CO_2 101

Analytical Procedures for Carbon Dioxide Quality

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The Gold Standard for Gas Analysis

Agenda

- Introduction
- History of CO_2 Quality
- Impurities of interest
- Sampling Equipment
- Analytical Techniques
- Summary

Who is this guy?

- Ralph Ciotti
- President / CEO of Atlantic Analytical Laboratory
- 30 years of analytical experience in compressed gases
- 20+ years working with beverage grade Carbon Dioxide

History of CO_2 Quality

Regulatory History

- Compressed Gas Association - CGA
  - Founded in New York in 1913 (as CGMA)
  - Primary focus – cylinder and gas manufacturing safety
  - 12 Different standards covering various carbon dioxide issues (manufacturing, storage, quality, safety)
  - Carbon Dioxide Commodity Specification G-6.2

Regulatory History

- International Society of Beverage Technologists - ISBT
  - Founded in Washington, DC in 1953
  - Primary focus – science and technology of beverages and their ingredients
  - Over 1,000 members worldwide
  - First basic CO_2 Guideline published in 1986
  - Formal CO_2 Guideline adopted in 1999, most recent revision released in January 2021 (rev 4)

The CO2 Quality “Bible”

isbt | international society of beverage technologists ®

Bulk Carbon Dioxide
Quality & Food Safety Guidelines

And

Analytical Methods
And Techniques
Reference

Beverage Grade Testing

Result	Parameter, Chemical Formula (Units)			DL	Method	ISBT Guideline Limit
99.99	Carbon Dioxide Purity	CO_2	(% v/v)	5.	ISBT 2.0	99.90% v/v min
nd	Moisture (Water Vapor)	H_2O	(ppm v/v)	1.0	ISBT 3.0	20.0 ppm v/v max
nd	Oxygen	O_2	(ppm v/v)	4.0	ISBT 4.0	30.0 ppm v/v max
nd	Carbon Monoxide	CO	(ppm v/v)	0.5	ISBT 5.0	10.0 ppm v/v max
nd	Ammonia	NH_3	(ppm v/v)	0.5	ISBT 6.0	2.50 ppm v/v max
nd	Oxides of Nitrogen	NO_x	(ppm v/v)	0.5	ISBT 7.0	5.0 ppm v/v max
nd	Nitrogen Dioxide	NO_2	(ppm v/v)	0.5	ISBT 7.1	2.50 ppm v/v max
nd	Nitric Oxide	NO	(ppm v/v)	0.5	ISBT 7.2	2.50 ppm v/v max
nd	Non-volatile Residue	NVR	(ppm w/w)	1.0	ISBT 8.0	10.0 ppm w/w max
nd	Non-volatile Organic Residue	NVOR	(ppm w/w)	1.0	ISBT 8.0	5.0 ppm w/w max
nd	Methanol	MeOH	(ppm v/v)	0.2	ISBT 9.0	10.0 ppm v/v max
nd	Total Hydrocarbons as Methane	THC	(ppm v/v as CH_4)	0.1	ISBT 10.0	50.0 ppm v/v max
nd	Total Non-Methane Hydrocarbons	TNMHC	(ppm v/v as CH_4)	0.1	ISBT 10.1	20.0 ppm v/v max
nd	Acetaldehyde	AA	(ppm v/v)	0.05	ISBT 11.0	0.20 ppm v/v max
nd	Aromatic Hydrocarbon	AHC	(ppm v/v)	0.002	ISBT 12.0	0.020 ppm v/v max
nd	Total Sulfur	TS	(ppm v/v as S)	0.02	ISBT 13.0	0.10 ppm v/v max (excl. SO_2)
nd	Sulfur Dioxide	SO_2	(ppm v/v)	0.02	ISBT 14.0	1.0 ppm v/v max
	Sensory Tests					
PASS	Odor in Water			na	ISBT 16.0	No foreign odor
PASS	Taste in Water			na	ISBT 16.0	No foreign taste
PASS	Appearance in Water			na	ISBT 16.0	No color or turbidity

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Can we analyze that?

What to look for?

