# Automatic Determination of Greenhouse Gases by GC

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# 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]

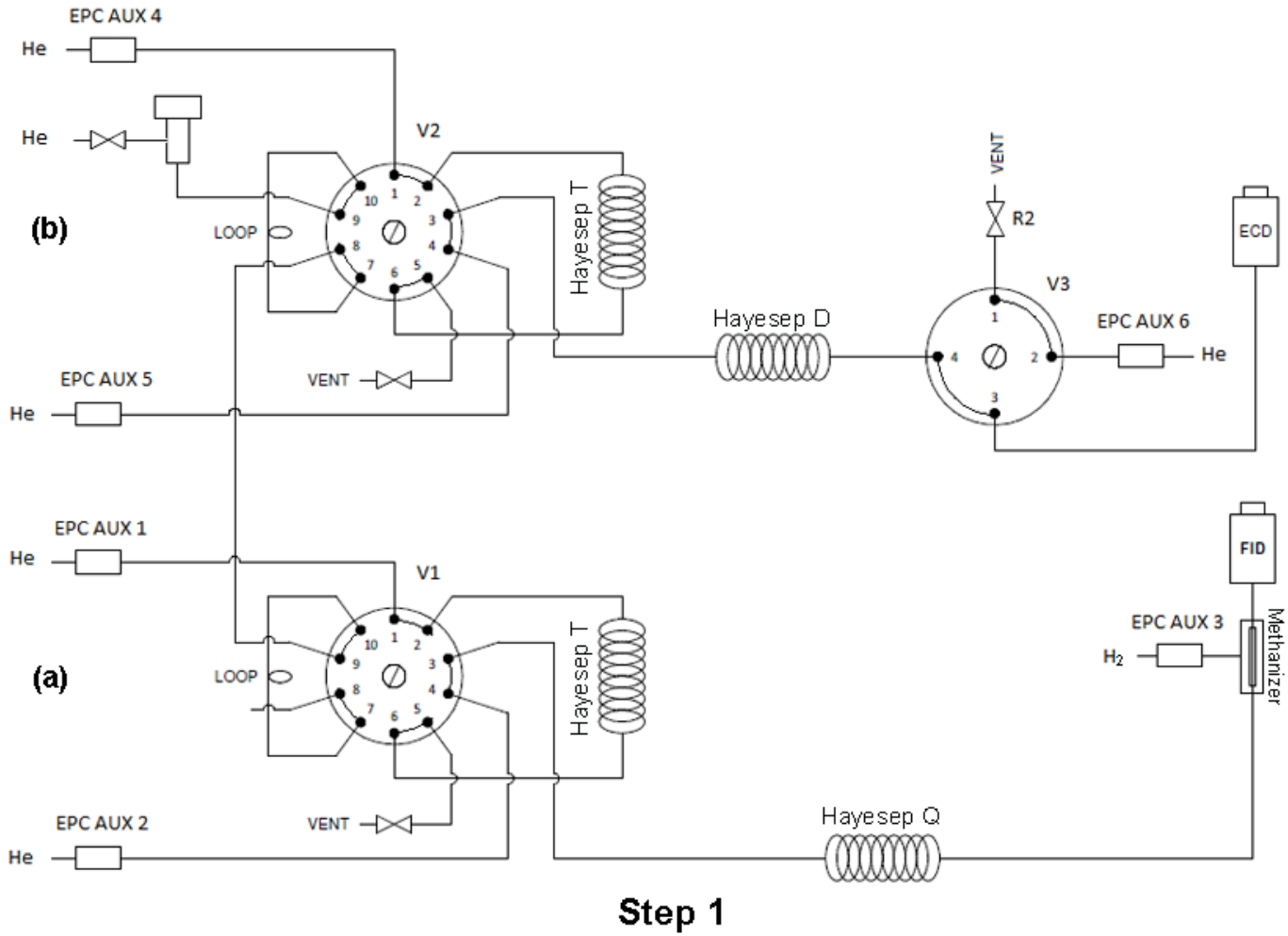
# Introduction

- The Greenhouse Gas compounds usually considered in the emission estimations are:
  - Carbon Dioxide ($CO_2$)
  - Nitrous Oxide ($N_2O$)
  - Methane ($CH_4$)
  - Hydrofluorocarbons (HFCs)
  - Perfluorocarbons (PFCs)
  - Sulfur Hexafluoride ($SF_6$)
- 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



