Recent developments on quality assurance of fuel cell hydrogen

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Gas Metrology Group – NPL

Cutting Edge Research for Gas Metrology, CCQM-GAWG (13 Oct 2016)

Overview of presentation

A Growing Hydrogen Economy

Four Metrology Challenges for the Hydrogen Industry

NPL’s Hydrogen Impurity Enrichment Device

A Growing Hydrogen Economy

Hydrogen vehicles

Hyundai ix35

Honda Clarity

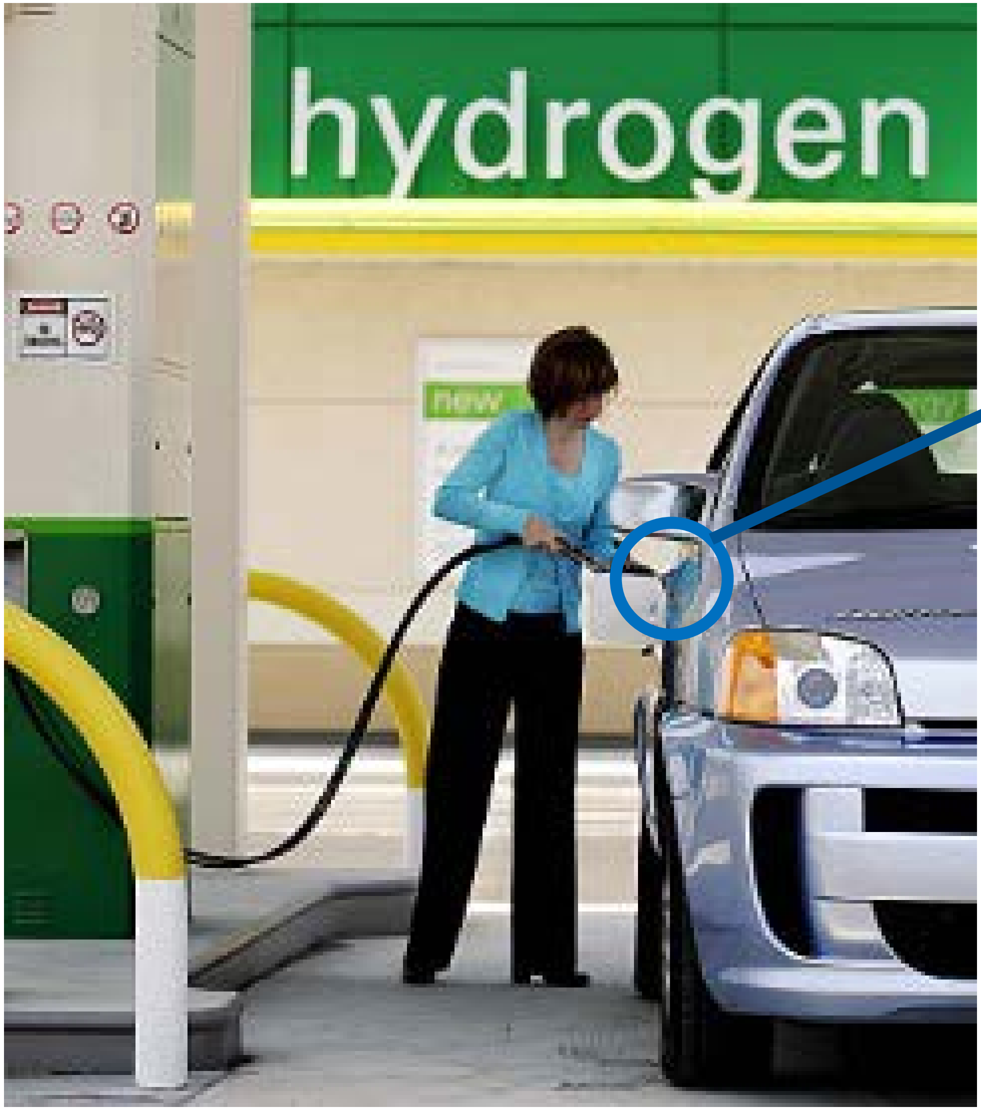
Toyota Mirai

Riversimple

	Fuel cell Vehicles
Exhaust	Only water
Emissions (CO_2, NOx, SO_2, particulates)	Zero
Range	500 km
Top speed	160 km/hr

