Automatic Determination of Greenhouse Gases by GC

Massimo Santoro, *Thermo Fisher Scientific*
Cristiane de Oliveira Silva, Henrique Franciscato Melo
Danilo Vinicius Pierone, * NovaAnalitica, Brazil
Introduction

• Greenhouse gases (GHG) are defined as trace components of the atmosphere that absorb infrared radiation emitted by the Earth's surface.

• Increases in GHG have the effect of reducing atmospheric heat loss into space and keeping the Earth warmed.\(^1\)\(^,\)\(^2\)
Introduction

• In 1997, the Kyoto Protocol established commitments for reducing or limiting GHG emissions to be met by industrialized countries between 2008 and 2012. In 2011 at Durban, South Africa, the deadline for the implementation of those commitments was extended for another five to eight years.³

• At COP 194, held in Warsaw (PL) in November 2013, it was decided that a new global agreement to reduce emissions will have to be approved by the first quarter of 2015.⁴

• Brazil is included in the group of developing countries and so has no quantified targets to meet, however, it established the National Policy on Climate Change which sets a national voluntary commitment to reduce its GHG emissions.⁵
Introduction

• The Greenhouse Gas compounds usually considered in the emission estimations are:
  • Carbon Dioxide (CO₂)
  • Nitrous Oxide (N₂O)
  • Methane (CH₄)
  • Hydrofluorocarbons (HFCs)
  • Perfluorocarbons (PFCs)
  • Sulfur Hexafluoride (SF₆)

• Changes in the atmospheric GHG concentration are usually determined by gas chromatography and used for calculating the rates of emission or absorption.
Greenhouse Gas Analysis Instrumentation

• The analysis is performed using the Thermo Scientific™ TriPlus™ RSH autosampler with the Thermo Scientific™ TRACE™ 1310 Gas Chromatograph controlled by the Thermo Scientific™ Chromeleon™ 7.2 Chromatography Data System software.
Two-Detector Configuration, Load Position

Step 1

Diagram showing the Two-Detector Configuration with labeled parts such as EPC AUX 1, EPC AUX 2, EPC AUX 3, EPC AUX 4, EPC AUX 5, EPC AUX 6, V1, V2, V3, LOOP, VENT, Haysep T, Haysep Q, He, ECD, FID, and Methanizer.
Two-Detector Configuration, Inject Position

(b) EPC AUX 4
He

(b) EPC AUX 5
He

(a) EPC AUX 1
He

(a) EPC AUX 2
He

V2

LOOP

Hayesep T

VENT

Hayesep D

EPC AUX 6
He

V3

R2

VENT

Step 2

(b) EPC AUX 4
He

(b) EPC AUX 5
He

(a) EPC AUX 1
He

(a) EPC AUX 2
He

V1

LOOP

Hayesep T

VENT

Hayesep Q

EPC AUX 3
H2

FID

ECD

ThermoFisher SCIENTIFIC
## Analytical Method

### Chromatographic Parameters of the GHG Analysis

- Loop purge: 20 mL/min of He for 12 s
- GC oven temperature: 50 °C
- Auxiliary oven temperature: 50 °C isothermal
- Carrier gas: He, flow rate: 18 mL/min

<table>
<thead>
<tr>
<th>Detector</th>
<th>Temperature (°C)</th>
<th>Flow rate (mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FID</td>
<td>250</td>
<td>350 (synthetic air)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25 (H₂)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12 (N₂ make-up)</td>
</tr>
<tr>
<td>μECD</td>
<td>350</td>
<td>30 (N₂ make-up)*</td>
</tr>
<tr>
<td>TCD</td>
<td>110</td>
<td>1.0 (N₂ make-up)</td>
</tr>
</tbody>
</table>

*Note: The flow rate for μECD detector with N₂ make-up is not specified in the original text.
Three-Detector Configuration, for Oxygen or High CO2 Concentrations
TRACE 1300 Series GC: Tailor Instrument Configuration

- Proprietary, patent-pending Thermo Scientific Instant Connect modules
- Modules are user-installable in less than two minutes
  - Just remove three screws and put the new module in place
  - No special training, dedicated tools or on-site service engineers required
- Every injector and detector is self-sufficient
  - Contains the Integrated Electronic Control (IEC) modules
  - Storing module calibration
Standards and Sample

- Four standard mixtures of CO$_2$, CH$_4$, N$_2$O and SF$_6$ in different concentrations in helium were analyzed to plot the calibration curves.
- A sample of rumen gases from cattle was analyzed by external standard calibration.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ (ppm)</td>
<td>252.7</td>
<td>502.2</td>
<td>1027</td>
<td>1998</td>
</tr>
<tr>
<td>CH$_4$ (ppm)</td>
<td>0.514</td>
<td>1.027</td>
<td>3.150</td>
<td>5.117</td>
</tr>
<tr>
<td>N$_2$O (ppb)</td>
<td>253.7</td>
<td>506.2</td>
<td>1000</td>
<td>2096</td>
</tr>
<tr>
<td>SF$_6$ (ppt)</td>
<td>34</td>
<td>100</td>
<td>1009</td>
<td>n.c.</td>
</tr>
</tbody>
</table>
Typical Chromatograms Obtained for One Mixture

(a) FID / Methanizer
He: Carrier

(b) ECD
N₂: Make-up gas
He: Carrier
The repeatability was evaluated through the relative standard deviation (RSD) of the peak area average. Mixtures of GHG were analyzed in triplicate and the peak areas were used for the calculation of the RSD. The low RSD values obtained indicate excellent repeatability.

