Airborne Labs International Inc.

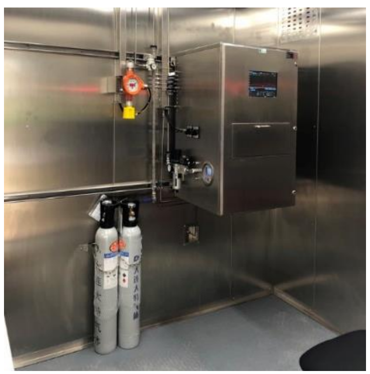
ASDevices

On-Line Analysis Strategy for SAE-J2719 / ISO 14687-2020 H_2 Fuel Quality Control

By: Mark Taylor, Dr. Don Pachuta, ALI, Dr. Marc-Antoine Langevin and André Lamontagne, ASD

Airborne Labs International 22C World's Fair Drive Somerset, New Jersey 08873 USA
www.AirborneLabs.com P: +1.732.302.1950 E: sales@airbornelabs.com

SAE-J2719 / ISO 14687-2020 H_2 Fuel Specs
(The Analytical Challenge)



Constituent	Chemical Formula	Limits
Hydrogen fuel index (minimum mole fraction)	H_2	≥99.97%
Total non-hydrogen gases	TNHG	300
Maximum concentration of individual contaminants		
Water	H_2O	5
Total hydrocarbons except methane[a] (C_1 equivalent)	TNMHC	2
Oxygen	O_2	5
Methane	CH_4	100
Helium	He	300
Nitrogen	N_2	300
Argon	Ar	300
Carbon dioxide	CO_2	2
Carbon monoxide[b]	CO	0.2
Total sulfur compounds[c]	TSC	0.004
Formaldehyde	HCHO	0.2
Formic acid	HCOOH	0.2
Ammonia	NH_3	0.1
Halogenated compounds (halogen ion equivalent)[d]	TXC	0.05
Particulate Concentration	NVR	1mg/kg

Commercial H_2 Fuel Gas
Feed Gas Sources
(Grey – Blue – Green Categories)

(Feed Source-Based Impurity Profile - Risk Variables)

- Steam Methane Reformation of Natural Gas (≈95%)
- Electrolysis (various electrical power sources)
- Renewable Liquids (ex. Ferm-alcohols, plant based oils)
- Commercial Chemical Processes
- Biogenic Processes (biomass related)

Feed Gas Sources for H_2 Fuel constantly growing!
(Analytical Versatility needed)

Airborne Labs International Inc.

ASDevices

Potential Negative Effects of Key Fuel Impurities on PEM-Based Electric Vehicles

- **Many key fuel contaminants can reduce fuel cell efficiency**
- Some impurities cause **reversible** fuel cell damage
- **CO + Sulfur-based** compounds can cause **irreversible damage** to fuel cell components
- **Total Sulfur Content** (TSC) current limit = **4 ppb (as S).**
- Note: Due to its effect on fuel cells, future standards may require ***lower*** **TSC** concentrations.
- Several types of volatile sulfur compounds (VSCs) can be found in typical H_2 fuel sources (ex. Natural Gas Steam Reformation)

Analytical Strategy for H_2 Fuel Producers

- **H_2 Feed gas source & Impurity Profile** = basic risk factors should be **1st consideration** in selecting an H_2 Analyzer System
- **Critical Impurities** (ex. that cause most serious fuel cell damage) should be monitored in **all** cases (ex. Std CoC Reports for customers)
- **Risk / Benefit** analysis must **also** include **Costs - Complexities – Robustness** of the analytical system
- **Passivated hardware + Rapid Analysis required** after sampling due to highly adsorptive & reactive impurities (ex. VSCs, VOXs, Halogens, NH_3)
- Freedom from **trace hardware leaks** is essential for safety and **reliable** impurity data
- **Detector(s)** need to be **Ultra-Sensitive**, **Universal** in Response and **ALSO** have some **Selectivity & Specificity** (to be explained)
- Ability to do **Continuous On-Line** + Periodic "**Batch**" Testing is Ideal

Desired Analytical Measurement Specs

(Range - MDL – Linearity – Specificity – Ruggedness – Speed – Cost)