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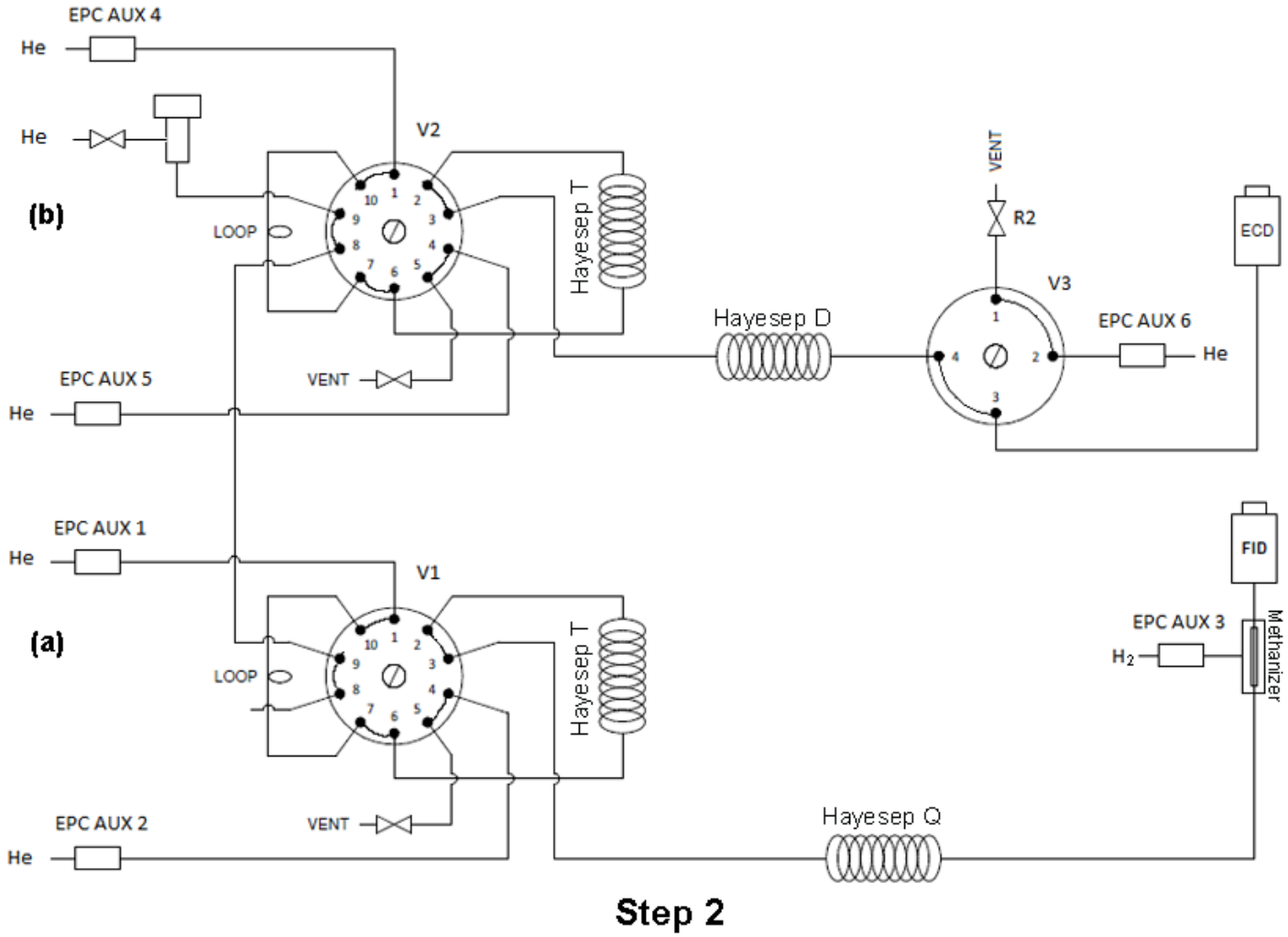
# Two-Detector Configuration, Inject Position




**Step 2**



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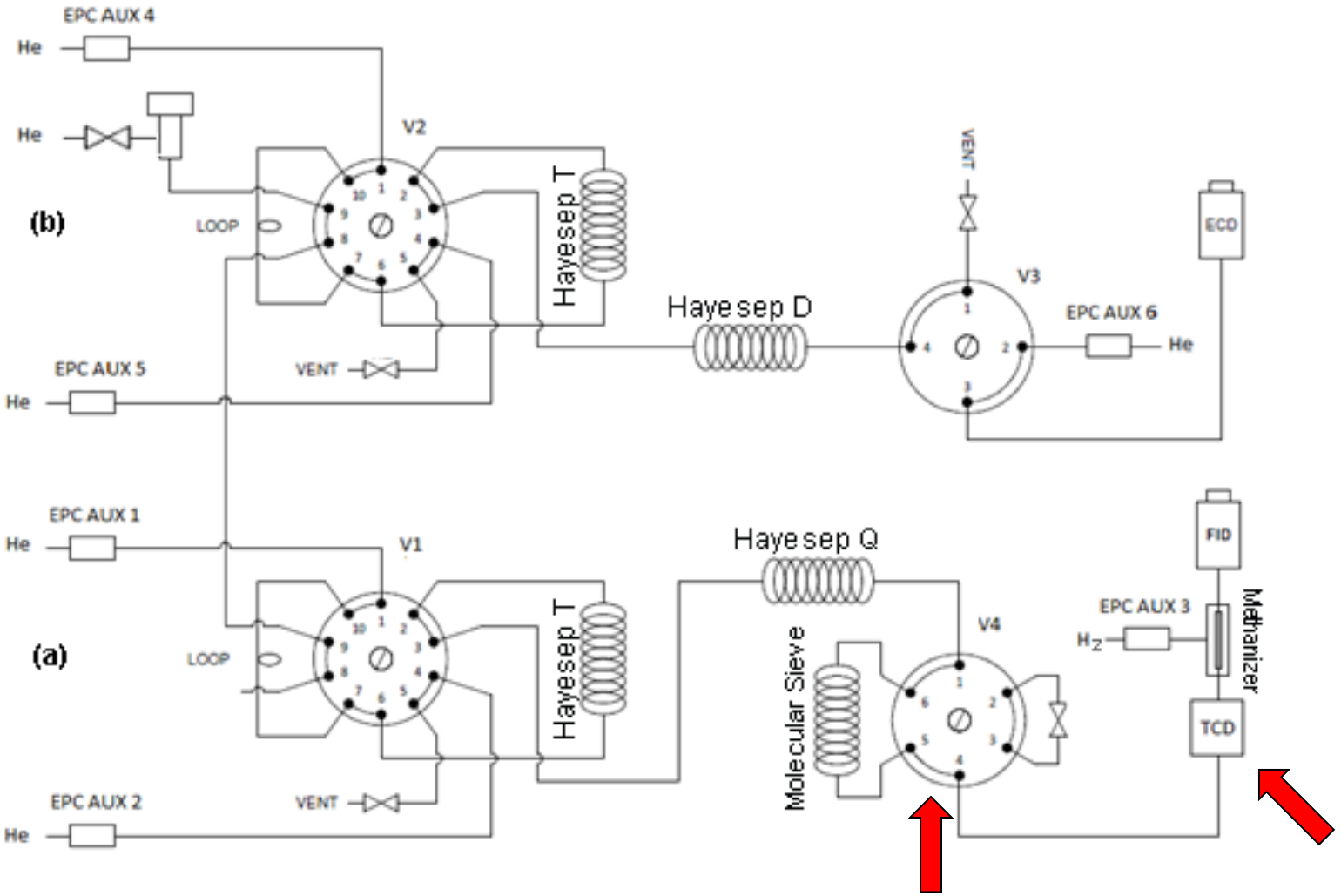
# Analytical Method

