On-line gas chromatography

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Research and Development

Money in the Pipeline
Delft, 2 November 2010
Why Gas chromatography?

Energy (MJ) = Quantity (m$^3$) x Quality (MJ/m$^3$)

- quantity = flow measurement
- quality = calorific value $\rightarrow$ composition
  $\rightarrow$ gas chromatography

Error / uncertainty in both parts have the same impact!!
What is gas chromatography?

Separation by Chromatography
Gas Chromatography: calibration

Gas chromatogram of calibration gas (with Elster Encal 3000)

Peak area is proportional to concentration
Gas composition is used to calculate the Calorific Value (inferior and superior), Wobbe index, compressibility, density, viscosity (Reynolds number), V.O.S. (ultrasonic flow meter), etc.

Validation is required by contracts
Objectives for validation

Need for reliable measurement results
- Confidence and trust between buyer / seller
- Comply to contractual issues
- Comply to legislation

In practice:
Comply to EN1776:
Gas supply – Natural gas measuring stations – Functional requirements

For on-line GC: comply to ISO 10723:
Natural gas – Performance evaluation for on-line analytical systems
4.8 National regulations may require that the inspection and testing have to be witnessed and accepted by independent experts

6.3.1 Gas chromatograph operating conditions determined from a performance evaluation complying with ISO10723

6.3.2 The quality of the calibration gas is the key issue for the quality of the results of the measuring system

6.4.2 These calibration gases shall be prepared according to ISO6142 or ISO6143 or certified according to ISO6141. The traceability of the calibration gas shall be established.

7.1.4.1 The measurement instruments shall be calibrated with traceability to national standards … and shall be done by accredited laboratories
(VSL) implementation of EN1776/ISO10723 (+additional issues)

- Factory Acceptance Test (FAT)
  - At VSL or at the manufacturer’s site

- Site Acceptance Test (SAT)
Factory Acceptance Test

- GC performance (peak separation)
- Use of 7 traceable Primary Standard Gas mixtures to test:
  - Repeatability
  - Reproducibility (calibration interval)
  - Detector linearity
Detector linearity check with 7 PSM

- during field operation: single point calibration!

- Advise on calibration gas composition
- Take non linearity effect as additional uncertainty in calculation
Site Acceptance Test

- Performance
- Repeatability

- Test with two independent traceable VSL gas mixtures (matched to the line gas composition)
  
  - Analytical result should match to the VSL certificate within uncertainty criteria of ISO10723

  → Validation of the complete system!
Example of impact of error in GC analysis

Example:
Mixture of
- 94% CH₄ (mol/mol)
- 3% C₂H₆ (mol/mol)
- 3% N₂ (mol/mol)

What is (are) the most critical component(s) for the analysis?
**Initial GC measurement result: raw data**

<table>
<thead>
<tr>
<th>Component</th>
<th>$x$ (kg/kg)</th>
<th>$H$ (MJ/kg)</th>
<th>$x \cdot H$ (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0.900</td>
<td>55.52</td>
<td>49.97</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.050</td>
<td>51.90</td>
<td>2.60</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.050</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>1.000</td>
<td></td>
<td>52.56</td>
</tr>
</tbody>
</table>

In case of error in measurement/calibration: Raw data!

<table>
<thead>
<tr>
<th>Component</th>
<th>$x$ (kg/kg)</th>
<th>$H$ (MJ/kg)</th>
<th>$x \cdot H$ (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0.895</td>
<td>55.52</td>
<td>49.69</td>
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<tr>
<td>Ethane</td>
<td>0.050</td>
<td>51.90</td>
<td>2.60</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.050</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>0.995</td>
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<td>52.29</td>
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</table>

<table>
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<tr>
<th>Component</th>
<th>$x$ (kg/kg)</th>
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<th>$x \cdot H$ (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0.9000</td>
<td>55.52</td>
<td>49.97</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.0450</td>
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<tr>
<td>Nitrogen</td>
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<tr>
<td>Total</td>
<td>0.9950</td>
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<td>52.30</td>
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<tr>
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<tr>
<td>Ethane</td>
<td>0.050</td>
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<td>2.60</td>
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<tr>
<td>Nitrogen</td>
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</tr>
<tr>
<td>Total</td>
<td>0.995</td>
<td></td>
<td>52.56</td>
</tr>
</tbody>
</table>
## GC measurement results in practice

<table>
<thead>
<tr>
<th>Component</th>
<th>x (kg/kg)</th>
<th>H (MJ/kg)</th>
<th>x·H (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0.900</td>
<td>55.52</td>
<td>49.97</td>
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<tr>
<td>Ethane</td>
<td>0.050</td>
<td>51.90</td>
<td>2.60</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.050</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>1.000</td>
<td></td>
<td>52.56</td>
</tr>
</tbody>
</table>

### after normalization:

<table>
<thead>
<tr>
<th>Component</th>
<th>x (kg/kg)</th>
<th>x’ (kg/kg)</th>
<th>x’ H (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0.895</td>
<td>0.899</td>
<td>49.94</td>
</tr>
<tr>
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<tr>
<td>Nitrogen</td>
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<td>0.050</td>
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</tr>
<tr>
<td>Total</td>
<td>0.995</td>
<td>1.000</td>
<td>52.55</td>
</tr>
</tbody>
</table>

**no effect**

### peak separation between N₂ and CH₄ is very important

### Nitrogen (and CO₂) very critical
- nitrogen most vulnerable to air leakage (also in cal line!)
- peak separation between N₂ and CH₄ is very important
VSL offers

- Factory Acceptance Test

- Site Acceptance Test
  - Including metrological and analytical issues

- Uncertainty calculation for energy (including flow, temperature, pressure and composition)

- Certification of calibration gas mixtures

- Training course on “gas flow metrology”
  - In Delft, but also on location
Any Questions?

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