-H_2 Gas Mfgs will need to **continuously monitor** their process to ensure constant fuel grade quality + ***quickly detect*** impurity trends / upsets. The ability for use 1L Sample Cylinders for **batch testing** applications is a desired bonus

Range: At least **2X** the Impurity Spec. Max (Ideally > **10-100+X** above Spec Max)

Minimum Detection Limit: Minimum < 50% spec limit – Ideally <10% spec limit

Linearity: Linear or Software-corrected from MDL to > X10 - 100+ spec limit

Detector Specificity: Varies from **Universal** (ex. N_2+Ar) – to Impurity "**Family**" Selective (VSCs, VHCs, VOX, VXC's) to ***Highly* Specific** (ex. CO, CO_2, H_2O, O_2, NH_3, He, CH_4)

Ruggedness: OK in **Production Apps** –Easy to Operate – Low Maintenance

Speed: Reasonable (ex. <10 min for results = ideal)

Cost: Affordable for the intended application

Basic On-Line H_2 Purity Analyzer Configuration Strategy

(Addressing the Most Critical & Common SMR Source Impurities)

Standard – Most SMR source Critical

Explosion-Proof Chassis

- **Total Sulfur Content** including: H_2S, COS, SO_2, CS_2, Mercaptans, Sulfides, Disulfides as ppm (S)
- **Carbon Monoxide** (CO)
- **Carbon Dioxide** (CO_2)
- **TNMHC**
- **N_2** (In SMR + *blanketing gas* in new storage tanks)
- **CH_4**

Common Options – Add-ons

- **Helium (He)**
- **H_2O Vapor (mostly contaminant related)**
- **Trace O_2 (mostly contaminant related)**

Airborne Labs International Inc.

ASDevices

Basic On-Line H_2 Purity Analyzer Configuration

(Basic H_2 Analyzer Operations Overview – how does it work?)

<u>Standard Fuel Grade Hydrogen Analyzer System</u>

- **Gas Chromatography (GC)** with all passivated hardware – leak-fee PLSV Valves + **Enhanced Plasma Discharge Detector** (**Epd**)*
- – for **TSC-CO-CO_2-N_2-CH_4** - (**GC/Epd**)

* Epd Basic operation to be explained later

<u>Add-on Analyzers & Custom Solutions</u>

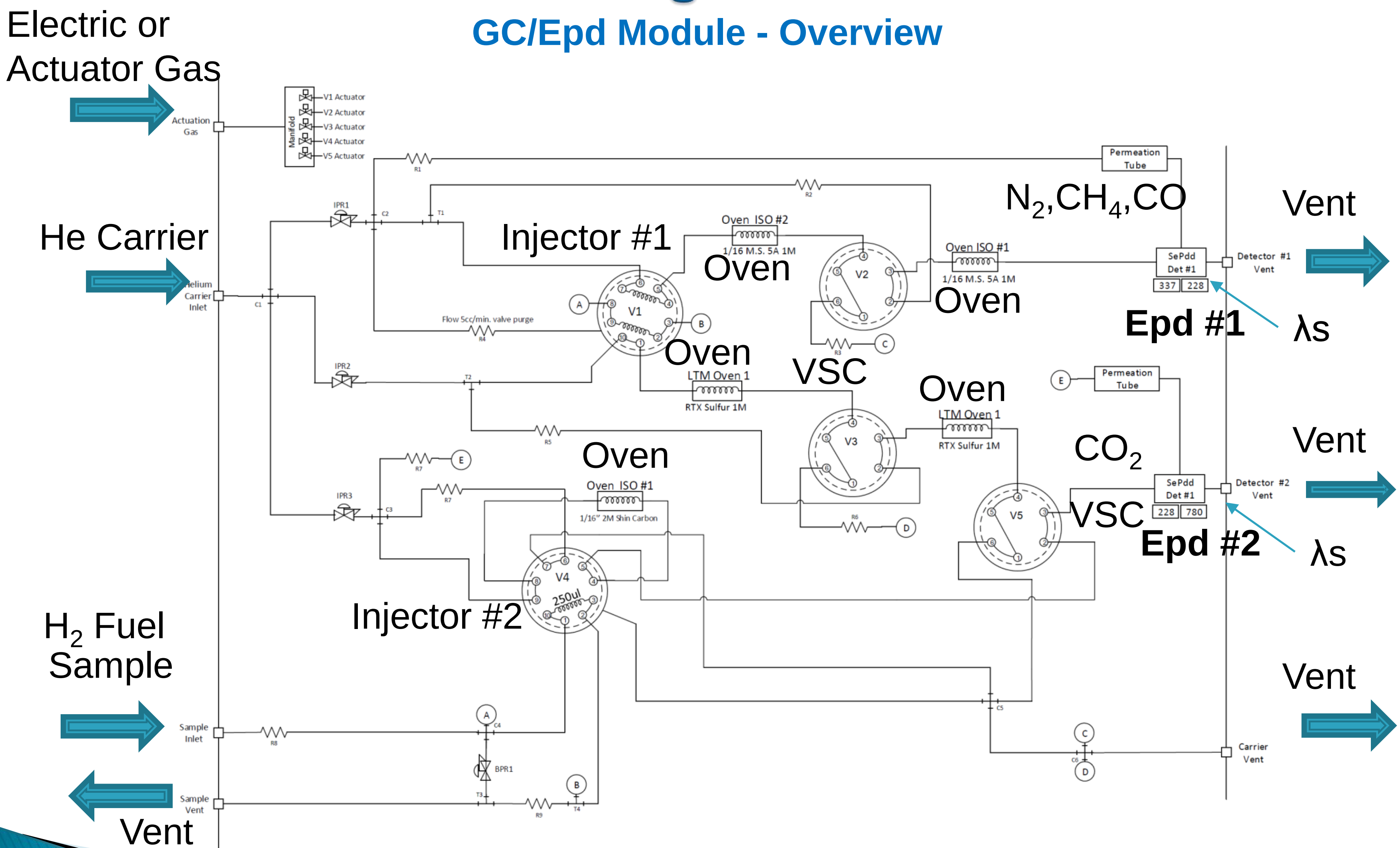
- Gas Chromatography with a Thermal Conductivity
- Detector (TCD) - for **He** (**GC/TCD**)

