



HyCoRA 2nd OEM Workshop

Hydrogen purity analysis development in HyCoRA project

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Brussels, 2015-10-09

Motivation

- HyCoRA main Goal
 - Develop strategy for cost reduction for hydrogen fuel quality assurance
- HyCoRA WP2 Goals
 - Development and validation of novel analytical methods and traceable gas standards for key analytes within the ISO 14687 specification that does not exist
 - Develop traceable gas standard mixtures
 - **Simply and reduce cost of QC by reducing the number of analytical methods required**
 - **Develop strategy for pre-concentration of impurities in samples**
 - **Provide traceable validation of the performance of online analyzers**
 - Test and validate online analyzers
- NMI's not part of HyCoRA (NPL, VSL)

Analytical methods tested within HyCoRA

- SINTEF
 - Long Path Fourier Transform InfraRed Spectroscopy (LP FTIR)
 - Gas Chromatography with Mass Spectrometry Detector (GC-MS)
 - GC with Pulsed Discharge Helium Ionization Detector (GC-PDHID)
- VTT LTD
 - GC-PDHID
 - GC Thermal Conductivity Detector (GC-TCD)
 - GC Electron Capture Detector (GC-ECD) (Pulse discharge detector in ECD mode)
- CEA
 - Ion Molecule Reaction MS (IMR-MS)
 - Optical Feedback Cavity Enhanced Absorption Spectroscopy (OFCEAS)

Grouping of analytes (NPL AS 64)

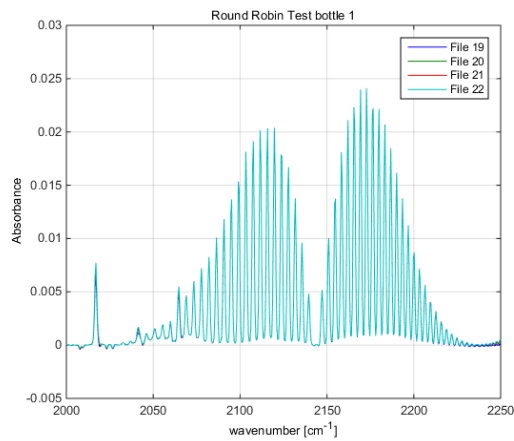
		Analytical method														
		Dew point analyser	Electrostatic capacity moisture meter	Vibrating quartz analyser	FTIR	Galvanic cell analyser	GC-FID with methaniser	GC-FID	GC-TCD	GC-MS	GC-PDHID*	GC-SCD	GC-ECD	Combustion – ion chromatography	Absorption – ion chromatography	Gravimetry
Species	Water	■	■	■	■											
	Total hydrocarbons			■		■	■		■	○						
	Oxygen				■											
	Helium								■	■						
	Nitrogen								■	■	■					
	Argon								■	■	■					
	Carbon dioxide			■		■			■	■	■					
	Carbon monoxide			■		■			■	■	■					
	Total sulphur											○		■		
	Formaldehyde			■			■			○	■				■	
	Formic acid			■						○	■				■	
	Ammonia			■											■	
	Total halogenated									○			○		■	
	Particle concentration															■

