Alternative Monitoring Technologies: A Brief Overview

a technical solution to meet every need...

Cemtek Environmental Inc.
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What’s New?

- Mercury
- Particulate
- Tunable Diode Laser Spectroscopy - TDLAS
  - NH₃, HCl, H₂S, HCN, O₂, +
- Fourier Transform Infrared Spectroscopy – FTIR
  - NH₃, HCl, NO, NO₂, CO, CO₂, SO₂, +
- Cavity Ring Down Spectroscopy – CRDS
  - HCl, CO, SO₃, NH₃, O₂, HF, H₂O, +
- Wavelength Scanning Spectroscopy (WSS)
  - CO, CO₂, CH₄, H₂S, H₂O + more
- Quantum Cascade Lasers
  - CO, NO, NO₂, CO₂, SO₂.
Mercury Monitoring Systems
Detection Technologies

Continuous Monitoring

Cold Vapor Atomic Fluorescence
Example: Thermo Freedom Mercury Series

Continuous Batch Measurement

Pre-Concentration on Gold Filter, Thermal Desorption, Atomic Fluorescence
Example: Tekran Series 3300

Long Term Batch Measurement

Sorbent Trap or Appendix K
Example: Apex Instruments
The Mercury Freedom System

- Dilution Based Measurement
- Inertial Filter Sample Conditioning
- Conversion at the Stack
- Direct Measurement CVAF
- High Sensitivity
- True Real-Time Monitoring
- Modular Design
- iSeries Platform
Model 80/Hg Analyzer

- Direct Measurement CVAF
  - Continuous measurement
  - No additional gasses required
- Diluted Sample
  - Lower moisture, less reactive
- Speciating
  - Measures either Hg$^+$ or Hg$^0$
- Analyzer Detection Limit: Currently ~1 ng/m$^3$ (~0.1 ppt)
- No Cross Interference with SO$_2$
Hg Fluorescence

\[
\text{Hg} + h\nu (254 \text{ nm}) \rightarrow \text{Hg}* \\
\text{Hg}* \rightarrow \text{Hg} + h\nu (254 \text{ nm})
\]

\[
I_a = I_o[1-e^{-ax(Hg)}]
\]

\[
I_f = I_oax(Hg) \text{ or } K(Hg)
\]

High Intensity Hg Lamp
Reflective Filtering
Enhanced Light Baffling
Bandpass Filter
Continuous Batch Monitoring
Tekran

M&C Hg Probe

Model 3320 Sample Conditioner

Model 2537A AF Analyzer

Model 3310 Calibration Unit

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Principles of Operation

- Mercury in sample gas is pre-concentrated onto (pat’d) pure gold cartridge
- Adsorbed mercury is thermally desorbed
- Detected by atomic fluorescence detector
- Two cartridges are used to alternately sample and desorb allowing continuous operation
  - No gaps in data stream
Flow Diagram of Mercury Analyzer (Pat’d)
HGP Dual Trap Sampling Probe

Configuration:
- Heated Sample Probe – Dual Probe Heaters
- Length (4, 6, 9, 12ft Standard)
- Material – C276 Hastelloy or 316 SS
- Enclosure – Insulated SS Junction Box
- Trap Sizes – 10mm Large Standard
- Optional 6mm Small Trap Adapter
- Paired trap holders
- Pitot Tube – Optional S Type Pitot

(shown with optional pitot)
Sorbent Trap

Configuration:
- Section 1: Sample Collection Section
- Section 2: Breakthrough Indicator Section
- Section 3: Vapor-Spike Section to Measure Recovery
Particulate Monitoring Systems
Particulate

- **Wet FGD Scrubber Particulate Monitoring**
  - Saturated stack applications
  - Opacity monitors cannot transmit light through saturated stack
  - Example: Sick FWE 200 Particulate Monitor

- **Dry Stack Particulate Monitoring**
Particulate

Sick FWE 200 Principle of Operation

NON-DISPERSIVE PHOTOMETER PRINCIPLE

The FWE200 is based on the scattered light principle (forward scattering). Smallest particle concentrations can be recorded thanks to the extremely high sensitivity of this principle.