- Conductimetric **H_2O** Analyzer

- Fuel-Cell Based Trace **O_2** Analyzer

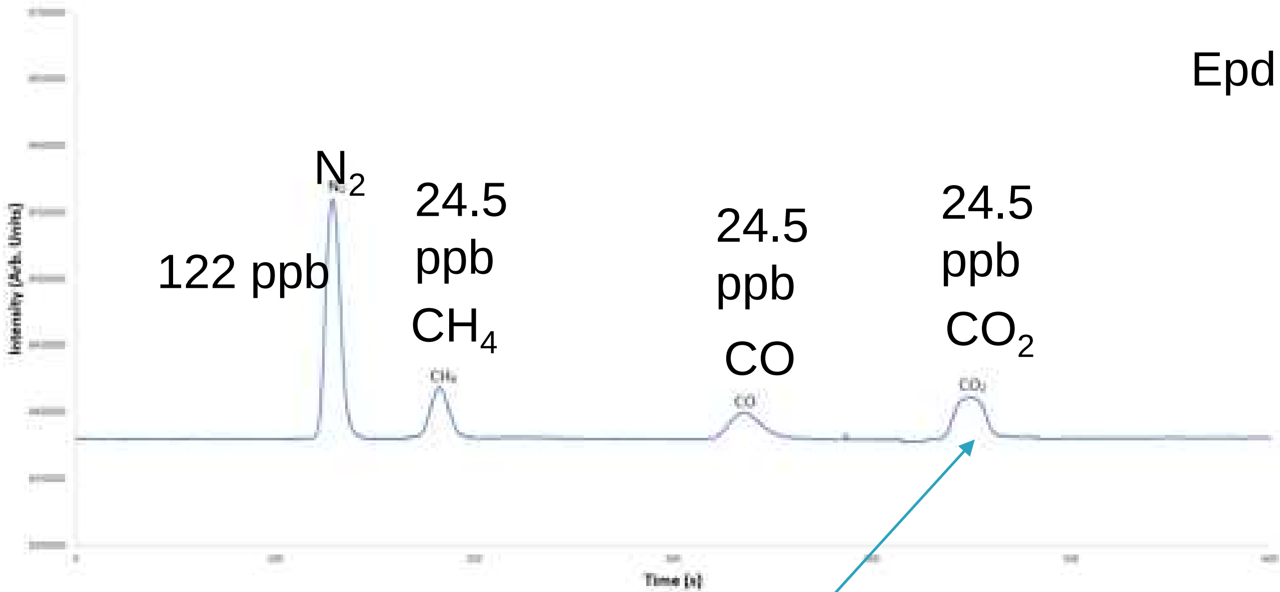
Standard On-Line H_2 Purity Analyzer Configuration