## Chromatographic Parameters of the GHG Analysis

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

| Detector | Temperature ($^0$C) | Flow rate (mL/min) |
|---|---|---|
| **FID** | 250 | 350 (synthetic air)<br>25 ($H_2$)<br>12 ($N_2$ make-up) |
| **µECD** | 350 | 30 ($N_2$ make-up)* |
| **TCD** | 110 | 1.0 ($N_2$ make-up) |

# Three-Detector Configuration, for Oxygen or High CO2 Concentrations



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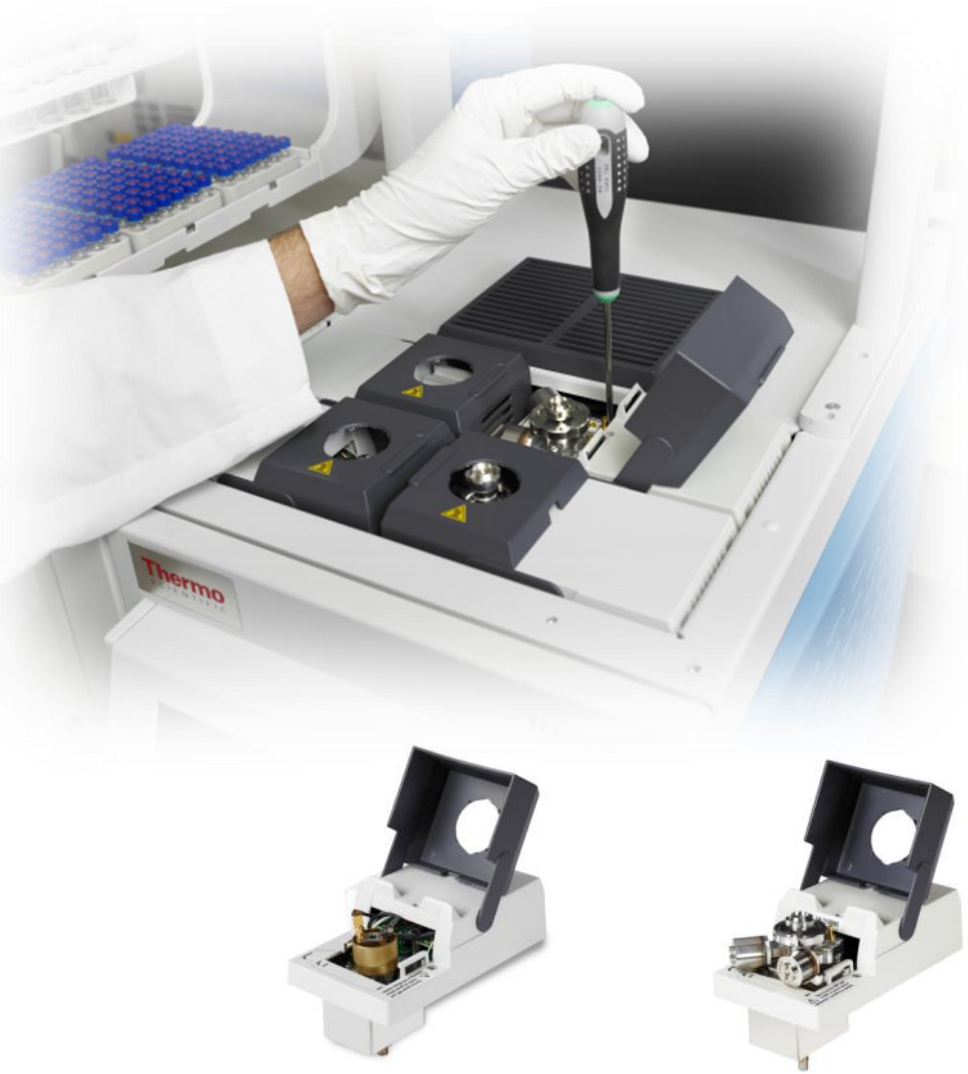
# TRACE 1300 Series GC: Tailor Instrument Configuration