For any gas analysis, the impurities of interest should be based on two main factors:

- **The source of the gas**

  What impurities could possibly be present?

- **Intended use for the gas**

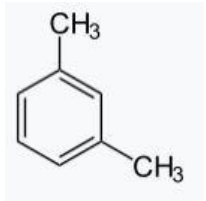
  What impurities will impact your product?

Common CO_2 Sources

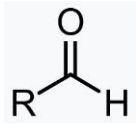
- Chemical Processing (ethylene oxide, ammonia, etc)
- Acid Neutralization
- Geothermal / Well Sources
- Combustion Processes
- Syngas Production
- **Fermentation**

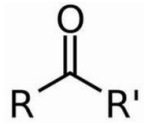
Fermentation Source Impurities

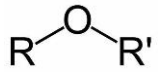
- Oxygen (O_2)
- Carbon Monoxide (CO)
- Oxides of Nitrogen (NO_x)
- Volatile Hydrocarbons (C_1-C_6)
- Aromatic Hydrocarbons (BTEX)
- Volatile Sulfur Compounds (VSC)
- Water Vapor (H_2O)

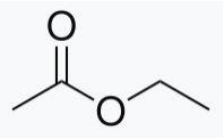


- Volatile Oxygenates (VOX)
  - Alcohols (Methanol, Ethanol, etc)
  - Aldehydes
  - Ketones
  - Ethers
  - Ethyl Acetate









Impact of Impurities

- Oxygen – Product oxidation, off odors and taste
- Oxides of Nitrogen (NOx) – Regulatory requirement
- Aromatic Hydrocarbons (BTEX) – Regulatory requirement
- Volatile Hydrocarbons (C_1-C_6) – Sensory impact, off odors and taste
- Volatile Oxygenates – Sensory impact, off odors and taste
- Volatile Sulfur Compounds (VSC) – Sensory impact, off odors and taste
- Water Vapor – Processing issues (freezing in cryogenic lines)

Sampling Equipment

The most important step in any analytical program is collecting an accurate sample that is truly representative of the source from which it was collected.

Sampling Equipment Types

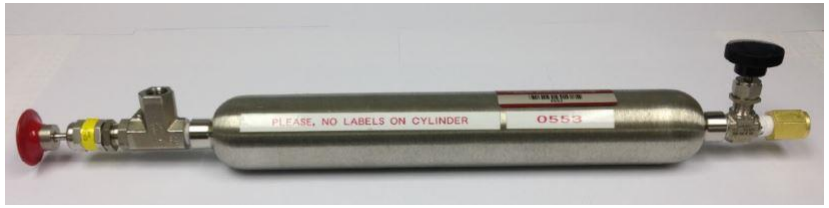
- Polished Beaker: Used for oil/particulate impurities (NVR/NVOR)

  Filled with dry ice or snow generated from liquid CO_2

Sampling Equipment Types

- **Cylinders:** Typically used for atmospherics and water only

  Filled with liquid (cryogenic) or gas phase (vaporized) CO_2



Sampling Equipment Types

- Polymer / Aluminized Bags: Used for all other impurities

  Filled with gas phase CO_2 only

Using Polished Beakers for Sampling

PROS

- Easy to ship
- Non-HAZMAT
- Eliminates need to ship liquid CO_2
- Multi-use – no maintenance
- Indefinite shelf life

CONS

- Potential for over-pressurization
- Easy to contaminate
- Cryogenic liquid handling safety
- Only good for NVR/NVOR testing

Using Cylinders for Sampling

PROS

- Impermeable to air and water
- Liquid sampling possible
- Can run all tests from one vessel
- Multi-use
- Long-term stability

CONS

- Heavy
- Expensive
- Potentially HAZMAT (liquid or high pressure)
- Stainless steel will absorb sulfurs
- Maintenance & cleaning
- Hydrotest requirements (5 years)

Using Bags for Sampling

PROS

- Inexpensive
- Easy to ship
- Non-HAZMAT
- Can be used for most impurities

CONS

- Permeable to air and water
- Fragile
- Potential to overfill & rupture
- Single use
- Potential outgassing of impurities
- Long-term stability issues (>3 weeks)

Cylinder, Beaker, and 2 – 1L tedlar bags

All low-pressure samples

Ships as non-HAZMAT

Indefinite shelf life

Best Option?