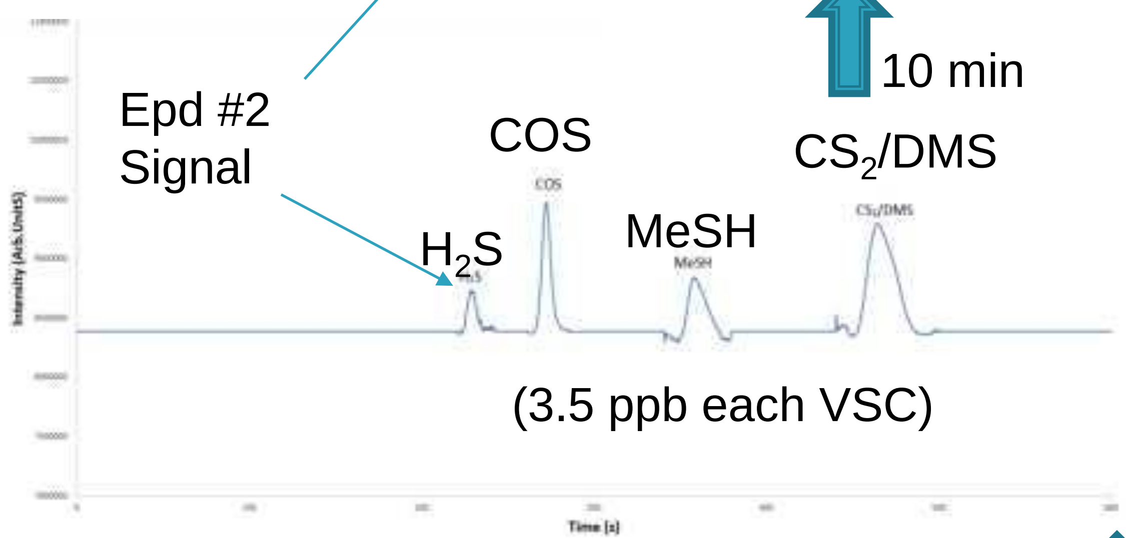
GC/Epd Module - Overview



Basic TSC / CO / CO_2 / CH_4 / N_2

GC/Epd H_2 Purity Analyzer Peak Display





10 min

Example VSC elution profile (TSC is Calculated)

