Tunable Diode Laser Spectrometrie
voor zuurstof analyse

Arthur Groenbos
Yokogawa Europe Solutions
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Quick overview of the session

- What you will bring after the session?
  - New method of gas analysis
  - How to migrate from legacy analyzer

- Which applications you will enjoy the benefit?
  - Oxygen analysis in process gas for safety
  - Analysis of Oxygen and Combustibles for advanced combustion control

- What are the enablers?
  - TDLS: Tunable Diode Laser Spectroscopy

- How does it work?
Yokogawa Europe

- Industry Automation
  - Instrumentation
  - Control Systems
  - Safety systems

- Business areas:
  - Oil & Gas
  - Refining
  - Petrochemicals
  - Chemicals
  - Power

- Manufacturing

- Sales support

- Technical Support
Application Laboratory
- Established in 2007 for GC, NIR and TDL
  - 180 m² application and run out area for 15 GC's simultaneously
  - Fume cupboards exist for the more toxic applications
Analysis and Quality Control

- **Liquid Analysis**
  - pH-/Redox
  - Conductivity
  - Dissolved Oxygen

- **Gas Analysis**
  - Zirconia Oxygen Detection
  - Zirconia Moisture Detection
  - TDL Tunable Diode Laser

- **Multi Component Analyzers**
  - FT-NIR Spectrometer NR800
  - Process Gas Chromatograph GC1000 Mark II
Realizing safe combustion and energy efficiency

Better explained in this document than I can do:

Instrumentation, Control, and Protective Systems for Fired Heaters

API RECOMMENDED PRACTICE 556

1 SCOPE
1.1 Purpose
1.1.1 This document provides guidelines that specifically apply to instrument, control, and protective system installations for gas fired heaters in petroleum refinery, petrochemical, and chemical plants.

3.2.4 Flue Gas Analyzers
3.2.4.2 Oxygen
3.2.4.3 Combustibles
3.2.4.4 Carbon Monoxide

But there is more to tell about TDLS
Legacy Oxygen analyzer: Paramagnetic

- Oxygen is a molecule with magnetic properties

- When placed in a magnetic field the rotation of the dumb-bell is proportional to the Oxygen concentration

- Wonderful analysis method in previous millennium still in use today
NIR Basics - Non Dispersive IR (NDIR)

For a simple Infrared analyser looking at one component it is necessary to filter out all the light except the wavelengths that are absorbed by the component of interest.

This is because the detector cannot distinguish individual wavelengths of light and just sees total light intensity of all wavelengths together.
Legacy (NDIR) Infrared Gas Analyzers

- We are used to seeing spectra as shown with smooth peaks.

- Photometers operate at low resolution (typical infrared filter is 10-20nm). Because of this, photometers are limited to large measure and reference wavelength absorption areas.

- In order to make an interference free analysis, there can be no stream component overlap within the filter areas.
Single peak Spectroscopy

At high resolution especially simple gas molecules exhibit fine structure (peaks within the peak, group of absorption bands ⇒ rotation bands)

Examples are O₂, CO, CO₂, SO₂, NO, C₂H₂, NH₃, HF, HCl, ……

While the entire absorption band is typically 10s of nanometers (nm), each individual peak is typically .1-.2nm wide
New Method of gas analysis:
An Infrared analyzer that measures also Oxygen

Stretching and bending of the bonds within molecules occurs at a frequency that is specific to that particular bond. If the vibration causes a change in dipole of the molecule then light at a particular frequency in the infrared band will be absorbed.
Spectral interference CO$_2$ - H$_2$O

- 10 nm (typical optical filter width) spectra of CO$_2$ and H$_2$O
- A low resolution spectrometer would report this entire section as one absorbance value
- No possible discrimination between CO$_2$ and H$_2$O. Results in H$_2$O interference with CO$_2$ measurement.
Single peak Spectroscopy

Diode lasers have very narrow wavelength emission (line width), typically 0.00004nm (0.04 pm = 0.04 *10^{-12} m) wide which allows hundreds or thousands of data points across the peak.

Therefore, they can focus on a single defined peak that has no overlap.

The laser scans the bandwidth, measuring the peak and baseline.
The laser is held at a fixed temperature as a coarse wavelength adjustment.

A current ramp is fed to the laser as the fine wavelength adjustment.