Hybrid Sampling Kit

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There’s definitely a story here.

Analytical Techniques

Non-Volatile Residue (NVR) and Non-Volatile Organic Residue (NVOR)

- Only tested on “product” cryogenic (liquid) CO_2
- Primary Concern

  Oil contamination – reported in ppm by weight
- Main Analytical Method

  Gravimetric (from solid, liquid, or snow vaporization)
- Alternate Analytical Methods

  None

Oxygen (O_2) & Atmospherics

- **Main Analytical Method**

  Mass Spectrometry

- **Alternate Analytical Methods**

  Electrochemical O_2 analyzer (oxygen only)

  Gas chromatography

Nitrogen
Oxygen
Argon
Hydrogen
Helium

Water (H_2O) / Moisture Content

- **Main Analytical Method**
  - Electrometric moisture analyzer
- **Alternate Analytical Methods**
  - Absorption spectroscopy
  - Mass spectrometry
  - Physical dew point analysis (Dew Cup)

Total Hydrocarbons (THC)

- Reported as Methane (CH_4) equivalent
- Main Analytical Method

  Gas chromatography - FID
- Alternate Analytical Methods

  Absorption spectroscopy

  Mass spectrometry

Volatile Hydrocarbons (VHC)

- **Primary Concern**

  Methane (CH_4)

- **Main Analytical Method**

  Gas chromatography - FID

- **Alternate Analytical Methods**

  Absorption spectroscopy

  Mass spectrometry

Methane
Ethylene
Ethane
Propylene
Propane
Isobutane
n-Butane
Butenes
Isopentane
n-Pentane
Pentenes
C_6+

Aromatic Hydrocarbons (BTEX)

- **Primary Concern**

  Benzene

- **Main Analytical Method**

  Gas chromatography - PID

- **Alternate Analytical Methods**

  Absorption spectroscopy

  Mass spectrometry / GC-MS

  Colorimetric detector tube

Benzene
Toluene
Ethyl Benzene
m+p Xylene
o-Xylene

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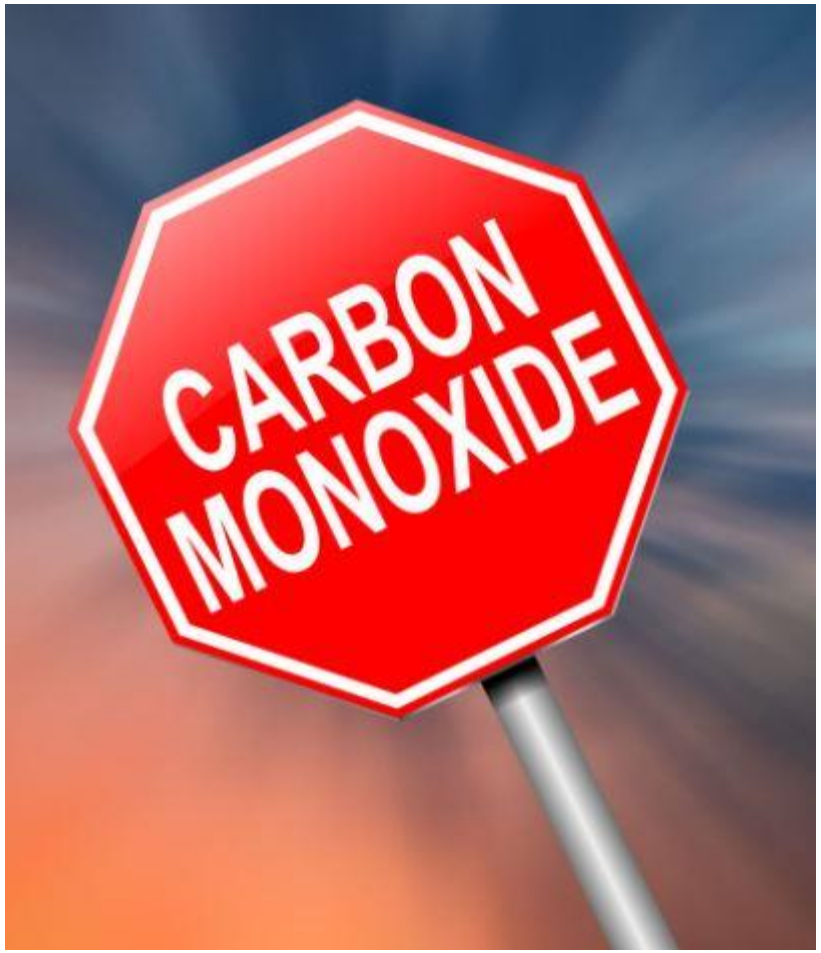
My favorite sampling job