- 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

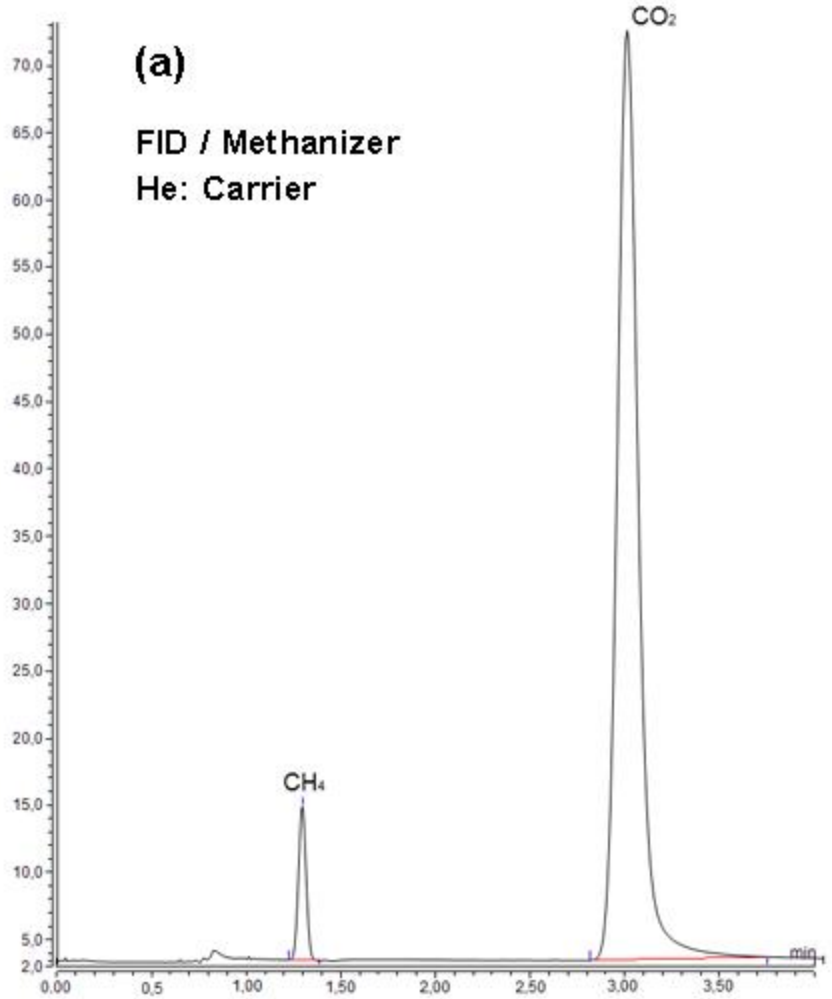
# Standards and Sample

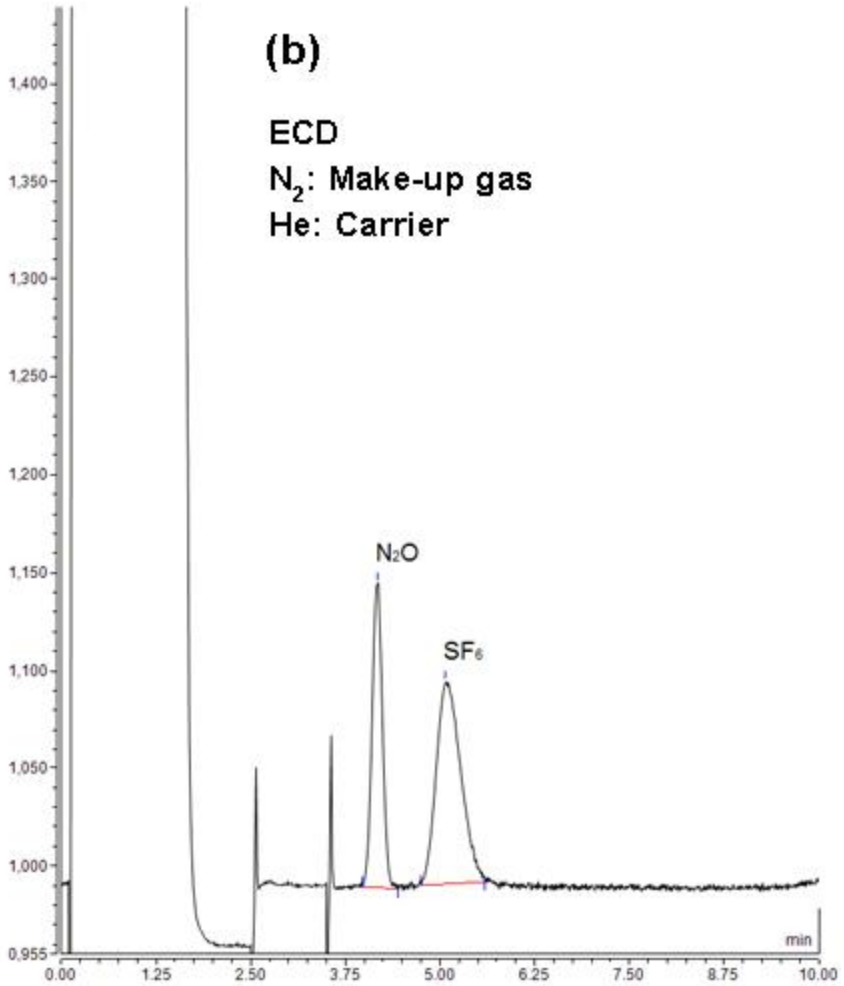
- Four standard mixtures of $CO_2$, $CH_4$, $N_2O$ and $SF_6$ in different concentrations in helium were analyzed to plot the calibration curves.
- A sample of rumen gases from cattle was analyzed by external standard calibration.