○ = with pre-concentration device

* GC-pulsed discharge helium ionization detector

LP FTIR

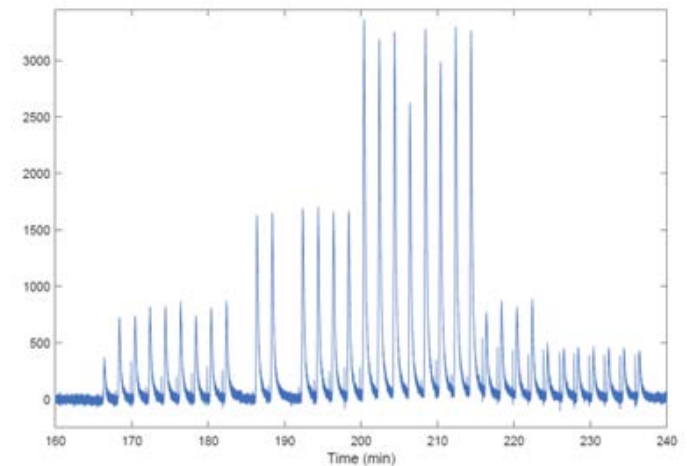
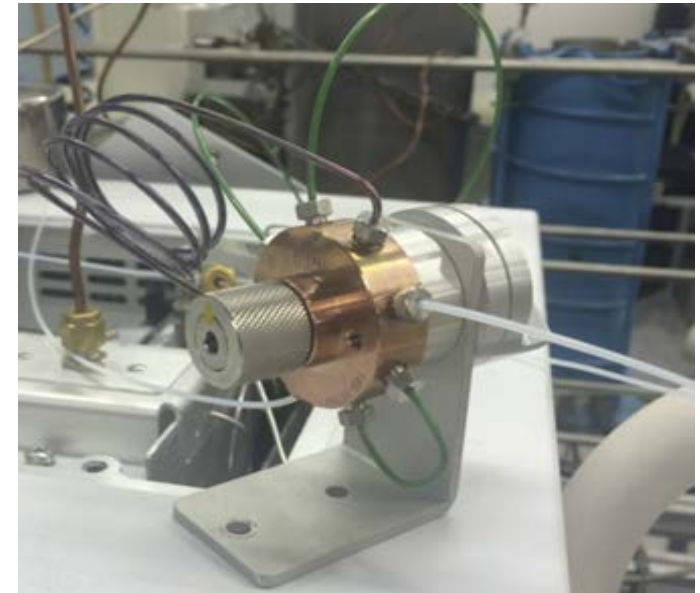
- Excellent sensitivity
- No application to homonuclear species
- LOQ CO 5 ppbv
- Applied to CO, CO₂, H₂O, SO₂, THC, HF, HCl
- Online application later in project



GC-MS

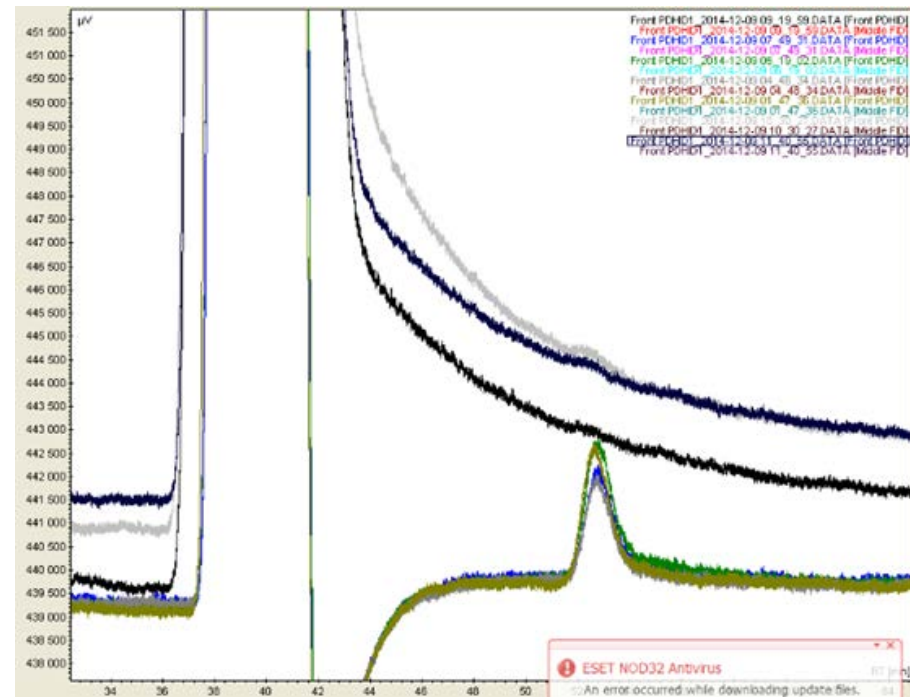
- Frequent calibration to compensate for drift
- Valco multivalve
- Software for quantitation
- Air leaks challenging

