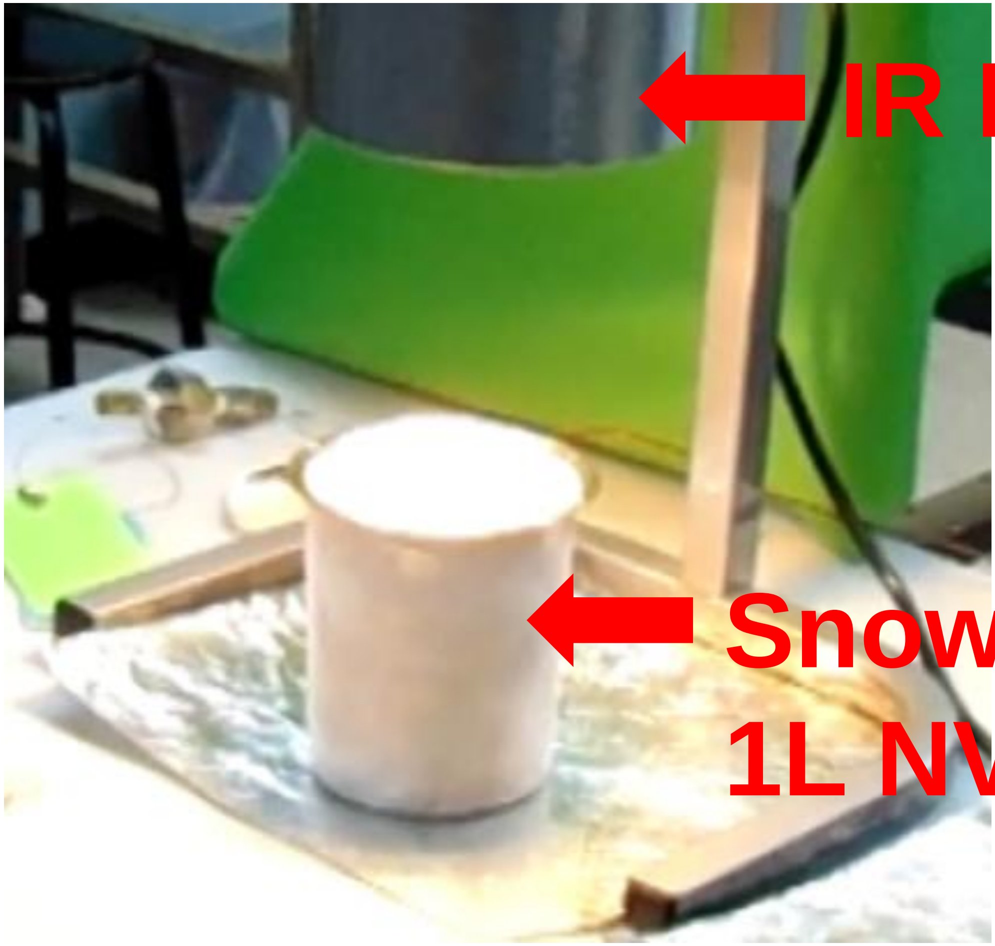
ISBT Method 8.0 Procedure A

Step 2: Weight (g) of snow is taken (200 – 400+g)

Basic Analytical Methods

ISBT Method 8.0 Procedure A

Step 3: Weighed Snow Is Evaporated (Sublimed).



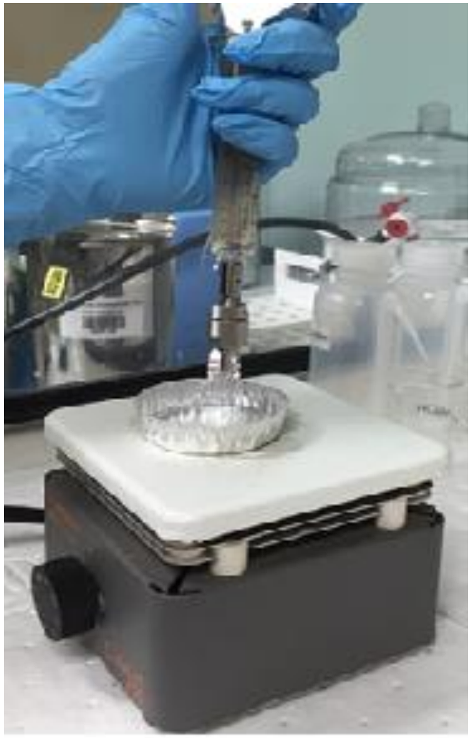
IR Lamp

Snow-filled 1L NVR Can

Basic Analytical Methods

ISBT Method 8.0 Procedure A

Step 4: NVR filtration, solvent evaporation, & organic residue weight is taken. NVOR is calculated with snow generation device “efficiency factor”.