Carbon Monoxide (CO)

- **Main Analytical Method**
  - Gas chromatography - PDID
- **Alternate Analytical Methods**
  - GC-Methanizer
  - Absorption spectroscopy
  - Colorimetric detector tube



Volatile Oxygenates

- **Primary Concerns**

  Acetaldehyde, Ethanol

- **Main Analytical Method**

  Gas chromatography - FID

- **Alternate Analytical Methods**

  Absorption spectroscopy

  Mass spectrometry

  Colorimetric detector tube (single impurity)

Acetaldehyde
Ethylene Oxide
Dimethyl Ether
Methyl Ethyl Ether
Methanol
Propionaldehyde
Acetone
Ethanol
Isopropanol
Ethyl Acetate
t-Butanol
n-Propanol
2-Butanol
Isobutanol
n-Butanol
Isoamyl Alcohol
Isoamyl Acetate

Volatile Sulfur Compounds (VSC)

- **Primary Concerns**

  Hydrogen sulfide, sulfur dioxide, carbonyl sulfide

- **Main Analytical Method**

  Gas chromatography - SCD

- **Alternate Analytical Methods**

  Absorption spectroscopy

  Mass spectrometry

  Colorimetric detector tube

Hydrogen Sulfide
Carbonyl Sulfide
Sulfur Dioxide
Methyl Mercaptan
Ethyl Mercaptan
Dimethyl Sulfide
Carbon Disulfide
i-Propyl Mercaptan
t-Butyl Mercaptan
n-Propyl Mercaptan
Methyl Ethyl Sulfide
sec-Butyl Mercaptan
i-Butyl Mercaptan
Diethyl Sulfide
n-Butyl Mercaptan
Dimethyl Disulfide
Diethyl Disulfide
Other Sulfurs
Total Sulfur Content

Ammonia (NH_3), Vinyl Chloride (C_2H_3Cl), Phosphine (PH_3), Hydrogen Cyanide (HCN), Oxides of Nitrogen ($NO + NO_2$)

- "Source Specific" Impurities
- Main Analytical Method
  - Colorimetric detector tubes
- Alternate Analytical Methods
  - Absorption spectroscopy
  - Gas chromatography
  - Mass spectrometry

Carbon Dioxide Purity

- Main ~~Analytical~~ Method

  Calculated by difference of all impurities from 100%

- Alternate Analytical Methods

  Absorption spectroscopy

  Gas chromatography

  Mass spectrometry

  Wet chemical absorption (Zahm & Nagel)

Odor, Taste, and Appearance

- **Measured in Gaseous and/or Aqueous Form**
- **Safety Concerns**

  Always perform last – only if no failing results
- **Main Analytical Method**

  Visual, olfactory, organoleptic
- **Alternate Analytical Methods**

  e-Nose analyzer

Review

- History of CO_2 Quality
- CO_2 Sources
- Impurities of Interest
- Sampling Equipment
- Analytical Techniques

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My favorite price quote

Thank you!

Any questions?

Ralph Ciotti

President / CEO

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The Gold Standard for Gas Analysis

ISO/IEC 17025:2017
Accredited
PJLA
Testing
Accreditation # 59415