Analyte	Level 1	Level 2	Level 3	R ²	LOQ
CO ₂	0.5	1	2	0.98	0.40
N ₂	5	10	20	0.92	17
O ₂	2	4	8	0.94	5
Ar	1	2	4	0.98	0.91



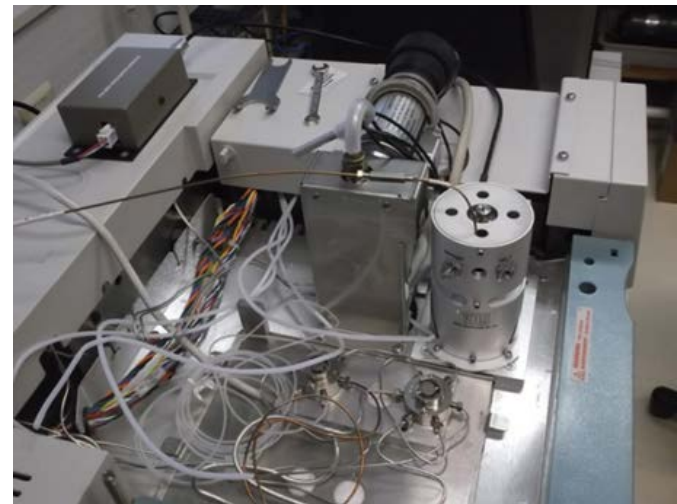
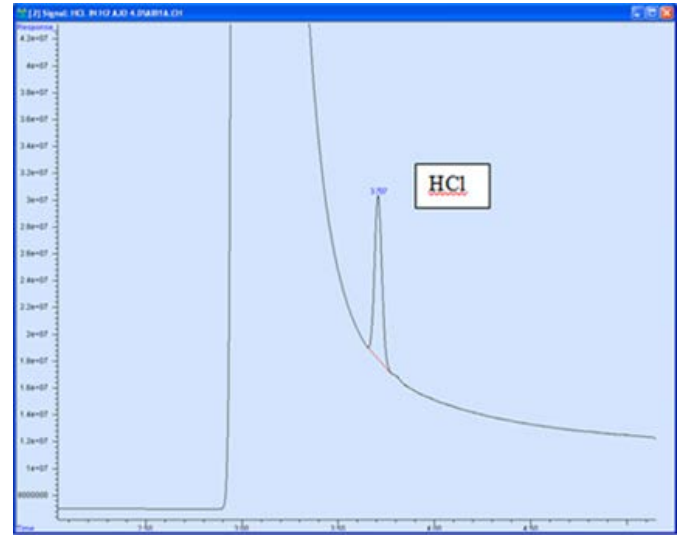
SINTEF GC-PDHID

- 1 ppm H₂S test not successful
 - Separation from H₂ peak difficult
 - LOQ > 10 ppm
- More applicable to homonuclear species and CO_x.



VTT GC-PDHID

- Evaluation of HCl performance
- LOD ~5 ppm
- Inferior performance to μ GC
 - Poraplot –U
 - Thermal Conductivity detector
- Now testing indirect method in ECD mode
 - Chloroethane conversion of HCl



IMR-MS

- Soft ionization of molecules, low fragmentation
- CO/N₂ interference avoided
 - Kr should not ionize N₂
- CO application did not work out
- Application to H₂S successful
 - LOD ~ 2ppb