A laser diode directs a beam of modulated light in the visible range (wavelength approx. 650 nm) at the dust particles in the gas flow. The light scattered by the particles is recorded by a highly sensitive detector which is positioned in an angle of approx. 15° to the beam axis.

The received signal is electrically amplified and supplied to the measuring channel of a microprocessor as the central part of the measuring, control and evaluation electronics. The point of intersection between the transmitted beam and the receiver aperture defines the measuring volume in the gas duct.
Laser Based Analyzer Systems
TDL & QC Analyzers

- Unisearch TDL for NH3, HCl, HCN, CO, O2
- AP2E Cavity Ringdown for SO3
- Los Gatos Research/ABB Off Axis CRDS for ppb level measurements.
- Cemtek Instruments WSS Optical GC’s
- Cascade Technologies UK Multi-gas analyzers & In-Situ Probes using QC Lasers
- TDL Sensors UK. QCL rack mount analyzers for trace level CO, NO, N2O, HCl, SO2 etc.
Tunable Diode Lasers

What are Tunable Diode Lasers?

- Small crystals of Ga, As, Sb, P
- Similar to those used in telecommunications, CD players, and laser printers
- Emits laser radiation when an electric current is applied
- Laser center wavelength depends on composition of crystal
- Wavelength can be changed over a narrow range by changing current, or over a wider range by changing laser operating temperature
- Permits scanning over entire absorption feature
Tunable Diode Laser Ammonia Slip Measurement Techniques

CO, CO₂, NH₃, H₂O, O₂, NO₂, SO₂, NO, SO₃

Near Infrared (1500 nm)

Visible (700 nm)

Near UV (350 nm)

NIR TUNABLE DIODE LASER ABSORPTION SPECTROSCOPY

VIS-UV DIFFERENTIAL OPTICAL ABSORPTION SPECTROSCOPY
IR Spectroscopy

Emission Wavelength

Absorbance

$I = I_0 e^{-\sigma c l}$

- **Absorption region**
- **Side wavelengths, without absorption**
Dual Pass (Mono-static) Duct Configuration

Fiber-optic & coax cables

Analyzer
AP2E Cavity Ringdown Analyzer
Direct SO3 Measurement Without Interferences

SO₃

ProCees Spectrum (50 mbar/45°C)
SO3 100 ppm

200 DATA POINTS SPECTRA - 0.0012 nm OPTICAL RESOLUTION
CEMGAS: Direct SO₃ Measurement Without Interferences

ProCeas Spectrum (50 mbar / 45°C)

H₂O 20%  CO₂ 10%  SO₂ 100 ppm  SO₃ 100 ppm

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Operating at low pressure in the entire sampling line (from control point to sensor gas cell) allows to work at much lower dew point values for the condensable. E.G., working at 50 mbar pressure in presence of 5% vol. of H2O(g), allows to operate without water removal step to temperatures as low as -11.7°C (11F), the dew point of 5% vol. H2O at 50 mbar. If the sample line temperature drops below that dew point temperature or if the water vapor concentration increases, the sample line only needs to be traced at a temperature above the dew point.
In this spectrum of CO₂ (~30%), CH₄ (~30%) and H₂S (~300 ppm), we observe that:

→ If operating at (almost) atmospheric pressure, there still is spectral overlap leading to cross response between CH₄ and H₂S.

→ If operating at low pressure (e.g. 100 mbar), all spectral overlap has disappeared. The risk of cross response in measuring H₂S in trace concentrations has been removed.
SO$_3$ Summary of Improvements

1. Higher Sensitivity (more signal / less noise)
2. Multi-Gas Capable - No Interference
3. No Sample Conditioning - Low Maintenance
4. Low Fouling – Low Maintenance
5. Faster Transfer Time – Faster Gas Cell T90 – Faster Response
7. Self-Stabilizing – No Drift.