NVOR results reported in ppm w/w units

Basic Analytical Methods

Simple Snow Cone Screening Test

PASS

No Visible Oil

FAIL

60 ppm

Snow Screening – snow sample taken – sublimation – Observe Residue – Pass/Fail – if no NVR/NVOR observed = taken as a "Pass".

Basic Analytical Methods

Snow Cone Screening

PASS?

5 ppm

PASS?

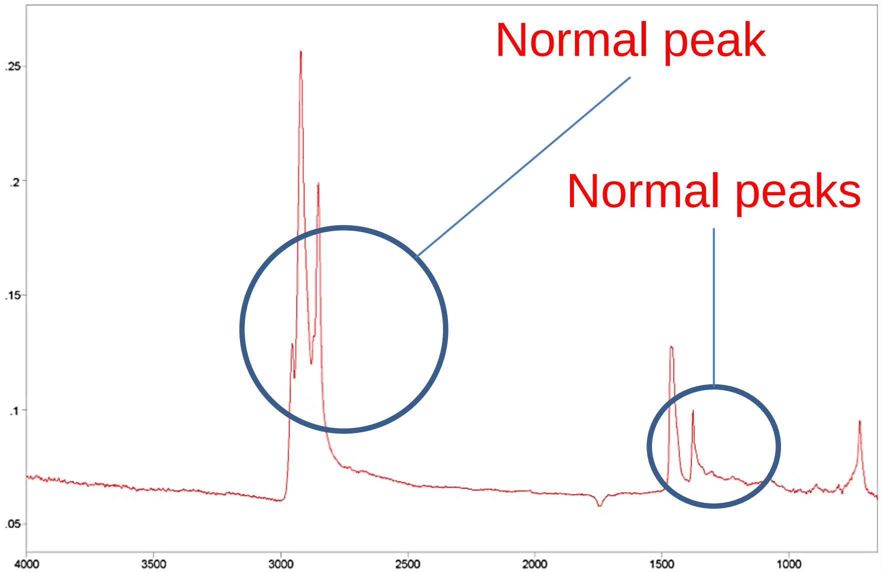
2 ppm

NVOR can even be **observed** at low 2 ppm level!