**GHG Concentrations in the Standard Mixtures**

| Mixture | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| $CO_2$ (ppm) | 252.7 | 502.2 | 1027 | 1998 |
| $CH_4$ (ppm) | 0.514 | 1.027 | 3.150 | 5.117 |
| $N_2O$ (ppb) | 253.7 | 506.2 | 1000 | 2096 |
| $SF_6$ (ppt) | 34 | 100 | 1009 | n.c. |

# Typical Chromatograms Obtained for One Mixture



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# Repeatability

- 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.

**GHG Concentrations in the Standard Mixtures**

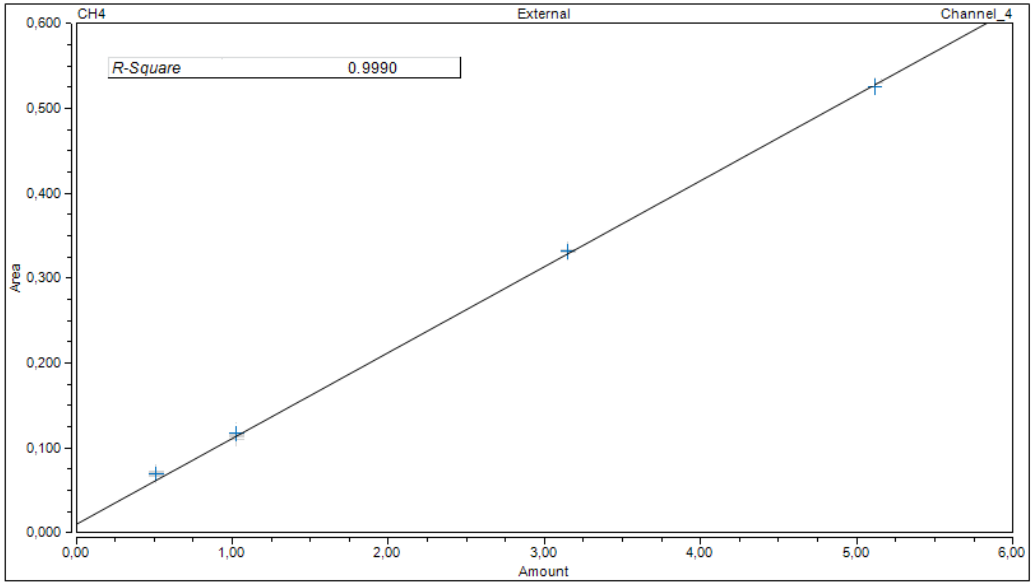
| GHG | Concentration | Area average (n=3) | Standard deviation | RSD % |
|---|---|---|---|---|
| $CO_2$ | 252.7 ppm | 22.6962 | 0.1738 | 0.8 |
| $CH_4$ | 1.027 ppm | 0.092 | 0.0008 | 0.8 |
| $N_2O$ | 506.2 ppb | 0.019 | 0.00016 | 0.8 |
| $SF_6$ | 34 ppt | 0.014 | 0.0002 | 1.4 |

# 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.

**$CH_4$ 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 |



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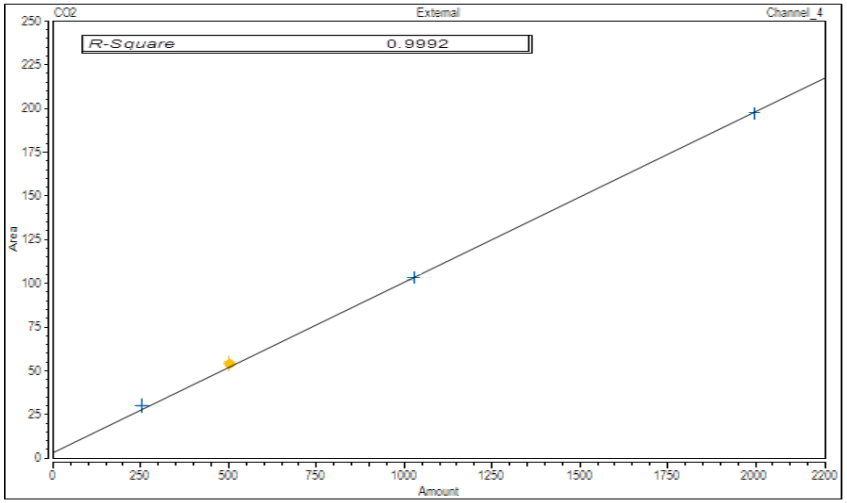
# Linearity