UK H2 Mobility report (2013)

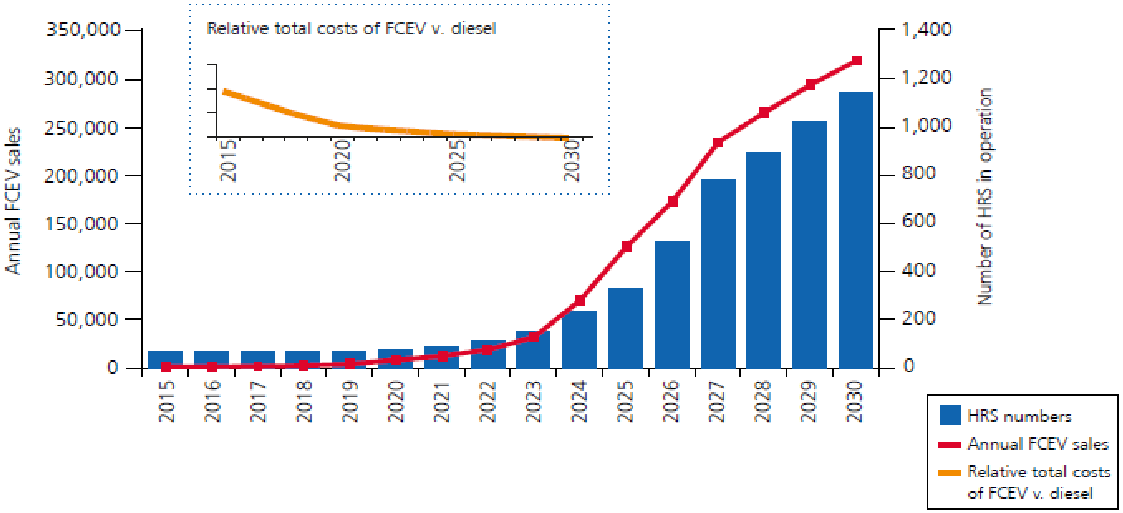
Hydrogen refuelling stations



- Supplied at 700 bar (or 350 bar)
- 5 kg per fill (full tank)
- 3 minutes to fill
- ~€50 for full tank
- Hydrogen produced by electrolysis or steam methane reforming

UK’s hydrogen economy 2030

A report by UK H2Mobility (2013)