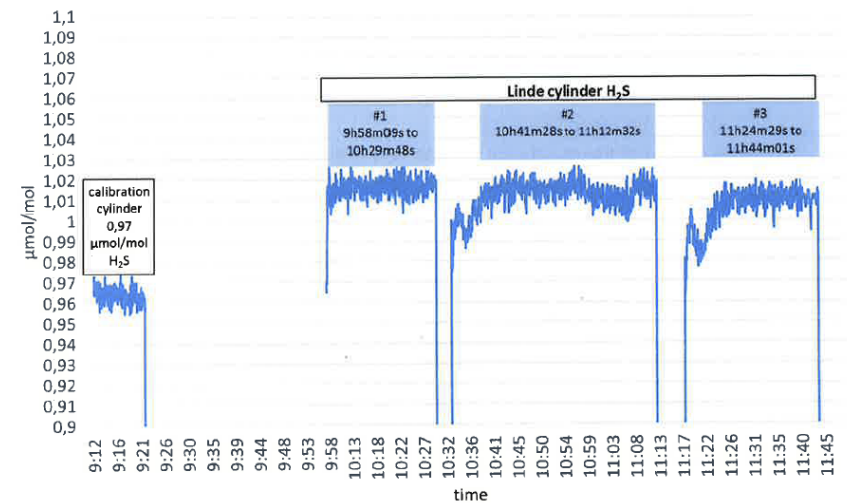


Figure 1: IMR-MS measurement of the H₂S LINDE cylinder (the 3 replicates)

OFCEAS

- Excellent performance
- Used by CEA for Euramet 1220 Round robin
- LOD (in air)
 - CO: 1 ppb
 - H₂S: 2 ppb

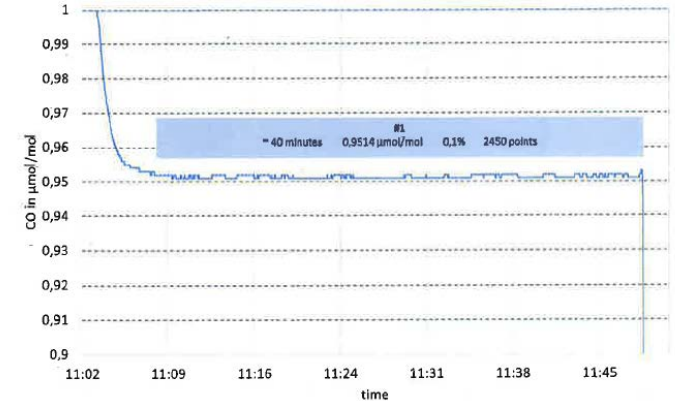


Figure 2: OFCEAS results for CO

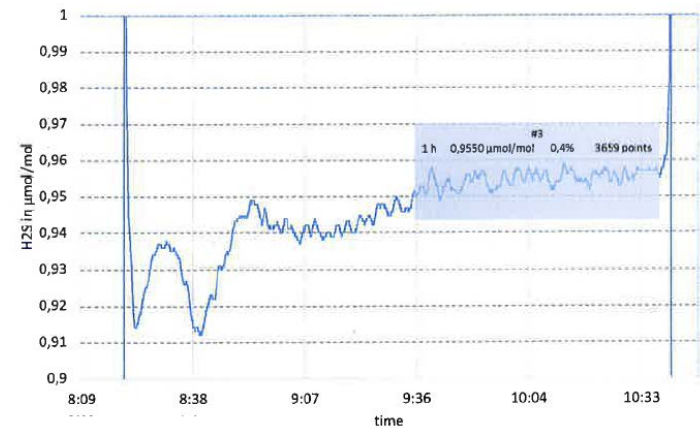
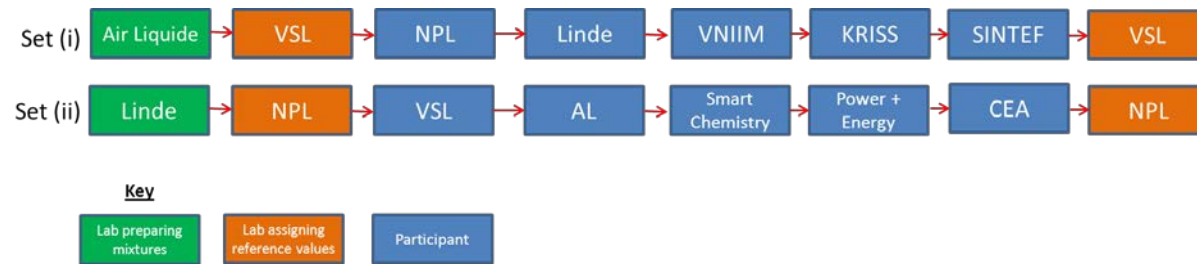