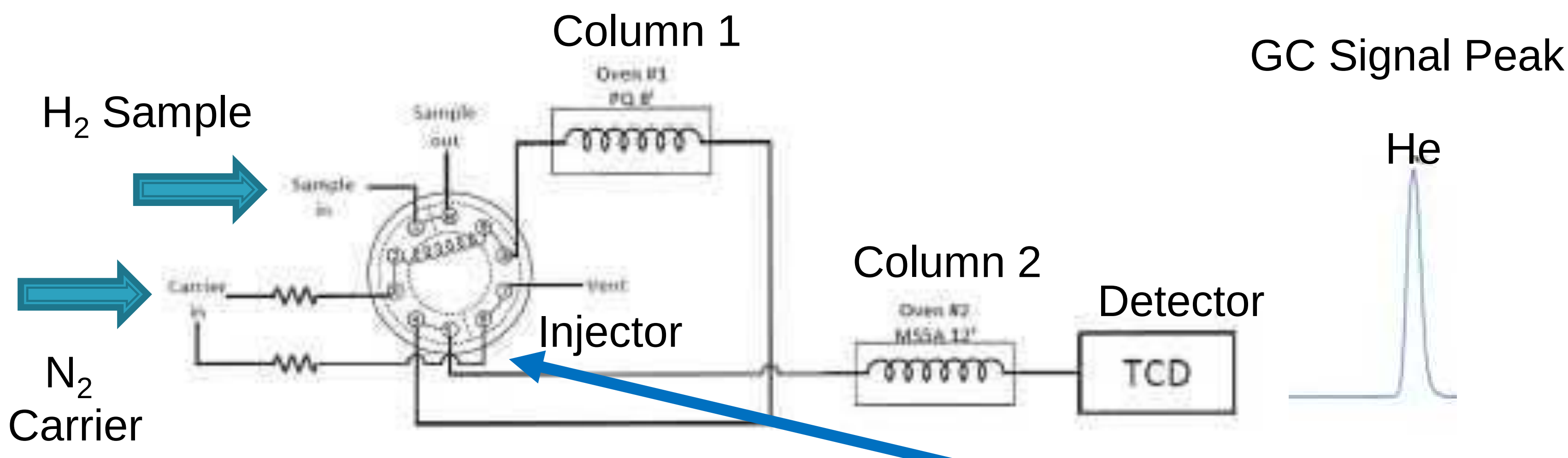
10 min

Airborne Labs International Inc.

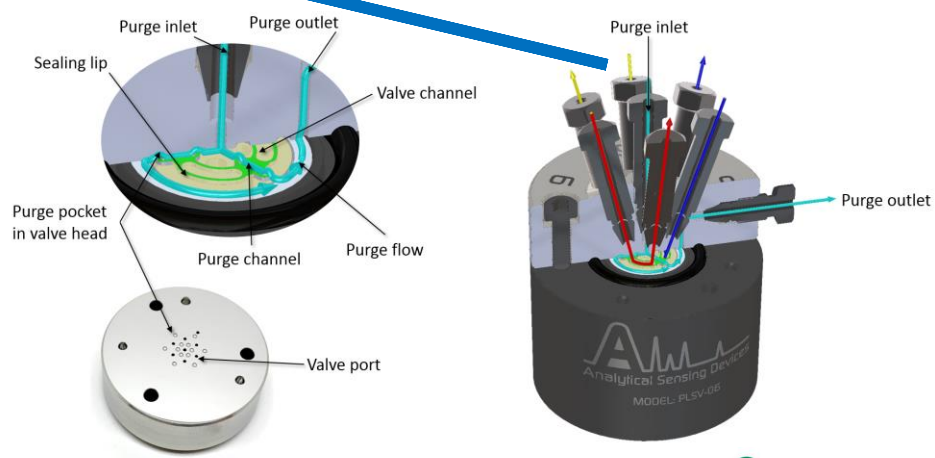
Optional GC/TCD Unit for He in SMR-sourced H_2 Fuel

GC/TCD

(For He Analysis only)



Leak-free Purge-Lip Sealing Valve (PLSV)



Airborne Labs International Inc.

ASDevices

H_2 Feed-Gas Source + Transport Contaminant Options

($Std\ H_2$ Analyzer Add-on Options)

- **Trace O_2 Analyzer** (ex. Fuel Cell sensor) = Transport Contaminant Source (Note: Zr Cell based units cannot be used in a H_2 matrix) GC/DID or GC/ePD's not cost effective.

- **Trace H_2O Analyzer** (ex. Conductimetric Sensor)
- = Source or Transport Contaminant.

- **Halogenated Impurities (VXC)** = Highly Source dependent Primarily a Transport Contaminant Source for SRM & other Feed gas based fuel.

- **Rare H_2 Fuel Source Specific** (ex. NH_3 ,Trace Metals = Highly Source Dependent)

Basic System Epd - How's Does it Work?

Overview / Background

Epd = Kind of a hybrid cross between a classic "Discharge Ionization Detector = **DID**" and a "Flame Photometric Detector = **FPD**"