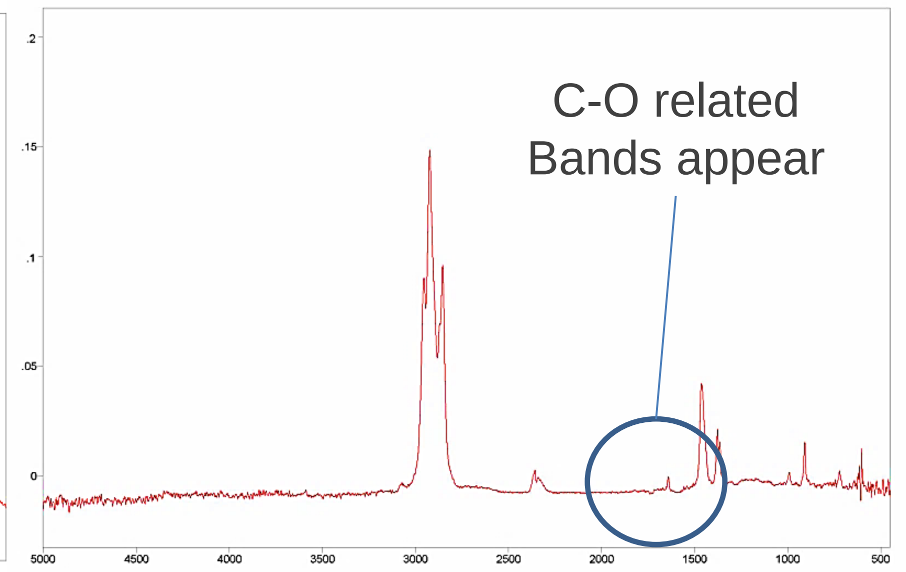
Advanced Analytical Methods

Infra-Red (IR) Spectrometry

Virgin PAO Synthetic Oil



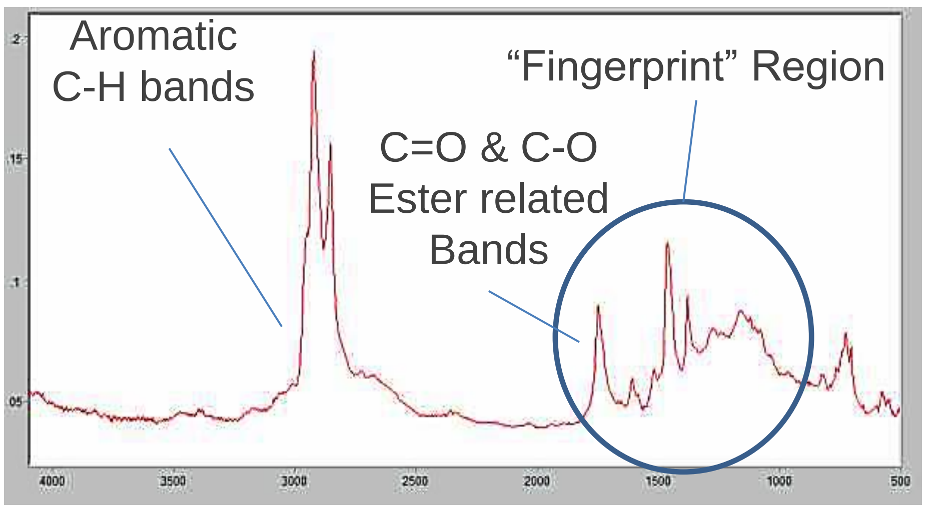
Slightly "Weathered" PAO Oil



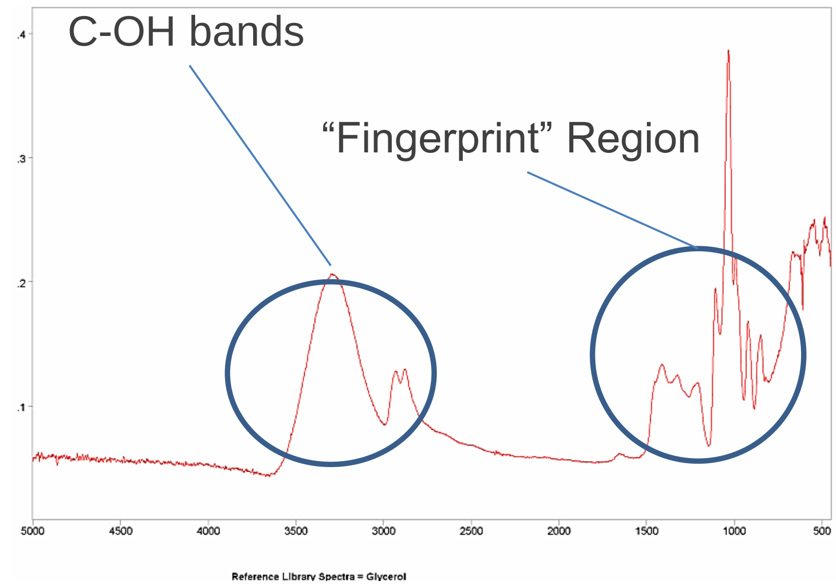
Advanced Analytical Methods