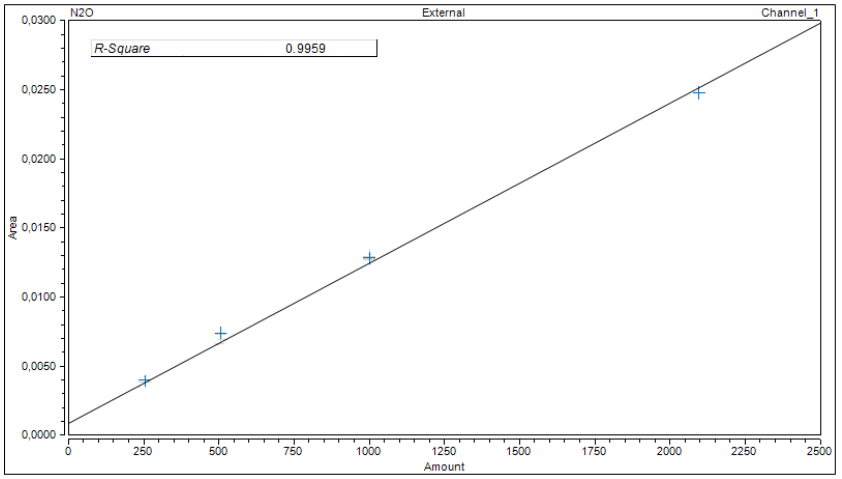
**$CO_2$ r = 0.9996**

| Conc (ppm) | Area average (n=3) |
|---|---|
| 252.7 | 22.696 |
| 502.2 | 54.453 |
| 1027 | 103.725 |
| 1998 | 197.388 |




**$N_2O$ r = 0.9979**

| Conc (ppb) | Area average (n=3) |
|---|---|
| 253.7 | 0.004 |
| 506.2 | 0.007 |
| 1000. | 0.013 |
| 2096 | 0.025 |



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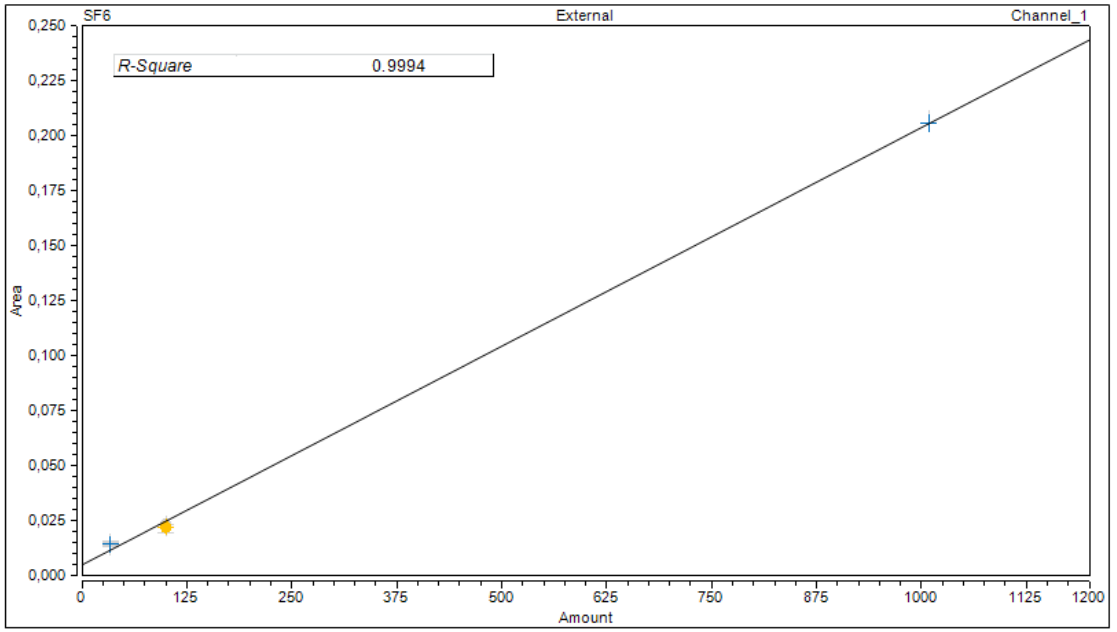
# Linearity




**$SF_6$ r = 0.9997**

| Conc (ppt) | Area average (n=3) |
|---|---|
| 34 | 0.014 |
| 100 | 0.022 |
| 1009 | 0.206 |

