

APPLICATION NOTE

LD16-13



Measurement of Greenhouse gases GHG



Energy (fossil fuel) and agriculture required for human activities on Earth produce Greenhouse gases (GHG) such as Carbon Dioxide (CO₂), Methane (CH₄), Nitrous Oxide (N₂O) and Fluorinated gases mainly Sulfur Hexafluoride (SF₆). These gases tend to absorb infrared radiation emitted by the Earth surface resulting to reduce the atmospheric heat loss into space and keeping Earth warmer.

The source of every GHG type is associated to different sectors resulting of human activities:

CO₂ → *Fossil fuel, industrial processes, forestry, land use for agriculture*

CH₄ → *Agriculture, waste management, energy use, biomass burning*

N₂O → *Agriculture (such as fertilizer use) and biomass burning*

F-gases (SF₆) → *Industrial processes and refrigeration*

For this reason, the Kyoto Protocol was established in 1997 by the industrialized countries with an objective to measure, control and decrease the GHG in order to reduce the continuous global warming.

Figures 1, 2 and 3 show some data that demonstrate the impact of human activities to increase the Greenhouse gases level worldwide.

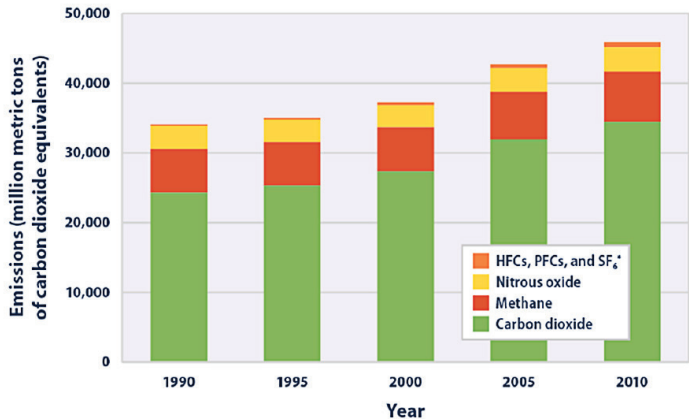


Figure 1:
Global Greenhouse gas emissions by gas type, 1990-2010

(Data sources WRI 2014, FAO 2014) ¹

This figure shows worldwide emissions of carbon dioxide, methane, nitrous oxide and several fluorinated gases from 1990 to 2010. For consistency, emissions are expressed in million metric tons of carbon dioxide equivalents. These totals include emissions and sinks due to land-use change and forestry.

*HFCs are hydro fluorocarbons, PFCs are per fluorocarbons and SF₆ is hexafluoride

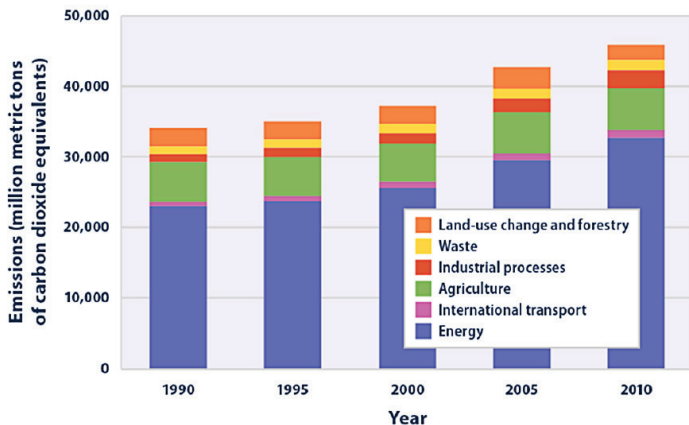


Figure 2:
Global Greenhouse gas emissions by sector, 1990-2010

(Data sources WRI 2014, FAO 2014) ¹

This figure shows worldwide gas emissions by sector from 1990 to 2010.

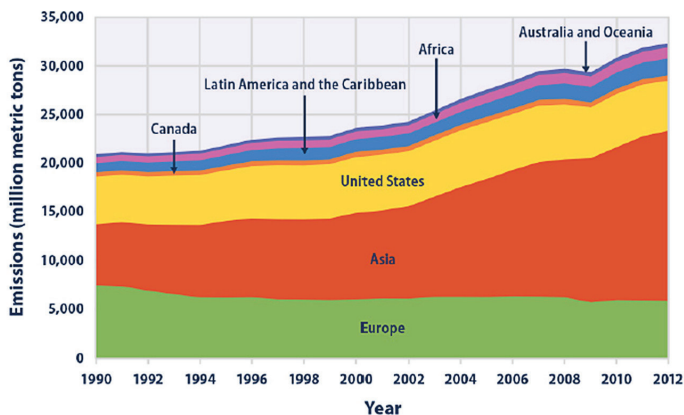


Figure 3:
Global Greenhouse gas emissions by regions, 1990-2012

(Data sources WRI 2015) ¹

This figure shows carbon dioxide emissions from 1990 to 2012 for different regions of the world.

¹Data and analysis come from the World Resources Institute's Climate Analysis Indicators Tool (CAIT), which compiles data from peer reviewed and internationally recognized greenhouse gas inventories developed by EPA and other government agencies worldwide.

The well known technique to measure and quantify the GHG is Gas Chromatography. It can determine the rate of emission or absorption. These rates are mainly measured using samples of soil, rice, maize or wheat from different areas. The measurement of ambient air is also used. The worldwide GHG can then be better measured and controlled to facilitate the proper actions to be taken to reduce the global warming.

