Air Contamination Quantification by FTIR Gas Cell

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Wallops Flight Facility

Wallops Flight Facility was established in 1945 by the National Advisory Committee for Aeronautics as a center for aeronautic research. Today, Wallops is NASA's principal facility for management and implementation of suborbital research programs.
Why is Gas Composition Important?

Gas quality is of utmost importance when supplied gas is required for breathing

- Firefighters require supplied breathing air in certain circumstances
- Pilots require aviators grade breathing oxygen at certain altitudes and when performing certain maneuvers
## Methods of Accreditation

<table>
<thead>
<tr>
<th>Impurity Requirements for Various Certifications of Air and Oxygen</th>
<th>ABO</th>
<th>ABO</th>
<th>ABO</th>
<th>ABO</th>
<th>Breathing Air</th>
<th>Breathing Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I (Gas)</td>
<td>Type II (Liquid)</td>
<td>Type I E (Gas)</td>
<td>Type II D (Liquid)</td>
<td>Grade D</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen Content</td>
<td>&gt;99.5%</td>
<td>&gt;99.5%</td>
<td>&gt;99.5%</td>
<td>&gt;99.5%</td>
<td>19.5 – 23.5%</td>
<td>19.5 – 23%</td>
</tr>
<tr>
<td>Moisture</td>
<td>&lt;6.6 ppm / -63.3 °C</td>
<td>&lt;6.6 ppm / -63.3 °C</td>
<td>&lt;6.6 ppm / -63.3 °C</td>
<td>&lt;6.6 ppm / -63.3 °C</td>
<td>&lt;67 ppm / -45.6 °C</td>
<td>&lt;24 ppm</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Remainder</td>
<td>Remainder</td>
<td>Remainder</td>
<td>Remainder</td>
<td>Remainder</td>
<td>75 - 81%</td>
</tr>
<tr>
<td>Rare Gases</td>
<td>Remainder</td>
<td>Remainder</td>
<td>Remainder</td>
<td>Remainder</td>
<td>Remainder</td>
<td>Remainder</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>&lt;10 ppm</td>
<td>&lt;5 ppm</td>
<td>&lt;10 ppm</td>
<td>&lt;5 ppm</td>
<td>&lt;1000 ppm</td>
<td>&lt;1000 ± 50 ppm</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>&lt;10 ppm</td>
<td>&lt;5 ± 0.5 ppm</td>
</tr>
<tr>
<td>Methane</td>
<td>&lt;50 ppm</td>
<td>&lt;25 ppm</td>
<td>&lt;50 ppm</td>
<td>&lt;25 ppm</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Acetylene</td>
<td>&lt;0.1 ppm</td>
<td>&lt;0.05 ppm</td>
<td>&lt;0.1 ppm</td>
<td>&lt;0.05 ppm</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Ethylene</td>
<td>&lt;0.4 ppm</td>
<td>&lt;0.2 ppm</td>
<td>&lt;0.4 ppm</td>
<td>&lt;0.2 ppm</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Non-methane Hydrocarbons as methane equivalent</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>&lt;25 ± 1 ppm</td>
</tr>
<tr>
<td>Non-methane Hydrocarbons as ethane equivalent</td>
<td>&lt;6 ppm</td>
<td>&lt;3 ppm</td>
<td>&lt;6 ppm</td>
<td>&lt;3 ppm</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Nitrous Oxide</td>
<td>&lt;4 ppm</td>
<td>&lt;2 ppm</td>
<td>&lt;4 ppm</td>
<td>&lt;2 ppm</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Halogenated Compounds (refrigerants)</td>
<td>&lt;2 ppm</td>
<td>&lt;1 ppm</td>
<td>&lt;2 ppm</td>
<td>&lt;1 ppm</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Halogenated Compounds (solvents)</td>
<td>&lt;0.2 ppm</td>
<td>&lt;0.1 ppm</td>
<td>&lt;0.2 ppm</td>
<td>&lt;0.1 ppm</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Other</td>
<td>&lt;0.2 ppm</td>
<td>&lt;0.1 ppm</td>
<td>&lt;0.2 ppm</td>
<td>&lt;0.1 ppm</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Condensed Hydrocarbons &amp; particulates</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>&lt;5 mg/m³</td>
<td>&lt;2 mg/m³</td>
</tr>
<tr>
<td>Odor</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>No / Slight Odor</td>
</tr>
</tbody>
</table>

Notes: ppm = parts per million; C = Celsius; N/A = Not Applicable; mg/m³ = milligrams per cubic meter
What is GC?