Infra-Red (IR) Spectrometry

“O” Residue - Phthalate Bands



Glycerol Profile

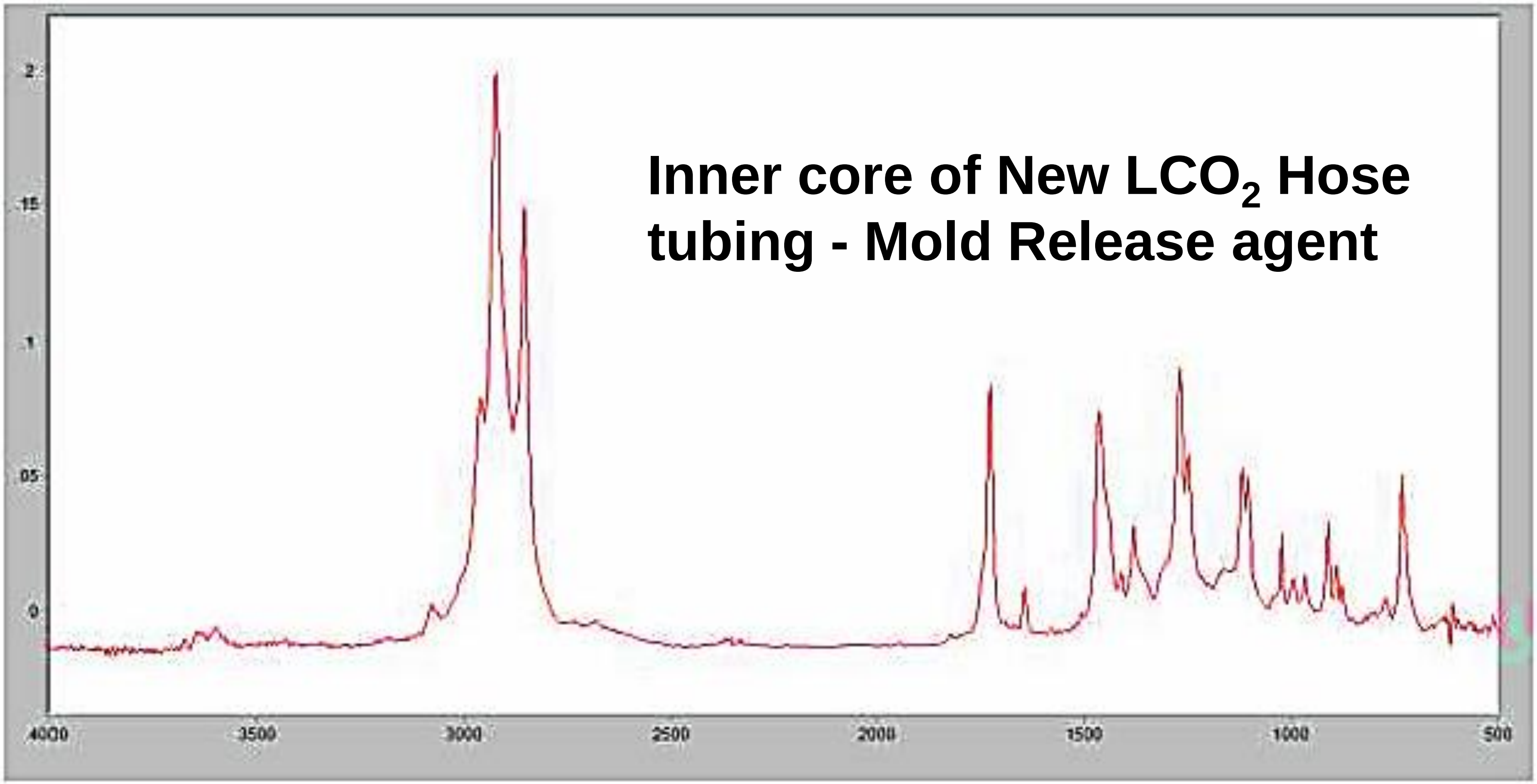


Hose Plasticizers & other classes of “O” are can often be easily distinguished from PAO or Mineral Compressor Oils using IR