Figure 3: OFCEAS results for H₂S

Round Robin Testing

- Important part of laboratory QC
- Euramet 1220



- H₂S (1 ppm), CO (1, 0.1 ppm)
- H₂FC (JRC)
 - SO₂, CH₄, CO, CO₂, O₂ mixture (5-15 ppm)

Euramet 1220

	Component	Method	Result ($\mu\text{mol/mol}$)	RSD (%)	Number of replicates
CEA	CO 1 $\mu\text{mol/mol}$	OFCEAS	0.950	5	2
	CO 0.1 $\mu\text{mol/mol}$	OFCEAS	0.096	5	2
	H ₂ S 1 $\mu\text{mol/mol}$	OFCEAS	0.931	5.08	4
		IMR-MS	1.013	5.2	3

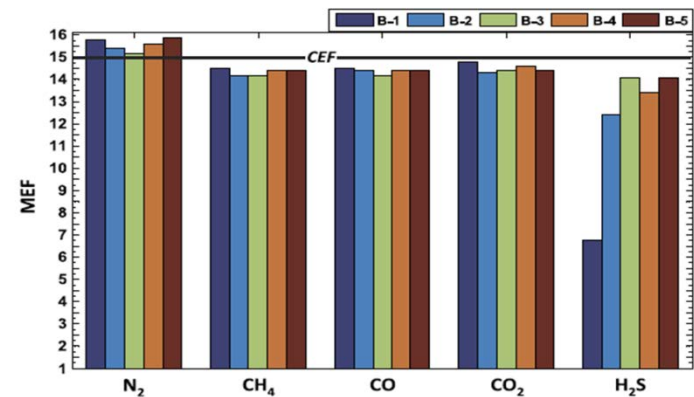
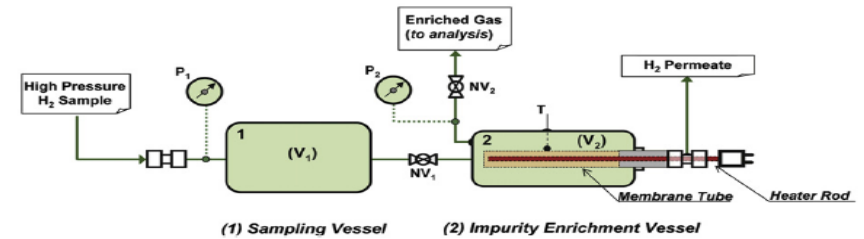
	Component	Method	Result (mol/mol)	RSD (%)	Number of replicates
SINTEF	CO 1 $\mu\text{mol/mol}$	FTIR	0.876 ppm	0.9%	4
	CO 0.1 $\mu\text{mol/mol}$	FTIR	0.064 ppm	4.7%	4
	H ₂ S 1 $\mu\text{mol/mol}$	GC-MS	1.05 ppm	6.2%	5

H2FC Round Robin (SINTEF)

Analyte	GC-MS (ppm)	SD (ppm)	FTIR (ppm)	SD (ppm)
CO			7.9	0.3
CH ₄	8.4	0.4	9.2	0.4
SO ₂	9.5	0.2	9.5	1.5
CO ₂	11.7	0.5	11.0	1.0
O ₂	10.4	0.5		
N ₂	9.7	1.5		

Pre-concentration efforts

- Collaboration with ANL
- Pd-membrane separation
- $CEF \sim \frac{V_1 P_1}{V_2 P_2}$. Increase V1 to $CEF > 500$
- Direct connect of 10 L sample cylinders (V1)
- New membranes with improved flux
 - Avoid irreversible Pd sulphide formation
 - High flux at low temperature to avoid catalysis of soot and methanation
- Currently pre-concentrating HRS samples



Online monitoring of fuel quality

- VTT soon to test ENVI MS analyser
 - Rental from Environics
- SINTEF will perform online application of LPFTIR
 - Existing instrumentation
- Protea developing FTIR instrument for online analysis of fuel QC as part of the project
 - 10 bar pressurized cell
 - 10 meter path length
 - To be manufactured