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Los Gatos Research

- High resolution absorption coupled with long pathlengths.
- Highly Specific to the target gas.
- No cross interference.
- No moving parts
- High degree of sensitivity - single ppb levels.
- Most sales have been in laboratory & research applications.
- Rugged design makes it suitable for industrial applications with the proper sample handling.
- Chemometrics enables quantification of multiple gases in complex mixtures
  - Single-laser instrument accurately reports multiple gas species
  - Industrial apps (C$_2$H$_2$ in olefin plants, H$_2$S in nat gas, industrial emissions)
    - Environmental applications (methane isotopes)
  - Emerging apps (chemical weapons, VOC monitoring, breath analyses)
Most Molecules Absorb Infrared (IR) Light:

- The patterns of IR wavelengths (colors) they absorb are unique to each molecule
- The amount of light they absorb is proportional to their concentration

As a Result:

- The presence of specific compounds can be unequivocally determined by the absorption patterns
- The concentration of the compounds can be measured by the strength of the absorption patterns
FTIR - Interior of Shell System
Cemtek Instruments WSS Optical GC

- Wavelength Scanning Spectroscopy.
- Gas specific optical filter & detector.
- Conventional Extractive or Dilution Extractive
- Single & Multi-pass Cells.
- Potential for open path & cross duct monitoring.
- Class 1 Div Options
- Potential to replace GC’s
Wavelength Scanning Spectroscopy (WSS)

- Non-contact, flow-through
  - no sensor poisoning
  - long-term stability

- Wavelength scanning
  - simultaneous multi-compound
  - high stability & selectivity

- Versatile platform
  - UV – IR wavelength regions
  - various kinds of light sources are easily coupled

- High Etendue optical system
  - High sensitivity
  - fast measurement (< 1 second)
  - “opaque” liquid & solid measurements

- Single-element detector
  - high performance-to-cost ratio

- Advanced signal processing
  - interference compensation
  - baseline stability

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Multiple Cell Configurations

- Modular, single-pass sensor design
- In-line configuration
- Short path liquid cell

- Double-pass sensor head
- Single-pass in a rackmount enclosure
Multiple Gas Analysis

Applications:
• Natural Gas composition
• Btu Content measurement
• Gas Turbine fuel control
• Alternate Biogas Fuels
• Zero cross - sensitivity
• Real Time operation to replace GC

Applications:
• C1 – C5 for total gas analysis
• CO, CO2, HCl, NH3, NO, NOx
• GC replacement potential for Isobutene, N-Hexane, Propane, Isopentane, N-Pentane, N-Butane, Methane, Argon,
## Multi-gas analysis