Advanced Analytical Methods

Infra-Red (IR) Spectrometry

NVOR leachate oil extracted from New LCO_2 Hose



Inner core of New LCO_2 Hose tubing - Mold Release agent

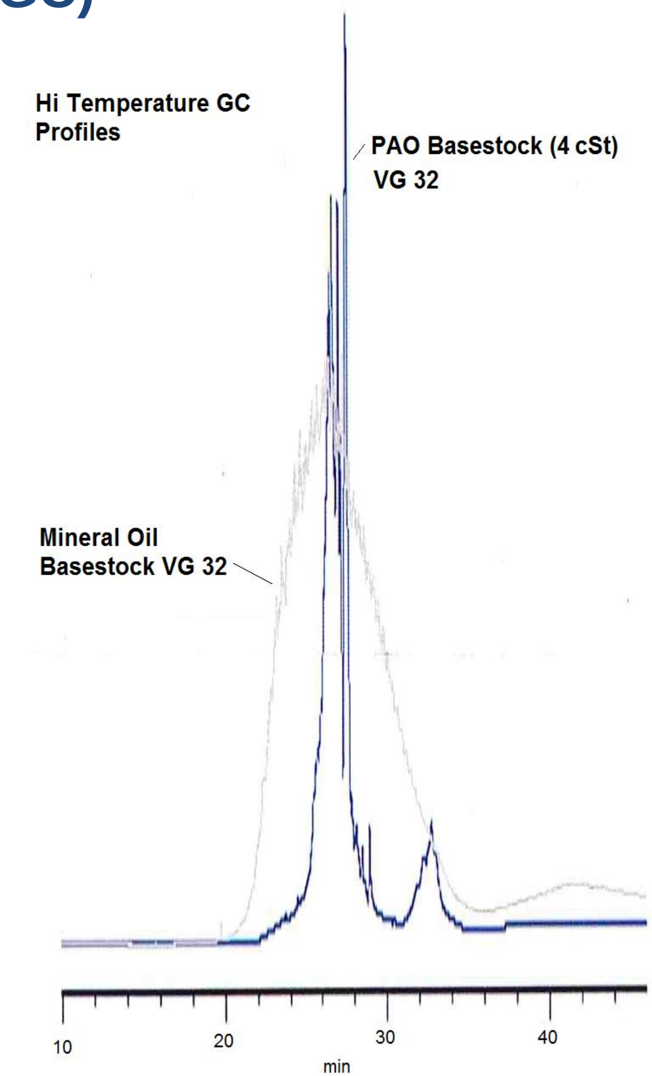
Airborne Labs International

Advanced Analytical Methods

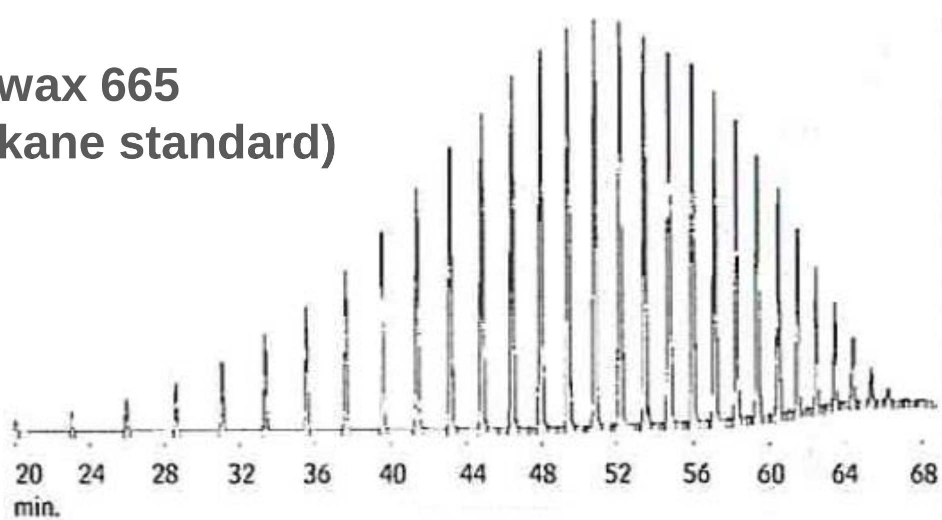
Gas Chromatography (GC)

Gas Chromatography: (ex. ***High Temperature*** 400+C (400 – 550+C) based methods – using FID or Mass Spec or NP-Selective detectors).

Good for basestock ID some *lower* VI compressor fluids, many plasticizer additives. PAO vs Mineral Oil type basestock discrimination possible.



Polywax 665 (n-alkane standard)



White Mineral vs PAO synthetic base stocks have different GC Profiles

V. Field Study "O" Experiences

ALI Lab Testing Data

PTS & LCO_2 Storage Tanks – Field "O" Data

- **Rare occurrences of high NVOR in LCO_2 samples from Mfg sources**.

- High NVR (particulates) more prevalent – but still low frequency.

- For LCO_2 sample cylinders

– sampling artifacts often suspected of causing High NVOR *errors*

V. Field Study “O” Experiences

Calculations - LCO_2 Production NVOR

Assumptions:

- Typical Rotary Screw Oil-Injected Compressor Weepage = 130 mL or less over 24 hr
- All oil weepage enters LCO_2 stream PTS & is soluble
- 24 hr LCO_2 Commercial Production: 100 TPD - 1,000 TPD
- Compressor Oil density = 0.8 g/mL
- Conversions: 1 US Ton = 2,000 lb = 90,800,000 g = 90,800 kg. 1 lb = 454 g, 1 µg = 1 x 10^{-6}g

V. Field Study "O" Experiences

Calculations - LCO_2 Production NVOR

Calculated NVOR Results

- @ 100 TPD production = **1.1** **ppm w/w NVOR max**
- @ 400 TPD production = **0.28** **ppm ww NVOR max**
- @1,000 TPD production = **0.11** **ppm w/w NVOR max**