Gas chromatography

• Separates chemicals by using a carrier gas to carry molecules through a long column

• Chemicals exhibit different retention times based on their physical and chemical properties in relation to a stationary phase
Why Use FTIR Instead of GC?

• Calibration time: 15 minutes vs 2-3+ hours

• The requirement of carrier gas and specific columns makes GC more expensive to maintain and operate

• GC is more susceptible to variation from changes in method and conditions such as carrier gas flow rate, column temperature, changes in columns, etc.

• Spectral features associated with FTIR do not vary in location due to changes in external conditions
Infrared Spectroscopy – Brief Overview

• Infrared light is passed through a sample and collected by a detector

• Molecules absorb infrared radiation at resonant frequencies that are characteristic of their structure

• Functional groups display predictable infrared properties that can be used to identify compounds of interest in a sample
Infrared Spectroscopy - Continued

• A spectrum is created with signal response vs. wavelength which acts as a “fingerprint” of the sample

• Only vibrations resulting in a change in dipole moment are detected
What is FTIR?

• Fourier Transform Infrared Spectroscopy

• FTIR differs from traditional IR spectroscopy in that it allows for the collection of a broad range of wavelengths simultaneously
FTIR Gas Cell

• A common method used with gas cells is the “Least Squares Fit” method
• Works best with pure standards
• Identifies molecules based on their entire spectral fingerprint, as opposed to individual functional group spectral features
• Gas cells allow for high signal throughput by taking advantage of the path length feature of Beer’s Law
Disadvantages of FTIR

- Infrared radiation has low energy - it can be difficult to obtain high levels of sensitivity

- Noise in one region of a spectrum can spread throughout the spectrum

- Only detects molecular vibrations causing a change in dipole moment - cannot be used for the detection of diatomic molecules
Instrument Set-up

FTIR – Agilent Cary 660
- Software – Resolutions Pro V 5.2.0
- Source – MIR Source
- Beam Splitter – Potassium Bromide (KBr)
- Gas Cell – Mars 2L/10M-SS Multi-Pass Gas Cell
- Detector – Mercury Cadmium Telluride (MCT)
- Resolution – 0.1 cm\(^{-1}\)
- Apodization – Happ-Ganzel
- Zero fill – 8
MCT Detector

• Mercury Cadmium Telluride
• Only common material that can detect IR radiation in both common atmospheric windows
  • Mid-wave infrared window  3300 cm\(^{-1}\) to 2000 cm\(^{-1}\)
  • Long-wave infrared window  1250 cm\(^{-1}\) to 830 cm\(^{-1}\)
• High quantum efficiency gives superior sensitivity
• Requires cooling with liquid nitrogen to reduce noise
Apodization

• The mathematical transformation of raw data used to create spectra

• Common apodization functions include boxcar, triangular, and Happ-Genzel

• Happ-Genzel results in lower resolution but minimizes the ripple effect caused by large peaks
Creating Calibration Curves

• Varying the pressure inside the gas cell can simulate different concentrations

\[ C = \frac{PSIg + 14.7}{14.7} \times X \]

• Limitations: Any uncertainty in the standards is expanded the further away the pressure in the cell is from 0 PSIg
Using the blank determination method gave us a quantitation limit of 0.37 ppm with an uncertainty of ± 0.09 ppm
Blank Determination Method

• Detection Limit = \( Avg_{Blank} + 3 \times Std\ Dev_{Blank} \)

• Quantitation Limit = \( Avg_{Blank} + 10 \times Std\ Dev_{Blank} \)

• Used when blank analysis yields results with nonzero standard deviation

• Weakness is that there is no evidence that low concentrations of analyte will actually produce a signal distinguishable from a blank sample
Concentration Dependent Bias

• Bias – Difference between the average of measurements made on the same object and its true value

• Does bias change throughout a curve?