<table>
<thead>
<tr>
<th>GHG</th>
<th>Concentration</th>
<th>Area average (n=3)</th>
<th>Standard deviation</th>
<th>RSD %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>252.7 ppm</td>
<td>22.6962</td>
<td>0.1738</td>
<td>0.8</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.027 ppm</td>
<td>0.092</td>
<td>0.0008</td>
<td>0.8</td>
</tr>
<tr>
<td>N₂O</td>
<td>506.2 ppb</td>
<td>0.019</td>
<td>0.00016</td>
<td>0.8</td>
</tr>
<tr>
<td>SF₆</td>
<td>34 ppt</td>
<td>0.014</td>
<td>0.0002</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Linearity

- Linearity was evaluated by the correlation coefficients (r) of the calibration curves. These calibration curves were obtained using the normal method of quadratic least squares fit. The (r) values greater than 0.99 indicate a good linear correlation achieved between the peak areas and the GHG concentrations determined with FID and ECD detectors.

\[ \text{CH}_4 \quad r = 0.9990 \]
Conc (ppm)    Area average (n=3)
0.514         0.070
1.027         0.123
3.150         0.332
5.117         0.525
Linearity

**CO₂**  
\[ r = 0.9996 \]  

<table>
<thead>
<tr>
<th>Conc (ppm)</th>
<th>Area average (n=3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>252.7</td>
<td>22.696</td>
</tr>
<tr>
<td>502.2</td>
<td>54.453</td>
</tr>
<tr>
<td>1027</td>
<td>103.725</td>
</tr>
<tr>
<td>1998</td>
<td>197.388</td>
</tr>
</tbody>
</table>

**N₂O**  
\[ r = 0.9979 \]  

<table>
<thead>
<tr>
<th>Conc (ppb)</th>
<th>Area average (n=3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>253.7</td>
<td>0.004</td>
</tr>
<tr>
<td>506.2</td>
<td>0.007</td>
</tr>
<tr>
<td>1000</td>
<td>0.013</td>
</tr>
<tr>
<td>2096</td>
<td>0.025</td>
</tr>
</tbody>
</table>
Linearity

$\text{SF}_6 \ r = 0.9997$

<table>
<thead>
<tr>
<th>Conc (ppt)</th>
<th>Area average (n=3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
<td>0.014</td>
</tr>
<tr>
<td>100</td>
<td>0.022</td>
</tr>
<tr>
<td>1009</td>
<td>0.206</td>
</tr>
</tbody>
</table>
The limits of detection (LOD) of the developed analytical method were determined in successive chromatograms of GHG mixtures with decreasing concentrations. The lowest concentrations that generate analytical signals were considered as LOD. The limits of quantification (LOQ) were calculated based on the 10:1 ratio, i.e. 10LOQ: 1LOD.

<table>
<thead>
<tr>
<th>GHG</th>
<th>LOD</th>
<th>LOQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2 (FID)</td>
<td>7.432 ppm</td>
<td>74.32 ppm</td>
</tr>
<tr>
<td>CH4</td>
<td>0.056 ppm</td>
<td>0.56 ppm</td>
</tr>
<tr>
<td>N2O</td>
<td>32.76 ppb</td>
<td>327.6 ppb</td>
</tr>
<tr>
<td>SF6</td>
<td>4.35 ppt</td>
<td>43.5 ppt</td>
</tr>
</tbody>
</table>
32.76 ppb of N$_2$O detected by ECD; (b) 0.056 ppm of CH$_4$ and 7.432 ppm of CO$_2$ detected by FID/Methanizer
Low Concentration Chromatograms

Low concentrations of SF₆: (a) 100 ppt (b) 4.35 ppt
Rumen Sample from Cattle

- Two chromatograms of a ruminal gas sample and the concentrations of N$_2$O, CH$_4$ and CO$_2$ quantified by the external standard method

<table>
<thead>
<tr>
<th>ECD</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O</td>
<td>337.4 ppb</td>
</tr>
<tr>
<td>FID</td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>2.82 ppm</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>981.1 ppm</td>
</tr>
</tbody>
</table>
Conclusions

• The results obtained for area repeatability, linearity, efficiency of the analyte separation, limits of detection, and quantification show that the TRACE 1300 Series GC, in the configuration presented in this study, is a system perfectly suited for the analysis of greenhouse gases.

• The approach is very simple and easily automated and applicable to low- and high-level calibrations.

• Samples are completed in less than 10 minutes, giving high productivity.
References


Acknowledgements

- The authors thank Prof. Dr. Paulo Henrique Mazza Rodrigues from the Department of Nutrition and Animal Production, University of São Paulo, Pirassununga, SP, BR, for contributing to the improvement of the chromatographic system configuration, the Embrapa São Carlos, SP, BR, by giving the mixtures of GHG standards and Silvana Odete Pisani, Ph.D., from Nova Analítica, São Paulo, SP, BR, by the revision of this writing.
Thank You for Your Attention!

Questions?

Stay connected with us

Twitter
@ChromSolutions

Chromatography Solutions Blog
http://chromblog.thermoscientific.com/blog

YouTube
http://www.youtube.com/ChromSolutions

Facebook
http://www.facebook.com/ChromatographySolutions

Pinterest
http://pinterest.com/chromsolutions/