TOWARDS THE UNIFYING OF THE DETECTION SYSTEMS FOR THE MEASUREMENT OF THE MAJOR GREENHOUSE GASES AND RELATED TRACERS

B. Mitrevski, R. Langenfelds, D. Spencer, P. Salameh, P. Krummel, P. Steele
• GASLAB @ CSIRO, current status, technology, problems

• Alternatives?

• Pulsed Discharge Helium Ionization Detector (PDD)

• Results (precision, separation, comparison…)
  ▪ Hydrogen
  ▪ Nitrous Oxide
  ▪ Methane
  ▪ and a bit for Carbon Dioxide

• Advantages/disadvantages
established 1990, samples per year: from 2000 (90’s) to 800 (recent years)

- GC-FID (CH₄ and CO₂)
- GC-RGA (CO and H₂)
- GC-ECD (N₂O)
- IR MS (¹³C, ¹⁸O in CO₂)

Precisions:
2.4 ppb for CH₄
2.2 ppb for H₂
0.08 for CO₂
0.8 ppb for CO
0.4 ppb for N₂O

Strongly non-linear response!

Today, 27 years later: nearly the same technology, precision...

- data management issue (Unix, integrators, paper, floppy disks)
- requires strictly local operation (on site)
- safety issues (hydrogen cylinder, mercury/UV, radioactive source)
- obsolete instrumentation / spare parts source difficulties
Aim

To develop a modern methodology for:

- **simultaneous** measurement of all 5 trace gasses (universal detector)
- accurate, reproducible, fast, robust (consistent long term measurements)
- **small sample volume** capability (i.e. for ice core samples)
- automated (remote control and access essential)
- expanded capacity for flask samples (unattended operation)

A hunch… that one detector displays great promise…

PULSED DISCHARGE HELIUM IONIZATION DETECTOR (PDHID or PDD)
- High voltage discharge
- Helium atoms excited
- High energy photons emitted (13.5-17.5 eV)
- all other atoms/molecules ionized
- current measured (electrometer)

- Truly universal (ionize anything, except neon?)
- Sensitive (low ppm to ppb level)
- no safety concerns: (e.g. H₂ use, mercury or radiation source)
Cape Grim in-situ measurements for atmospheric hydrogen

Installed April 2015, in parallel to the existing GC-RGA
- trouble-free
- maintenance-free
Cape Grim in-situ measurements for atmospheric hydrogen

Insignificant bias

hydrogen in air (ppb)

time

GC-RGA
GC-PDD
Cape Grim in-situ measurements for atmospheric hydrogen

Average precision over 2+ years (same inlet):

RGA (0.8%)  
PDD (0.09%)  
or 0.5 ppb
PDD for **Methane**: Experimental setup

**GC**: Agilent 6890, oven at 30 °C  
**Column**: 20' Heyesep D (1/8”, 100/120 mesh)  
**PDD**: Pulsed Discharge Helium Ionization Det.
Results: separation on Heyesep D column (divinylbenzene)
Precision for methane: ± 1.22 ppb, over 100+ days

Precision: 0.07% (n=4000)
1723.99 ± 1.22 ppb

GASLAB CH₄ precision: 2.4 ppb

- Latest result: a tank at 1842.39 ± 0.56 ppb (n=47)
PDD linearity for **Methane**

$R^2 = 0.99999$
PDD linearity for **Methane**

\[ y = -2 \times 10^{-9}x^2 + 0.0006x - 5 \times 10^{-5} \]

\[ R^2 = 1 \]
PDD linearity for Methane

![Graph showing PDD linearity for Methane](image-url)
Non-linearity: within ± 0.5%
PDD calibration stability

- mean value for each cal batch is within the measurement uncertainty

![Graph showing PDD calibration stability with time]
Can we measure atmospheric $\text{N}_2\text{O}$ with GC-PDD?

Experiment:

- A mixture of ~6 ppm CH$_4$ and 1.2 ppm N$_2$O was prepared in UP air
- 8 dilutions with UP air were prepared from the “parent” mixture
- CH$_4$ was characterized on Carle GC-FID (linear response detector)
- One N$_2$O dilution was characterized on GC-ECD
- N$_2$O was also measured on GC-PDD
### Results, separation

5 mL dry air on Heyesep D (20’ x 1/8”, 100/120 mesh)

- 1 – neon
- 2 – hydrogen
- 3 – methane
- 4 – krypton
- 5 – carbon dioxide
- 6 – nitrous oxide
- 7 – xenon
N$_2$O results: linearity comparison with ECD, stats, more details

Comparison of GC-PDD linearity (non corrected) with the GC-ECD linearity (corrected)

There is a good agreement between them in the range 150-350 ppb
GC-PDD for N$_2$O, limited number of experiments…

Precision: 0.10 % (n=981)

Or in some instances, down to 0.057% (n = 82)
GC-PDD for CO\textsubscript{2}, limited number of experiments…

June 2016, 600+ analyses. Precision of 0.036 % or ± 0.14 ppm. Sometimes down to ± 0.07 ppm.

Less linear!!!
Conclusion

- PDD is a **sensitive** detector

- very reproducible (**high precision results**)

- It measures all species isotopes, unlike some optical instruments

- It is a simple, robust, and does not use/posses any safety risk

- **It is a promising alternative for the current old technology!**

<table>
<thead>
<tr>
<th></th>
<th>rel. precision (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Current (various)</td>
</tr>
<tr>
<td>hydrogen</td>
<td>0.5</td>
</tr>
<tr>
<td>methane</td>
<td>0.15</td>
</tr>
<tr>
<td>carbon monoxide</td>
<td>1.0</td>
</tr>
<tr>
<td>nitrous oxide</td>
<td>0.15</td>
</tr>
<tr>
<td>carbon dioxide</td>
<td>0.02</td>
</tr>
<tr>
<td>krypton</td>
<td>-</td>
</tr>
</tbody>
</table>