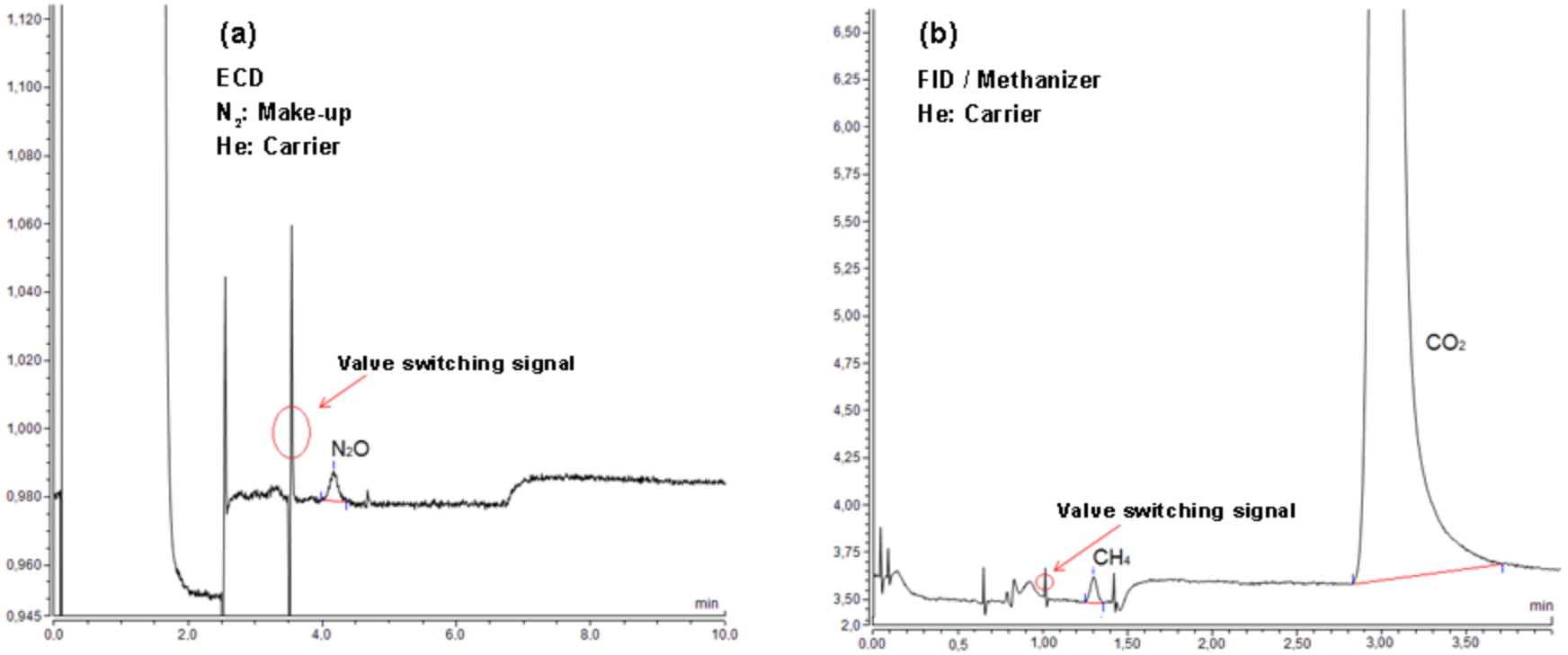
# Limits of Detection and Quantification

- 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.

**Limits of Detection and Quantification**

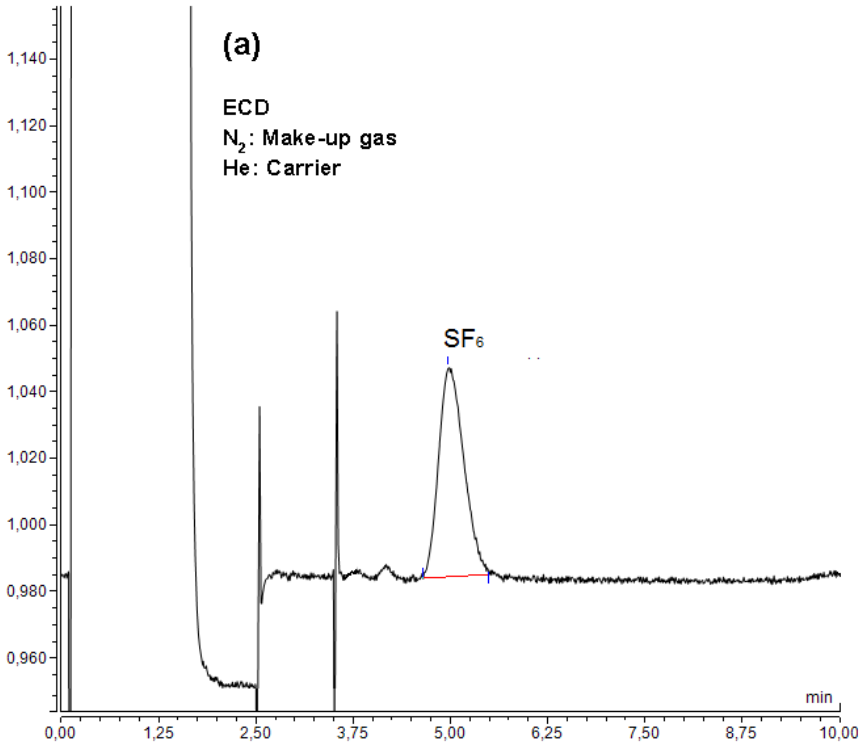
| GHG | LOD | LOQ |
|---|---|---|
| CO2 (FID) | 7.432 ppm | 74.32 ppm |
| CH4 | 0.056 ppm | 0.56 ppm |
| N2O | 32.76 ppb | 327.6 ppb |
| SF6 | 4.35 ppt | 43.5 ppt |