ALTERNATIVE SOLUTION USING GAS CHROMATOGRAPH

The use of multiple detectors in a gas chromatography system is generally necessary to cover the greenhouse application.

A FID detector and a methanizer system for detection of trace impurities of Methane (CH₄) and Carbon Dioxide (CO₂). Such detector requires Fuel (H₂), Air and the carrier gas source to make it works.

An ECD detector to measure traces Nitrous Oxide (N₂O) and Sulfur Hexafluoride (SF₆). This type of detector is a source of radioactivity and results in complication for storage, handling and transport.

A TCD is also required for measuring high concentration Carbon Dioxide (CO₂) when necessary.

It is then a solution combining multiple types of detection technology which makes the system more complex to operate and increases the operating cost.

OUR SOLUTION

Using the PlasmaDetek2 (PED) plasma detector and the MultiDetek2 compact gas chromatograph, the analysis of the most critical trace impurities in air can be achieved in one unit with a single detection technology (PED).

By default, the configuration has 2 channels to cover the analysis of Methane, Carbon Dioxide, Nitrous Oxide and Sulfur Hexafluoride. If additional options for the analysis of other impurities like fluorinated gases (F-gases) are required, then an additional channel still using a Plasma Emission Detector can be added in the same instrument.

Channel#1: This channel measures 0-1000ppm Methane (CH₄) and 0-5000ppm Carbon Dioxide (CO₂) using the PlasmaDetek2 (PED). Other measuring ranges can be configured. The system is protected against moisture using a pre column in back flush to vent configuration.

Channel#2: 0-10ppm Sulfur Hexafluoride (SF₆) and Nitrous Oxide (N₂O) still uses the PlasmaDetek2 (PED). Other ranges are also possible. A pre column to protect the system against moisture is also used in this channel.

Channel#3 (optional): Analysis of other fluorinated gases (F-gases) that would still be using the PlasmaDetek2 (PED) as detector.

The sample preparation is managed by the HTA Headspace auto sampler system mounted on the MultiDetek2 GC. The auto sampler tray configuration can be for 14 or 42 vials having size range of 10ml or 20ml depending of the application requirements. The oven can accept 1 or 6 vials for heating and shaking in preparation of analysis. The auto sampler offers syringe auto cleaning and a purge routine in between each sample collection. The syringe volume can be 2.5ml or 5ml depending of the application.

The Headspace can be controlled from its keypad, touch screen interface or from the software environment installed on an external PC or in the integrated PC of the MultiDetek2.

The data management is done with the MultiDetek2 interface. The unit can be control locally from the MultiDetek2 touch screen interface or remotely using LAN connectivity.

RESULTS

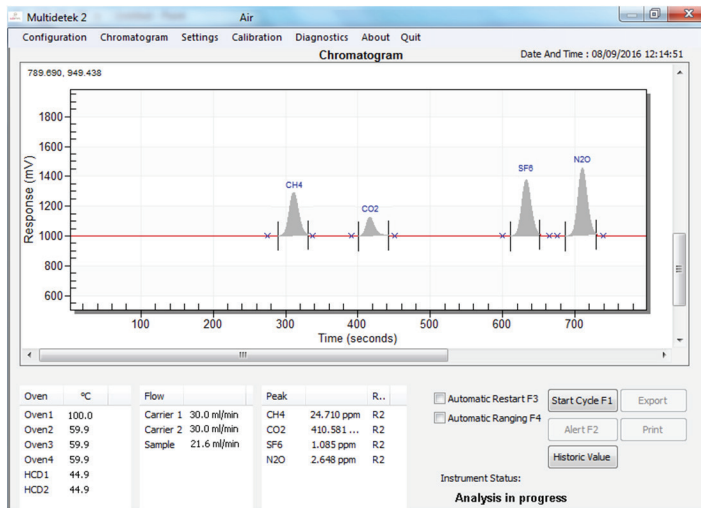


Figure 1:
chromatogram of trace impurities in balance air coming from a certified gas bottle.

For this application, a measuring range of 0-1000ppm was required for the CH4 with a LDL of 200ppb.

A measuring range of 0-5000ppm was required for the CO2 with a LDL of 500ppb.

A measuring range of 10ppm was required for the SF6 and N2O with a LDL of 20ppb.

The figure 2 shows a table where the LDL calculation was obtained with a noise/response ratio. It shows the system can achieve better specifications than what was required for the application. Lower detection limits can be obtained with the same system just by changing the injected sampling loop volume. An extended range with lower detection limit capabilities can be obtained with our optional multiple sampling loop injection system.

It becomes possible to measure ppt/ppb/high ppm with the same detector in the same instrument.

COMPONENT	CONCENTRATION	PEAK HEIGHT	NOISE	LDL (3X NOISE)
CH4	24.710 ppm	331 mV	0.4 mV	89.6 ppb
CO2	410.581 ppm	177 mV	0.06 mV	417.5 ppb
SF6	1.085 ppm	389 mV	1.6 mV	13.4 ppb
N2O	2.648 ppm	479 mV	0.9 mV	14.9 ppb

Note: other LDL could be obtained with different injection volume and chromatographic condition

Figure 2

CONCLUSION

The combination of the PlasmaDetek2 (PED) detector with the MultiDetek2 compact gas chromatograph and the HTA Headspace auto sampler becomes an interesting reliable and robust solution for the laboratory requirements where Greenhouse (GHG) gases must be measured.