1.6 million *fuel cell vehicles on the road in the UK*

1,100 *hydrogen refuelling stations in operation*

254,000 *tonnes of hydrogen produced a year*

Four Metrology Challenges for the Hydrogen Industry

Challenge 1 – Flow Metering

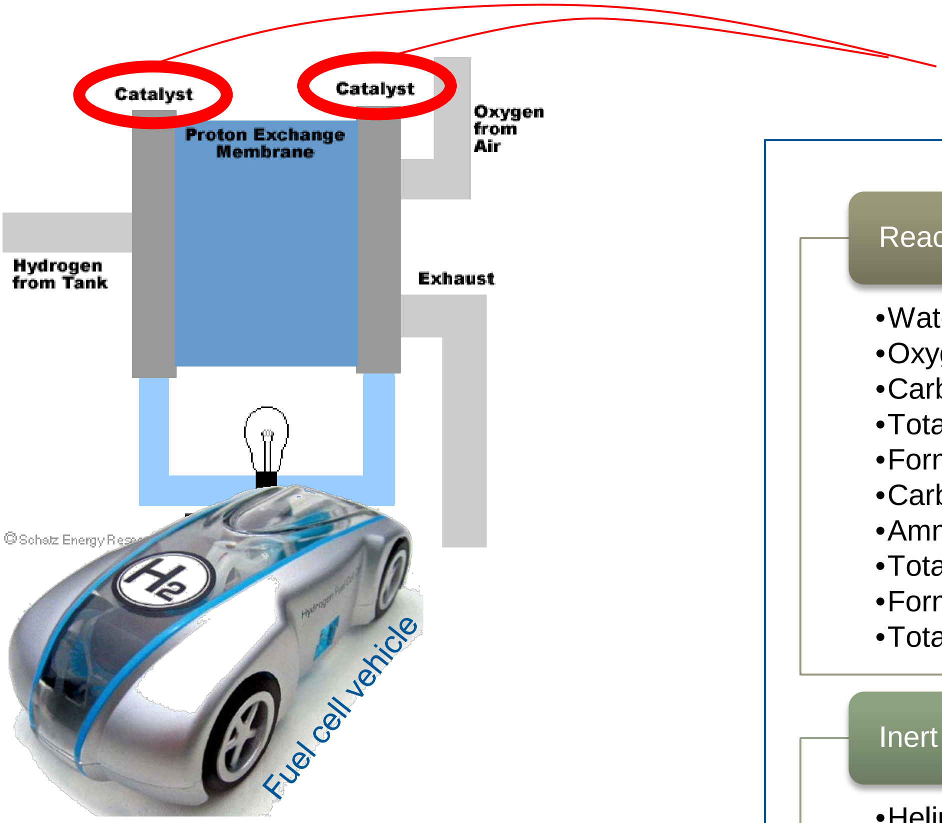
Refuelling stations cannot cost their customers with required accuracies

Flow meters in the refuelling station must be accurate to 1% (OIML R 139-1)

Hydrogen supplied can vary up to 700 bar in pressure and between -40 to 85°C during refuelling

Unknown mass of hydrogen is lost during venting

Challenge 2 – Quality Assurance



Usually platinum – can degrade in the presence of impurities (such as hydrogen sulphide or carbon monoxide)

Reactive gases

•Water	(5 µmol/mol)
•Oxygen	(5 µmol/mol)
•Carbon dioxide	(2 µmol/mol)
•Total hydrocarbon compounds	(2 µmol/mol)
•Formic acid	(0.2 µmol/mol)
•Carbon monoxide	(0.1 µmol/mol)
•Ammonia	(0.1 µmol/mol)
•Total halogenated compounds	(0.05 µmol/mol)
•Formaldehyde	(0.01 µmol/mol)
•Total sulphur compounds	(0.004 µmol/mol)

Inert gases

•Helium	(300 µmol/mol)
•Nitrogen	(100 µmol/mol)
•Argon	(100 µmol/mol)

Non-gases

•Particulates	(1 mg/kg)

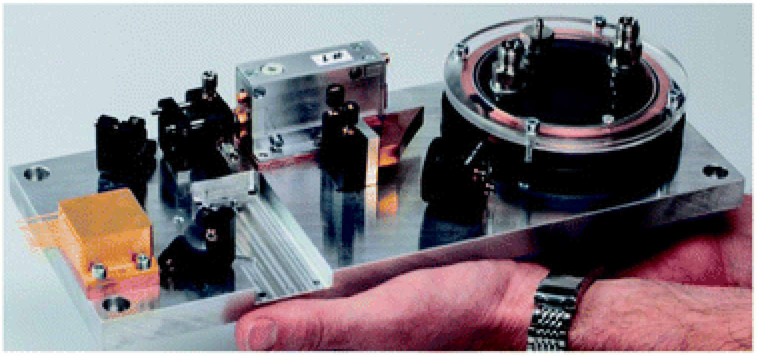
DIRECTIVE 2014/94/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 22 October 2014 on the deployment of alternative fuels infrastructure:

"The hydrogen purity dispensed by hydrogen refuelling points shall comply with the technical specifications included in the ISO 14687-2 standard."