• Eurachem Guide “Quantifying Uncertainty in Analytical Measurement”
Concentration Dependent Uncertainty

• Uncertainty – Estimate of how far an experimental value may be from the true value

• Uncertainty could be overstated or understated based on the concentration used to calculate it
Major Interferences

• Specificity - The extent to which a calibration is specific for a particular molecule

• Care must be taken to ensure specificity of calibration curves before signal to noise can be maximized

• If an interference is found, can use different IR region for identification
Water

- Biggest concern in gas analysis due to overlap of regions
- Water is a strong absorber of IR, combined with the 10 meter path length gives strong signals for small concentrations of water
Carbon Dioxide Measurements

- Carbon Dioxide is present in normal air and most calibration gases
- The most active region for carbon dioxide quantification saturates around 100ppm with my instrument parameters
Nitrous Oxide

- Nitrous Oxide contains similar functional groups to carbon dioxide and therefore exhibits similar IR modes
- Certifications requiring nitrous oxide measurements contain low concentrations of carbon dioxide

![Graphs showing IR modes of Carbon Dioxide and Nitrous Oxide](image)
Total Hydrocarbon Determination

• Certifications require grouped quantification of hydrocarbons

• Methane and ethane have unique IR modes that can be used to distinguish them from other hydrocarbons
Total Hydrocarbon Quantification

• All hydrocarbons exhibit C-H combination bands near 3000 cm\(^{-1}\)
• This curve only gives total hydrocarbons as methane equivalents, it cannot be used to distinguish between hydrocarbons such as propane and butane
Results and Conclusion

- Results from a comprehensive study of a certified standard at the limits set in NFPA 1989 prove the methods meet the required specifications

<table>
<thead>
<tr>
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<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>High Range Carbon Dioxide</td>
<td>1024.058</td>
<td>11.635</td>
<td>1038</td>
<td>13.942</td>
<td>2.272</td>
<td>23.27</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>5.174</td>
<td>0.077</td>
<td>5.012</td>
<td>-0.162</td>
<td>2.986</td>
<td>0.154</td>
</tr>
<tr>
<td>Total Hydrocarbons as Methane Equivalents</td>
<td>26.755</td>
<td>0.751</td>
<td>25.44</td>
<td>-1.315</td>
<td>5.614</td>
<td>1.502</td>
</tr>
<tr>
<td>Methane &amp; Ethane as Methane Equivalents</td>
<td>24.955</td>
<td>0.417</td>
<td>25.44</td>
<td>0.485</td>
<td>3.343</td>
<td>0.834</td>
</tr>
<tr>
<td>Ethane</td>
<td>13.014</td>
<td>0.142</td>
<td>12.72</td>
<td>-0.294</td>
<td>2.178</td>
<td>0.283</td>
</tr>
</tbody>
</table>
Results and Conclusion

• Five consecutive 100% passing CAPT round robin samples

<table>
<thead>
<tr>
<th>Analytes</th>
<th>LJT &amp; Associates, INC.</th>
<th>Average Value (n=11)</th>
<th>(mean+3σ)</th>
<th>(mean-3σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide</td>
<td>766.93</td>
<td>738.96</td>
<td>995</td>
<td>528</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>16.51</td>
<td>15.86</td>
<td>20.6</td>
<td>10.2</td>
</tr>
<tr>
<td>Total Hydrocarbons as Methane Equivalents</td>
<td>30.131</td>
<td>29.13</td>
<td>33</td>
<td>25.2</td>
</tr>
<tr>
<td>Methane</td>
<td>10.57</td>
<td>9.96</td>
<td>13.3</td>
<td>7.2</td>
</tr>
<tr>
<td>Ethane</td>
<td>10.02</td>
<td>9.88</td>
<td>11.4</td>
<td>8.4</td>
</tr>
</tbody>
</table>
References