### Table of recipes for Precise 5 Gas Analyzer (% level recipes listed only)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Recipe 142 (Natural Gas)</th>
<th>Recipe 143 (HPI blending)</th>
<th>Recipe 152 (LNG)</th>
<th>Recipe 153 (Sour Gas)</th>
<th>Recipe 154 (extended HPI)</th>
<th>Recipe 159 (LPG)</th>
<th>Recipe 161 (SynGas)</th>
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<td>Methane</td>
<td>( \text{CH}_4 )</td>
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<tr>
<td>iso-Butane</td>
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<td>✓ (0-100%)</td>
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<td>Carbon Monoxide</td>
<td>CO</td>
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<td>Carbon Dioxide</td>
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<td>1-Butene</td>
<td>( \text{C}_4\text{H}_8 )</td>
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<td>isobutylene</td>
<td>( 2\text{-methylpropene} )</td>
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<td>✓</td>
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<tr>
<td>1,3 Butadiene</td>
<td>( \text{C}<em>6\text{H}</em>{10} )</td>
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<td>✓</td>
<td>✓</td>
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<td>BTU calorific value</td>
<td>(&lt;\pm 0.05%) repeatability with 5 second averaging</td>
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<td>✓</td>
<td>✓</td>
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<td>✓</td>
<td>✓</td>
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<tr>
<td>Wobbe Index</td>
<td>(&lt;\pm 0.05%) repeatability with 5 second averaging</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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Subject to change.
Contact Precise for ranges, accuracy, repeatability and sample conditions.
<table>
<thead>
<tr>
<th></th>
<th>Certified Gas A</th>
<th></th>
<th>Certified Gas B</th>
<th></th>
<th>Certified Gas C</th>
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<td>Reference</td>
<td>Precise</td>
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<tr>
<td>CH4 (%)</td>
<td>86.29</td>
<td>86.183</td>
<td>83.37</td>
<td>83.284</td>
<td>82.10</td>
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<td>C2H6 (%)</td>
<td>8.47</td>
<td>8.542</td>
<td>3.07</td>
<td>3.056</td>
<td>3.88</td>
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<td>C3H8 (%)</td>
<td>1.84</td>
<td>1.963</td>
<td>0.40</td>
<td>0.460</td>
<td>0.88</td>
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<td>iC4H10 (%)</td>
<td>0.31</td>
<td>0.227</td>
<td>0.10</td>
<td>0.073</td>
<td>0.18</td>
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<td>nC4H10 (%)</td>
<td>0.48</td>
<td>0.422</td>
<td>0.11</td>
<td>0.093</td>
<td>0.17</td>
<td>0.148</td>
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<td>C5 lumped (%)</td>
<td>0.02</td>
<td>0.000</td>
<td>0.00</td>
<td>0.000</td>
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<tr>
<td>N2 (%)</td>
<td>1.10</td>
<td>1.120</td>
<td>11.23</td>
<td>11.344</td>
<td>9.80</td>
<td>9.793</td>
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<tr>
<td>CO2 (%)</td>
<td>1.55</td>
<td>1.543</td>
<td>1.72</td>
<td>1.690</td>
<td>3.01</td>
<td>2.979</td>
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<td>C6+ (%)</td>
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<td>N/A</td>
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<td>CV (Superior, Gross) (MJ/m3)</td>
<td>43.1638</td>
<td>43.107</td>
<td>35.9752</td>
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<td>36.7314</td>
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<td>Wobbe Index (MJ/m3)</td>
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<td>53.676</td>
<td>44.9728</td>
<td>44.971</td>
<td>45.3103</td>
<td>45.336</td>
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</table>
Acid or Sour Gas

- $\text{H}_2\text{S}$, $\text{CH}_4$, $\text{C}_2\text{H}_6$, $\text{C}_3\text{H}_8$, $\text{i-C}_4\text{H}_{10}$, $\text{n-C}_4\text{H}_{10}$, $\text{C}_5\text{H}_{12}$, $\text{CO}_2$, optional $\text{NH}_3$ &/or $\text{H}_2\text{O}$, BTU Calorific/heating value, Wobbe index
- SRU (Sulfur Recovery Units), feed-gas analysis, acid-gas removal, tail-gas treatment.

- Full C1 thru C5 speciation.

- All optical analyzer for H2S, Hydrocarbon & CO2 Measurements.
Olefins Analyzer

- \( \text{CH}_4, \text{C}_2\text{H}_6, \text{C}_2\text{H}_4, \text{C}_3\text{H}_8, \text{C}_3\text{H}_6, \text{i-C}_4\text{H}_{10}, \text{n-C}_4\text{H}_{10}, \)
  - upto 20 alkanes, alkynes, alkenes, CO, CO\(_2\), H\(_2\)S
  - and analog inputs including H\(_2\) and O\(_2\)

- Ethylene & Propylene Fractionation, & Acetylene Conversion process monitoring.


- Storage of Ethane & Ethylene
TDL Sensors

- TDL Gas analyzers
- QCL gas analyzers
- Low ppb sensitivity
- Rack mount, easy to use.
- Interface & control with laptop or DAHS
- CO, NO, NH3, N2O, NO2, CH4, H2S, SO2 etc.
- Higher cost than conventional rack mount but better accuracy. Simple - no moving parts.
Analyzer: Inside

Multi-pass optical cell

Control and signal processing electronics (embedded system)

TDL Sensors Rack Mount

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Fixed pathlength optical cell that is not dependant on mirror reflectivity

Robust, Stable Optical Cell
**Performance & Sensitivity**

Parts per billion resolution of CO concentration

**VERY high sensitivity!**

Mean = 0.201 ppm
\( \sigma = 0.008 \text{ ppm} \)

Latest version of instrument can achieve 2 ppb resolution

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Conclusion

Questions?

Thank You for Attending!

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