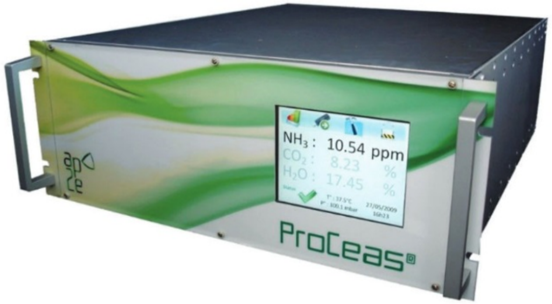
Challenge 3 - Quality Control

ISO 19880-8 recommends adding quality control measures in order to:

- Continuously monitor key impurities (rather that waiting for annual purity checks)
- Monitor levels of reactive species that could degrade the fuel cell
- Switch off pump as soon as any impurities are detected



Quantum cascade analyser by Cascade Technologies

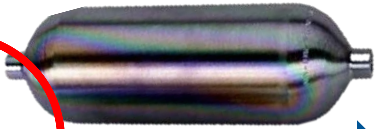


ProCeas by AP2E

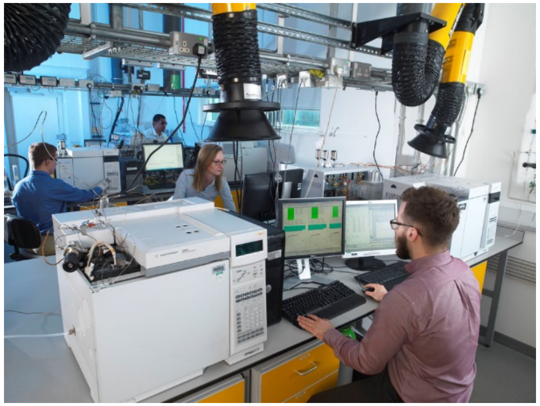
Online analysers are available but have not been tested for hydrogen quality control

Challenge 4 - Sampling

Hydrogen refuelling station



Hydrogen sample



Hydrogen purity laboratory

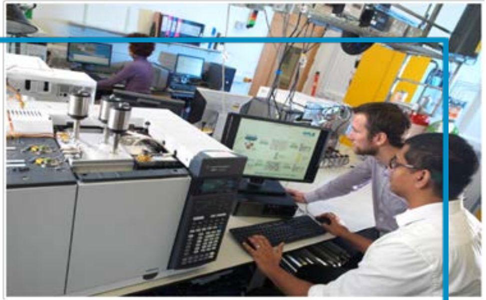
There are no official guidelines for sampling hydrogen and therefore stations may be using:

- Inaccurate technique for sampling (contamination issues)
- Inappropriate sampling device (e.g. stainless steel opposed to sulfinert)
- Wrong sampling vessels/cylinders

EMPIR Metrology for Hydrogen Vehicles

NPL
National Physical Laboratory


Flow metering


Quality assurance

Quality control


Sampling


Creating impact

Supported by 43 stakeholders including:

BMW
DAIMLER
TOYOTA
riversimple

20 project partners:

NPL National Physical Laboratory
FORCE TECHNOLOGY
SP
NEN
METAS
nel flow measurement services
CEM CENTRO ESPAÑOL DE METROLOGÍA
AIR LIQUIDE
Justervesenet
VSL Dutch Metrology
ap2e
THE LINDE GROUP Linde
CASCADE TECHNOLOGIES
CESAME-exadébit SA
Ha FUNDACIÓN PARA EL DESARROLLO DE LAS NUEVAS TECNOLOGÍAS DEL HIDRÓGENO EN ARAGÓN
IFE
ITM POWER Energy Storage | Clean Fuel
SINTEF
EMPA Materials Science & Technology
Shell