Summary: ≈ 0.1 – 1 ppm w/w calc'd NVOR range

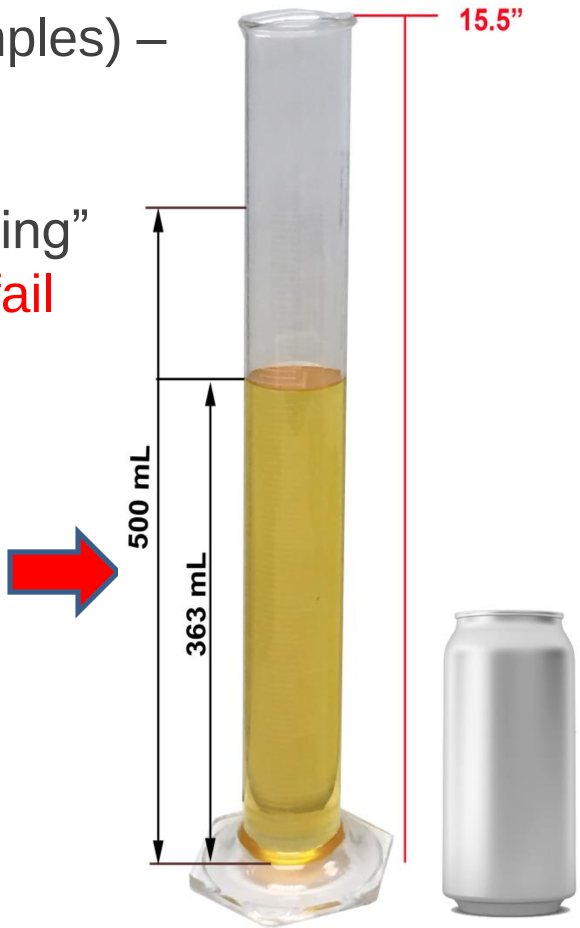
Calculated results supported by laboratory test data statistics & NVR can interior visual observations (non-detectable)

Very low incidence of high NVOR from large storage tanks with frequent LCO_2 withdrawal

V. Field Study "O" Experiences

ALI Study - MBT NVOR Data

- Much fewer samples analyzed to date (31 MBT samples) – field study in progress
- Status: MBT samples *Much higher frequency* of "failing" NVOR data observed (**29%** failure rate so far, **26%** fail USFCC NVR max)
- Some samples highly contaminated with "O" (ex. one 800+ ppm NVOR) = 291 g "O" = 363 mL in an 800 lb tank
- **Limited** qualitative ID data on source of high "O". Mostly ISBT gravimetric Proc. A.



V. Field Study "O" Experiences

ALI Lab Data - MBT samples to Date

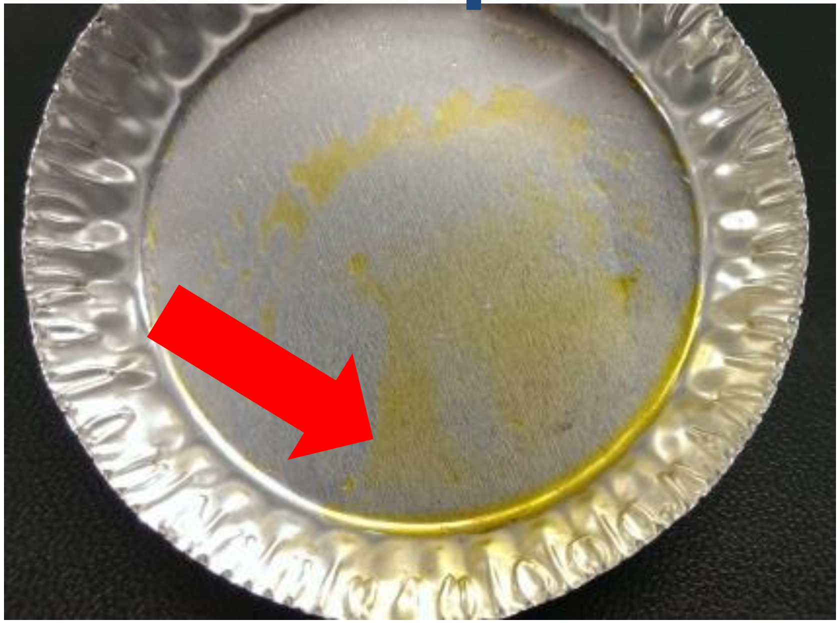
To Date: 31 MBT samples tested % ISBT NVOR failures = 29%
% USFCC Food Grade failures = 26%