The collimated light passes through the gas to be measured. The amount of light absorbed by the peak is proportional to the analyte concentration.

The light is then focused on a detector and this direct signal is used to quantify the light absorbed by the analyte.
The TruePeak measurement technique is specifically developed for process analysis. It allows measurement in processes where the pressure, temperature and background gases change.

By using the True Peak we can measure the area of the absorbance peak. This eliminates effects from changing background gases, allowing for simple pressure and temperature compensation.

Traditional TDL measurement methods distort the peak, this makes it difficult or impossible to deal with simultaneous pressure, temperature and background gas changes.

**The TruePeak Advantage**

**Direct Absorption Spectra**
(10% O2 in different background gases)

**Traditional TDL Spectra**
(10% O2 in different background gases)
Tunable Diode Laser Spectroscopy

TruePeak TDL Analyzer

Launch Unit/Laser

Laser beam

Detector

Process connection
1. **Electronics Box, consists of:**
   - CPU & software for signal processing
   - Data acquisition
   - Laser temperature and current control
   - User interface and display
   - Communications hardware (ethernet, measurement outputs)

2. **Laser module (inside), consists of:**
   - Laser
   - Collimating lens
   - Laser mount
   - Validation chamber

3. **Process Connection, consists of:**
   - Flanges (2-4”)
   - Process isolation windows (wedged)
4. Detector module (inside), consists of:
   - Detector
   - Focusing lens
   - Detector mount
5. Alignment mechanism
6. Detector electronics
Inst. options for increased optical pathlength

- 24° TO 14° CONCENTRIC REDUCER
- 24° PIPE
- MIN. 36° DPL

- 36° PIPE
- 39° TO 14° CONCENTRIC REDUCER
- MIN. 36° DPL

- MIN. 36° DPL
- RESTRICTION
What challenges are you facing now?

**Extractive**

- Perfect Analyzers that require clean and dry sample are unreliable, unsafe and inaccurate
  - Paramagnetic Oxygen Analyzers
  - Electrochemical Oxygen Analyzers
  - NDIR gas analyzers
  - $P_2O_5$ or similar sensor based Moisture Analyzers

What keeps you awake at night?
What challenges are you facing now?

→ In-Situ

→ In-Situ Analyzers present safety hazard, selectivity problems and reliability issues
  
  – Combustion Oxygen in gas fired furnaces
  – Combustion Oxygen analysis in corrosive gases
  – Process Oxygen in gases with organic material
  – Catalytic bead or hot-wire Combustible analyzer
  – X-stack NDIR analyzers

EExd II B + H2, T2
Ambient Temperature : -20 to +60 °C
What challenges are you facing tomorrow?

- Fuel and feedstock costs will increase again
- Emissions limits will continue to decrease (CO₂, CO, NOx, etc)
- Requirements for plant safety will increase (SIL)
- Higher efficiency and flexibility will be required for profitable operation

**Advanced process control needs Advanced Analysis**
**TDLS vs. Paramagnetic (1-cost)**

**Analyzer Cost Estimate**

<table>
<thead>
<tr>
<th>%O2 on Vent Header</th>
<th>Paramagnetic</th>
<th>TDL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyzer hardware</td>
<td>10,000</td>
<td>25,000</td>
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<tr>
<td>Sample system</td>
<td>25,000</td>
<td>10,000</td>
</tr>
<tr>
<td>Free standing Enclosure</td>
<td>15,000</td>
<td></td>
</tr>
<tr>
<td><strong>Analyzer Hardware Total</strong></td>
<td><strong>50,000</strong></td>
<td><strong>35,000</strong></td>
</tr>
<tr>
<td>Packaging</td>
<td></td>
<td></td>
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<tr>
<td>Sample transport lines</td>
<td>4,000</td>
<td></td>
</tr>
<tr>
<td>Calibration gases &amp; regulators</td>
<td>1,000</td>
<td>1,000</td>
</tr>
<tr>
<td>Spare parts (est. at 10% of HW and SS costs)</td>
<td>3,500</td>
<td>3,500</td>
</tr>
<tr>
<td><strong>Auxiliary Equipment Total</strong></td>
<td><strong>8,500</strong></td>
<td><strong>4,500</strong></td>
</tr>
<tr>
<td>Construction/On-site Installation</td>
<td>10,000</td>
<td>5,000</td>
</tr>
<tr>
<td>Other-Specify in remarks</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Field Installation Total</td>
<td>10,000</td>
<td>5,000</td>
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<tr>
<td>Contingency</td>
<td>12,400</td>
<td>8,600</td>
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<tr>
<td><strong>System Total</strong></td>
<td><strong>80,900</strong></td>
<td><strong>53,100</strong></td>
</tr>
</tbody>
</table>