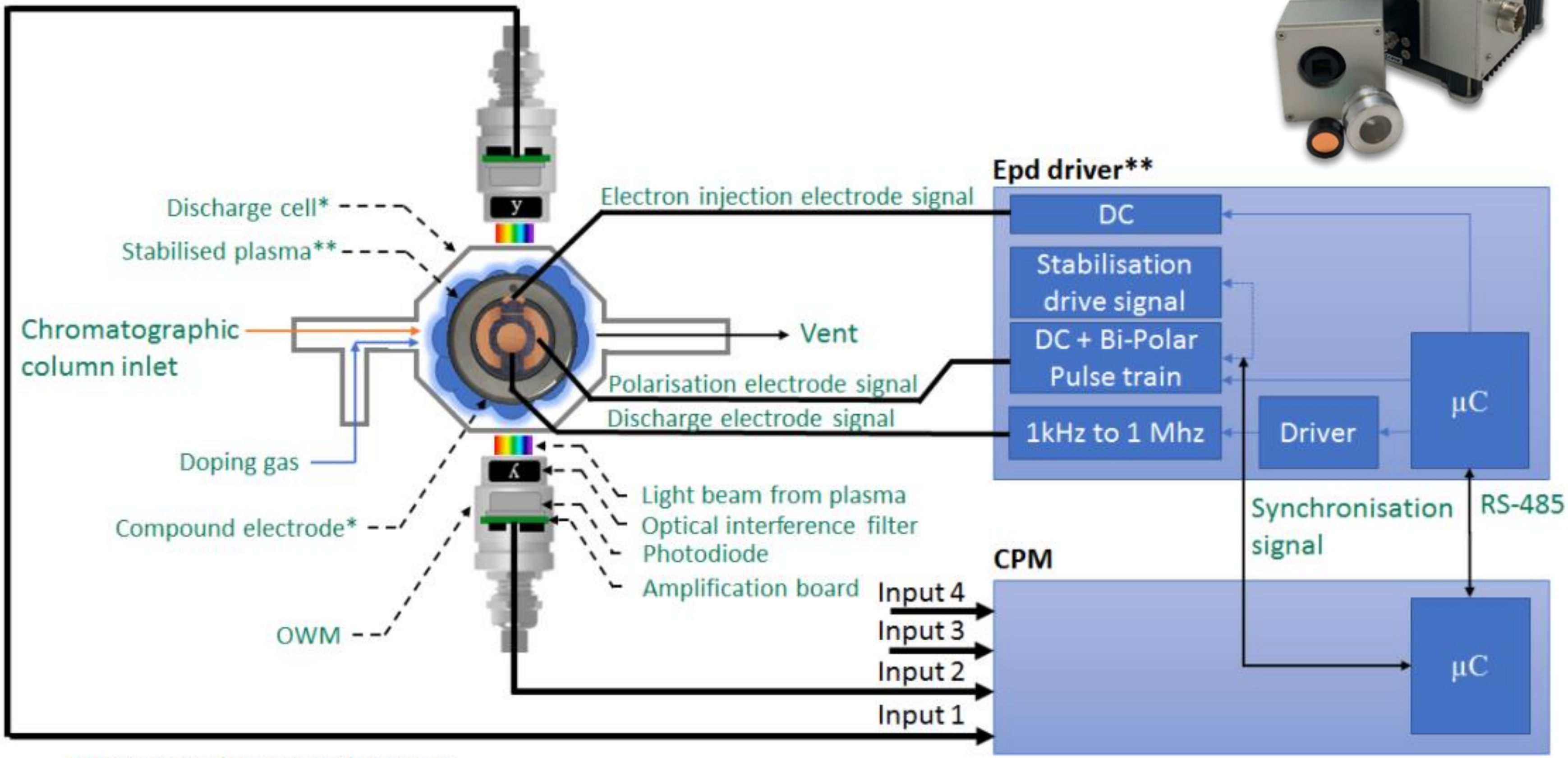
A "plasma" gas discharge created within the Epd causes "**universal**" ionization & **excitation** of the carrier gas PLUS **all eluting** impurities (like a DID).

Unlike a DID where an impurity-concentration related "**electrical ion current**" is used for impurity detection (**universal** = no selectivity)– An Epd looks at the **Plasma Emitted Light Photons** generated by the excited impurities for signal generation (like an FPD).

For "**Impurity Selectivity**" an optical **light filter** is located between the Plasma & a photo-diode detector which **only allows** those desired **emission** wavelengths generated by a **selective** "family" (ex. Sulfur agents) or, specific agents (ex. Halogens, CO, N_2, etc.) to be measured.

This process enhances the separation and measurement of various H_2 impurities by **BOTH** their GC elution **AND** light emission behavior.
This reduces the detectors needed (and **cost**) of a Basic H_2 Purity Analyzer.

Summary - Epd Advantages for H_2 Fuel Impurity Measurements



OWM: Optical Wavelength Module

CPM: Chromatographic Processing Module

Note: The plasma cell geometry is only for conceptual purpose and dimensions in this diagram are not representative of real design.