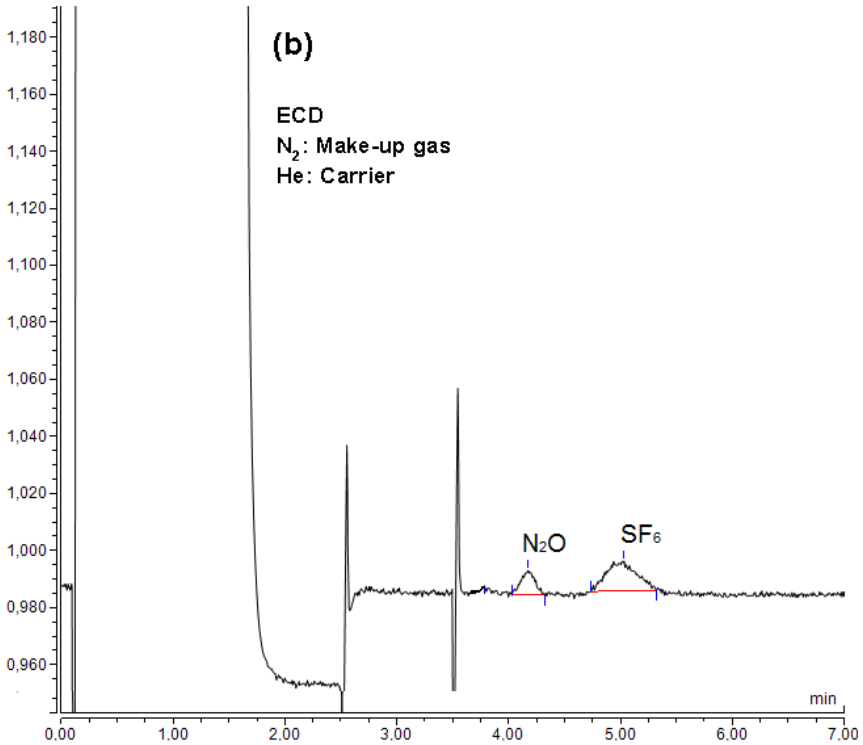
# Low Concentration Chromatograms




32.76 ppb of $N_2O$ detected by ECD; (b) 0.056 ppm of $CH_4$ and 7.432 ppm of $CO_2$ detected by FID/Methanizer

# Low Concentration Chromatograms



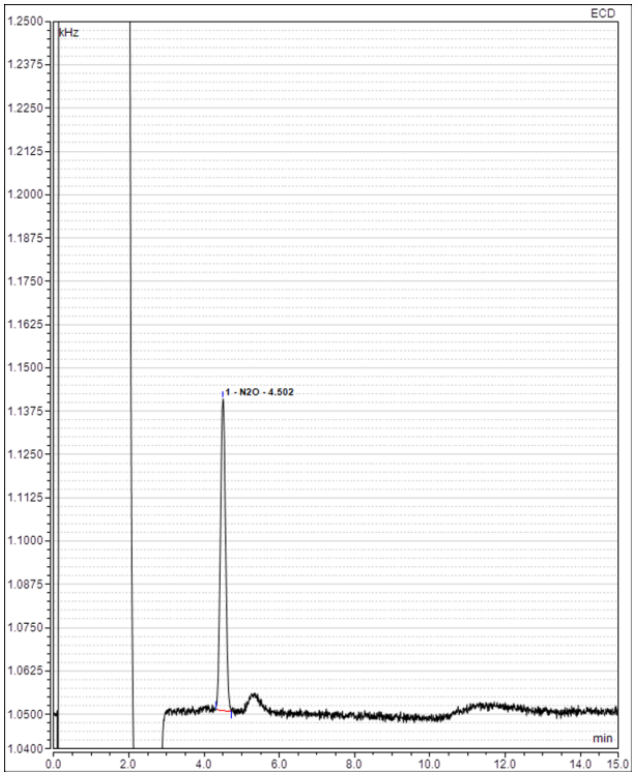



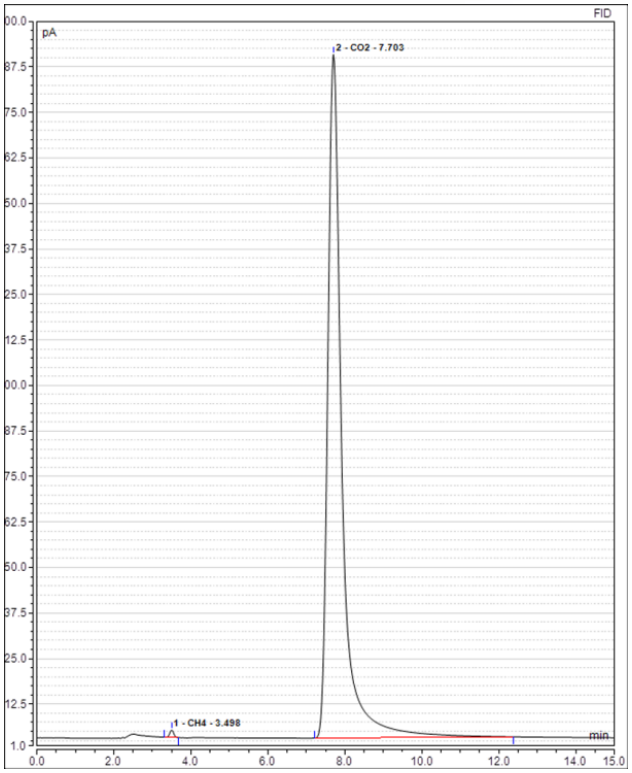

Low concentrations of $SF_6$: (a) 100 ppt (b) 4.35 ppt

# Rumen Sample from Cattle

- Two chromatograms of a ruminal gas sample and the concentrations of $N_2O$, $CH_4$ and $CO_2$ quantified by the external standard method

| | |
|---|---|
| **ECD** | Concentration |
| $N_2O$ | 337.4 ppb |
| **FID** | |
| $CH_4$ | 2.82 ppm |
| $CO_2$ | 981.1 ppm |



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# 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


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