**Reduced installation/operation Costs**

- No analyzer shelter required
- No sample system required (excl. P/T)
- Low maintenance
- High reliability
- Fast response
- No cross interference
- No sampling errors
Installations
Yokogawa solution for Process Oxygen?

- Solution for your immediate challenge
- Migration from legacy analyzer
- Eliminate Measurement Interferences
- Improve Accuracy
- Improve Response Time (Analyzer Response time 2-5 sec)
- Reduce Maintenance
- Improve Reliability
Yokogawa Solutions for combustion Oxygen?

ZO>ZA>ZR: first digital Zirconia with replaceable sensor
- Direct measurement (<700 °C)
- Low Maintenance
- High Reliability
- Low Cost of Ownership

ZR series limitations
- Dangerous errors in presence of combustibles
- Ignition source if flame goes out in gas fired oven
- Point measurement

TDLS200: first TDL with true peak area integration
- Direct measurement
- Low maintenance
- High reliability
- Low Cost of Ownership
- Average measurement
- Safe under all circumstances

TDLS limitations
- Price is higher than ZR
- Installation is more elaborate than ZR
General combustion chart

**Oxygen**
- Primary combustion efficiency measurement. Easy to use for control
- Typically also used as safety measurement

**CO**
- Ideal set point measurement (for excess air)
- Pre-cursor to combustibles breakthrough

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**FUEL RICH**
- Oxygen
- Carbon Dioxide
- CO & Combustibles
- Unsafe
- CO ‘VIOLATIONS’
- CO2 ‘EXCURSIONS’
- Efficiency Losses

**AIR RICH**
- NOx ‘VIOLATIONS’
- Efficiency
- CO2
- Oxygen

**% EXCESS AIR**
-20
-10
0
10
20
Combustion control: the right way!

- Control Fuel-Air ratio based on Oxygen analysis

- Determine Oxygen by averaging analysis

- Determine Oxygen set point by CO analysis

- Detect flame-out by CH₄ analysis
Why use TDLS200 for CO analysis?

Safe:
- Energy efficiency losses
- NOx “violations”

Unsafe:
- CO “violations”
- CO2 excursions
Traditional combustion analysis

You had to make a difficult choice

Measure in the combustion zone with *distribution errors*

OR

Measure past the combustion zone where *CO is false low and O₂ is false high*

TruePeak combustion analysis

You no longer have to compromise

O₂ Measurement can be made in the combustion zone to *eliminate tramp air effects.*

CO, CH₄ and H₂O Measurement can be *made in the firebox* before concentrations reduce due to afterburning.

AND

Across the combustion zone to *minimize distribution errors*
Conclusion on Combustion benefits

TDLS measurements can provide combustion diagnostics:

- CO measurement with cross firebox coverage
- Average $O_2$ value from one analyzer
- $O_2$/CO Matching for control
- $CH_4$ and gas temperature measurements at high speed and across the firebox
Summary

- TDLS has no sample contact with sensor
- Windows can be purged to eliminate analyzer-gas contact
- Spectra (stored on analyzer) can allow historical measurement validation
- Continuous diagnostics
- TruePeak diagnostics stored on the analyzer
- TruePeak allows automatic validation
- No moving parts
- High MTTF for all components
- Minimal calibration/validation requirements
Question 1

To control a gas fired heater we want to measure:

- \( \text{O}_2 \) for fuel/air ratio
- \( \text{CO} \) to determine best Oxygen value
- \( \text{CH}_4 \) to detect flame-out situation
- \( \text{H}_2\text{O} \) to detect tube leak
- Temperature to detect fast temperature changes in case of tube leak or flame out

If you want to perform all these measurements, how many TDLS200 analyzers do you need?
Answer question 1

Two analyzers:

- One for Oxygen and for Temperature (comparing absorption of two absorption peaks)
- One for CO, CH₄, and H₂O that have peaks in the same scanning range
Thank you for your attention!