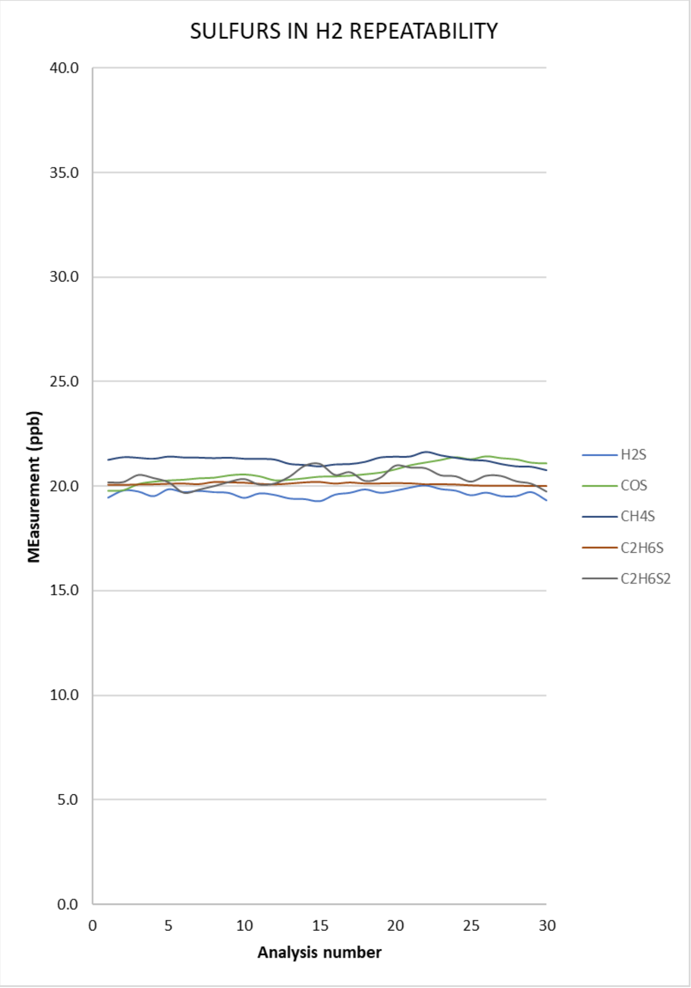
Summary - Epd Advantages for H_2 Fuel Impurity Measurements

- Can detect a **wide variety** of target H_2 impurities (permanent gases, VSC's, VHC's, NMHC, VOX, BTEX,, RX's halogens, etc.).
- The carrier gas (He, Ar or N_2) is used as the plasma discharge gas. **No Need for UHP Air / O_2 or flammable support gases.**
- **Range, LDR & MDL meets/exceeds SAE/ISO H_2 Fuel Spec Guidelines**
- **Calibration by 1-3 Cal Gas Mixtures: NCG's / VHC's/VSC's**
- **Low-maintenance**. Continuous production use possible for long periods.
- **Robust** = Ideal for trace analysis in a plant process operation.

Analytical GC/Epd TSC Performance Example

Excellent RSD & Sensitivity for TSC

	Results (ppb)				
Analyse	H2S	COS	CH4S	C2H6S	C2H6S2
1	19.5	19.8	21.3	20.1	20.2
2	19.8	19.8	21.4	20.1	20.2
3	19.8	20.1	21.4	20.1	20.6
4	19.5	20.2	21.3	20.1	20.4
5	19.9	20.3	21.4	20.1	20.2
6	19.7	20.3	21.4	20.1	19.7
7	19.8	20.4	21.4	20.1	19.8
8	19.7	20.4	21.4	20.2	20.0
9	19.7	20.5	21.4	20.2	20.2
10	19.5	20.6	21.3	20.2	20.4
11	19.7	20.5	21.3	20.1	20.1
12	19.6	20.3	21.3	20.1	20.1
13	19.4	20.3	21.1	20.1	20.5
14	19.4	20.4	21.0	20.2	21.0
15	19.3	20.5	21.0	20.2	21.1
16	19.6	20.5	21.1	20.1	20.6
17	19.7	20.5	21.1	20.2	20.7
18	19.9	20.6	21.2	20.1	20.3
19	19.7	20.6	21.4	20.1	20.4
20	19.8	20.8	21.4	20.2	21.0
21	20.0	21.0	21.4	20.1	20.9
22	20.1	21.1	21.7	20.1	20.9
23	19.9	21.2	21.5	20.1	20.5
24	19.8	21.4	21.4	20.1	20.5
25	19.6	21.3	21.3	20.0	20.2
26	19.7	21.4	21.2	20.0	20.5
27	19.5	21.3	21.1	20.0	20.5
28	19.5	21.3	21.0	20.0	20.3
29	19.7	21.1	20.9	20.0	20.1
30	19.3	21.1	20.8	20.0	19.8
Average (ppb)	19.67	20.65	21.26	20.11	20.39
Standard deviation (ppb)	0.18	0.46	0.20	0.06	0.35
MDL (ppb)	0.43	0.79	0.13	0.15	0.77
Repeatability (%)	0.9%	2.2%	0.9%	0.3%	1.7%