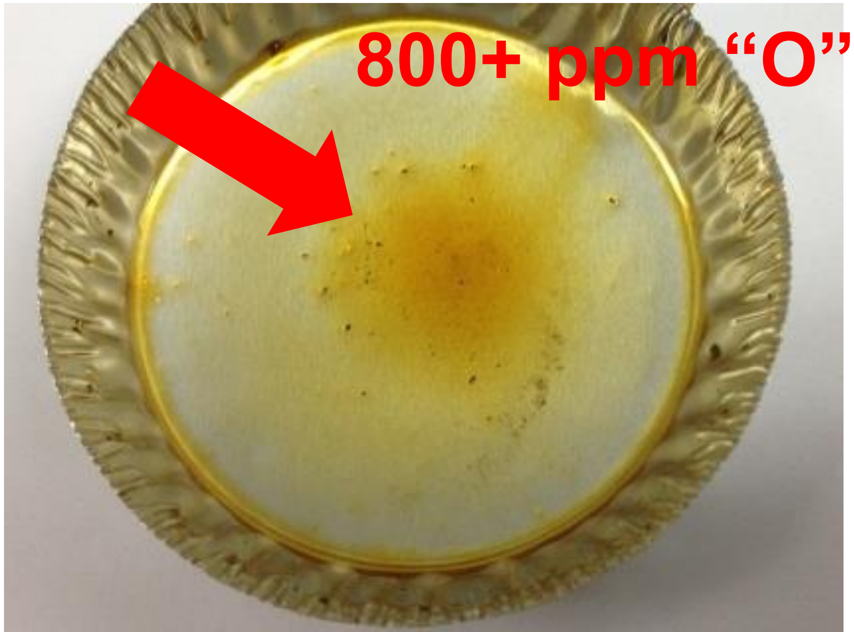
NVR Concentration (ppm)	NVR Description	NVOR Concentration (ppm)	NV0R Description	THC (ppm)
860	Pale, yellow oil and fine, dark paricles.	810	Pale, yellow oil.	7.3
8.3	Yellow oil and various, dark particles.	7.1	Yellow oil.	1.0
11	Various, black particles and clear, yellow oil.	10	Clear, yellow oil.	1.3
230	Dark, yellow oil and black particles.	210	Dark, yellow oil.	0.6
44	Fibers, yellow oil and black particles.	35	Clear oil and light, yellow oil.	--
92	Dark, yellow oil and black particles.	84	Yellow oil.	4
14	Dark, yellow oil residue and black particles.	10	Dark, yellow oil.	--
45	Fine, black particles and clear oil.	31	Clear oil.	6.5
32	Various, black particles, yellow oil and fibers.	29	Some yellow oil and clear colorless oil.	0.2

ISBT NVOR Limit for Bev-Grade CO_2 = 5 ppm w/w

USFCC Food Grade Limit for CO_2 = 10 ppm w/w NVR

Examples: MBT "O" Data





800+ ppm "O"

V. Field Study “O” Experiences

Calculations - MBT NVOR Build-up

Assumptions:

- All MBT loads @ calculated 0.1 - 1 ppm range from typical compressor weepage data
- 150 – 800 lb LCO_2 typical MBT capacity
- MBT Top-off 1X / month @ ≈ 40% remaining fill (0.6 tank capacity)
- Most of oil retained in LCO_2 phase of MBT
- No MBT Drainage for: 1, 2, 4, 8 yrs
- Typical “O” density = 0.8 g/mL
- Conversions: 1 US Ton = 2,000 lb = 90,800,000 g =90,800 kg. 1 lb = 454 g, 1 µg = 1 x 10^{-6}g

V. Field Study "O" Experiences

Calculations - MBT NVOR Build-up

Calculated total mL "O" & NVOR Results (worst case – typical compressor oil weepage only)

- 200 lb MBT after **1 yr** = 0.08 – 0.82 mL, **NVOR = 0.7 - 7 ppm w/w**
- 800 lb MBT after **1 yr** = 0.4 – 4 mL "O" load

- 200 lb MBT after **2 yrs** = 0.2 – 1.6 mL, **NVOR = 1.4 - 14 ppm w/w**
- 800 lb MBT after **2 yrs** = 0.8 – 6.4 mL "O" load

- 200 lb MBT after **4 yrs** = 0.4 – 3.2 mL, **NVOR = 2.8 - 28 ppm w/w**
- 800 lb MBT after **4 yrs** = 1.6 - 12 mL "O" load

- 200 lb MBT after **8 yrs** = 0.8 – 6.4 mL, **NVOR = 5.6 - 56 ppm w/w**
- 800 lb MBT after **8 yrs** = 3.2 – 26 mL "O" load

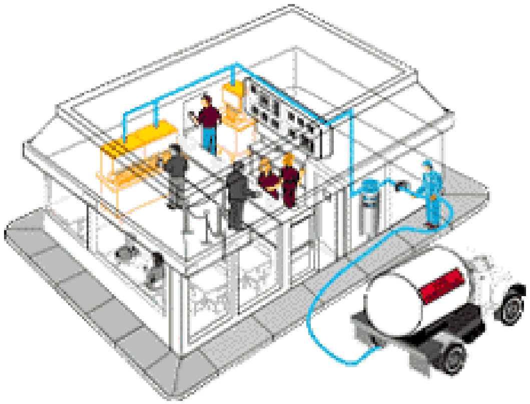
V. Field Study "O" Experiences

Field Data vs Calculated Data Interpretation

- **Historically, very low % data** of failing NVOR from large storage tanks & low calculated "worst case" contribution of NVOR from compressor weepage of 0.1 – 1 ppm NVOR max. - **BUT**