Field Experience to Date – GC/Epd System (China Olympics App)

- **Process-Oriented Solution**
  - Fully field validated
  - Process GC software
  - No need for highly trained personnel
- **Safety**
  - No support fuel or air / O_2 gas required
  - Only needs inert carrier / discharge gas
- **High Sensitivity**
  - **Epd** based Detector Technology
- **Robustness**
  - Low maintenance, leak-free Rotor Valves
  - All passivated hardware
- **Key specifications:**
  - LOD : < 4 ppb for H_2S + VSC

Summary / Conclusions

The Challenge

Constituent	Chemical Formula	Limits
Hydrogen fuel index (minimum mole fraction)	H_2	≥99.97%
Total non-hydrogen gases	TNHG	300
Maximum concentration of individual contaminants		
Water	H_20	5
Total hydrocarbons except methane[a] (C_1 equivalent)	TNMHC	2
Oxygen	O_2	5
Methane	CH_4	100
Helium	He	300
Nitrogen	N_2	300
Argon	Ar	300
Carbondioxide	CO_2	2
Carbonmonoxide[b]	CO	0.2
Total sulfur compounds[c]	TSC	0.004
Formaldehyde	HCHO	0.2
Formic acid	HCOOH	0.2
Ammonia	NH_3	0.1
Halogenated compounds (halogen ion equivalent)[d]	TXC	0.05
Particulate Concentration	NVR	1mg/kg

The Analytical Solution

- ✓ Yes – **By TCD or Software (PLC) subtraction**
- ✓ Yes – GC/Epd + GC/TCD **Option**
- ✓ Yes – H_2O Analyzer **Option**
- ✓ Yes – **Std** GC/Epd Unit
- ✓ Yes – O_2 Analyzer **Option**
- ✓ Yes – **Std** GC/Epd Unit
- ✓ Yes – GC/TCD **Option**
- ✓ Yes – **Std** GC/Epd Unit
- ✓ Yes – **Std** GC/Epd Unit
- ✓ Yes – **Std** GC/Epd Unit
- ✓ Yes – **Std** GC/Epd Unit
- ✓ Yes – **Std** GC/Epd Unit
- ? GC/Epd VOX Method Future Option
- ? GC/Epd VOX Method Future Option
- ? GC/Epd Method Future Option
- ? GC/Epd **VXC** Future Option

All current On-Line H_2 Analyzer methods meet/exceed SAE/ISO Method Performance Guidelines

Airborne Labs International Inc.

ASDevices

What's Next? – Future H_2 Analyzer Developments

- Development of an integrated GC/Epd Method / Module Options for **VXC Target List / Fatty Acids (RCOOH) / C1-C2 Aldehydes (VOX)** / **NH_3** analysis

- Incorporation of purged **Instrument sheds** for housing On-Line H_2 Fuel Purity Analyzers + H_2 Truck Sampling Stations.

- Use of special Manifold-Connected **Detector Tubes** & H_2 Fuel ASTM 7606 type Samplers for quick, **on-site** H_2 Fuel Station screening tests for critical H_2 Fuel Impurities

THANK YOU FOR YOUR TIME AND ATTENTION!

QUESTIONS?

Please Contact us

Mark Taylor – Mark.Taylor@airbornelabs.com

Dr. Don Pachuta – Don.Pachuta@airbornelabs.com

Dr. Marc-Antoine Langevin – malangevin@asdevices.com

André Lamontagne – alamontagne@asdevices.com