- **Relatively high (29%) MBT ISBT NVOR sample failures** to date – suggests non-compressor oil sources of "O" (ex. plasticizers from transfer hoses?) may be an important "O" source in MBT's. ***26% also Failed USFCC Food Grade CO_2 NVR max.***

- Hose Plasticizer Leachate MBT loading rate **unknown** to date

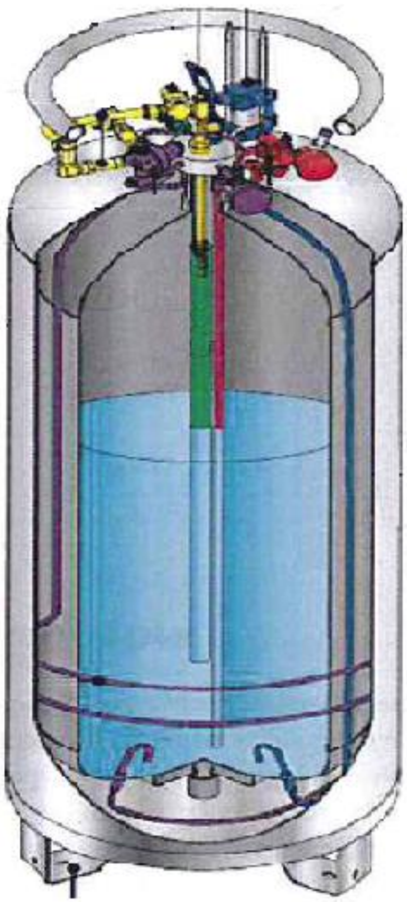


- Most MBT data obtained was only analyzed gravimetrically. ID of "O' not performed on most samples to date – more detailed data needed.

V. Field Study "O" Experiences

Fountain MBT Current Practices

- Myth: "O" is insoluble - floats to bottom" – **not so in LCO_2 phase much "O" is also soluble!**
- **Some Mfg's have no recommended PM tank drain / tank cleaning schedules – or customers ignore their PM recommendations**
- Some Mfg's have no recommended PM practices concerning periodic LCO_2 **quality screening checks**
- **Many current MBT models have <u>no drain port</u>**
- Bev-grade LCO_2 **not mandatory** by many fountain users.



V. Field Study "O" Experiences

Fountain MBT Current Practices

- **Direct Liquid withdrawal** options on some MBT's for high volume delivery requirements – will draw "O" out into plumbing circuit
- Pressure building circuit should trap some "O".
- **Pressure Regulator filter clogging – cloth staining test used for some "O" blow-out.**
- Some Mfg's have no recommendations regarding use of polishing filters & filter use is **not** mandatory by many fountain users

VI. Conclusions & Recommendations

Probabilities as Potential MBT "O" Sources

	LOWER Probability	HIGHER Probability
Compressor Oils	✓	
Elastomeric Transfer Hoses, Tubing, O-Rings		✓
Pipe Assembly Aids	✓	
Feed Gas Oil Residues	✓	

VI. Conclusions & Recommendations

- Only use LCO_2 compatible (food grade) compressor oils, transfer hoses, polymeric tubing & elastomeric hardware.

- MBT Tank Drain & Cleaning guidelines should be considered - time scheduled or "on-condition" based upon simple CO2 Purity Screening Tests
- MBT polishing filters recommended if no tank cleaning PM performed.

VI. Conclusions & Recommendations

- Field survey data of MBT “O” conditions are minimal at best. This study should be expanded – **internationally**.

- LCO_2 Transfer Hose Materials - Compatibility Charts, Test methods may need review & possible revisions made (ex. Neoprene, Buna N, plasticizer solubility etc.)

VII. Summary

"O" in MBT tanks needs more study & possible industry attention.

Psychological impact of high "O" in MBT's may be more potentially damaging to **Fountain Business** than actual sensory or health risks, especially when polishing filters are used.

Perception is Reality*?*

Acknowledgements

Thank you to the many CO_2 supplier, OEM hardware, Fountain & Beverage Industry Service Sources that contributed "O" data, pictures & field experience information.