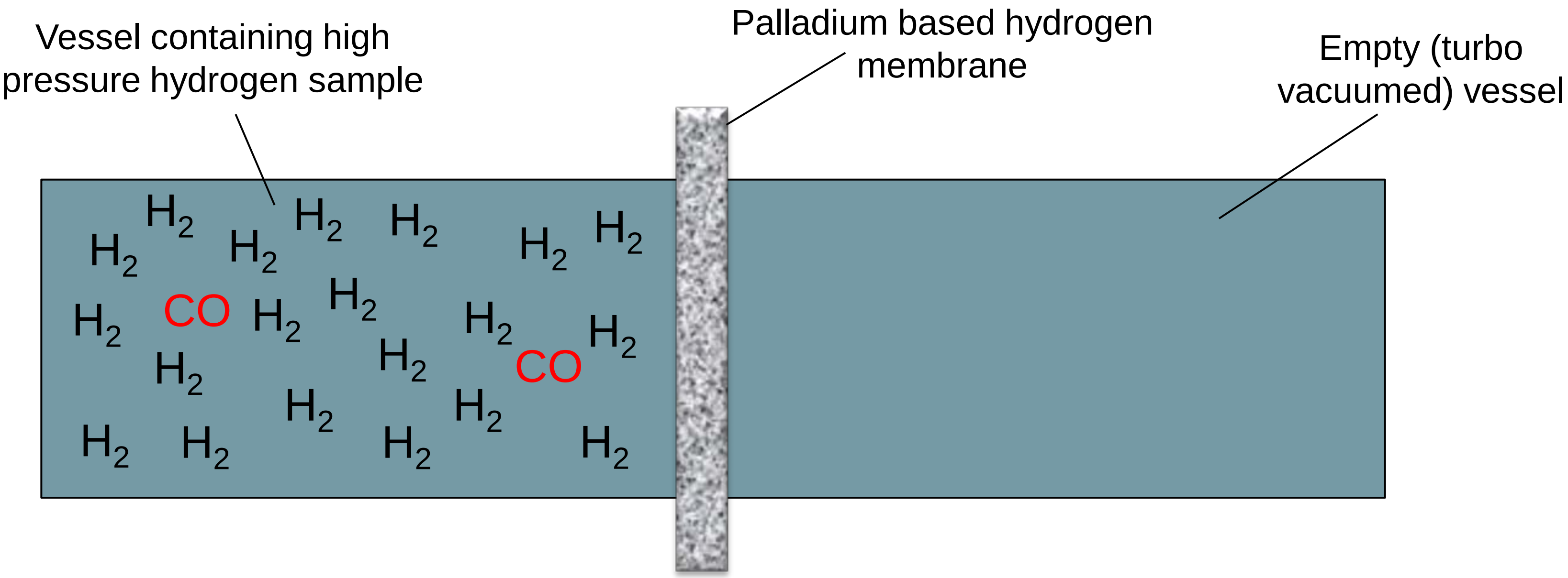
NPL’s Hydrogen Impurity Enrichment Device

Problems for commercial laboratories

A commercial hydrogen purity laboratory

- Number of instruments → 7
- Capital expenditure → ~€500k total
- Small volumes of sample → Cannot use low pressure in small vessels
- Limits of detection → Not feasible with routine instruments such as GC-MS
- Time for analysis → Too long (several instruments)

Hydrogen impurity enrichment



- ✓ Allows measurement of lower amount fractions
- ✓ Better signal-to-noise
- ✓ Can be used with any analyser

Problems for commercial laboratories

National Physical Laboratory

A commercial hydrogen purity laboratory

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Capital expenditure → ~€500k total

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Problems for commercial laboratories

A commercial hydrogen purity laboratory

Number of instruments → 2-3

Capital expenditure → ~€500k total

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Time for analysis → Too long (several instruments)

Problems for commercial laboratories

A commercial hydrogen purity laboratory

Number of instruments → 2-3

Capital expenditure → <€200k total (using routine GC-MS)

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Problems for commercial laboratories

A commercial hydrogen
purity laboratory

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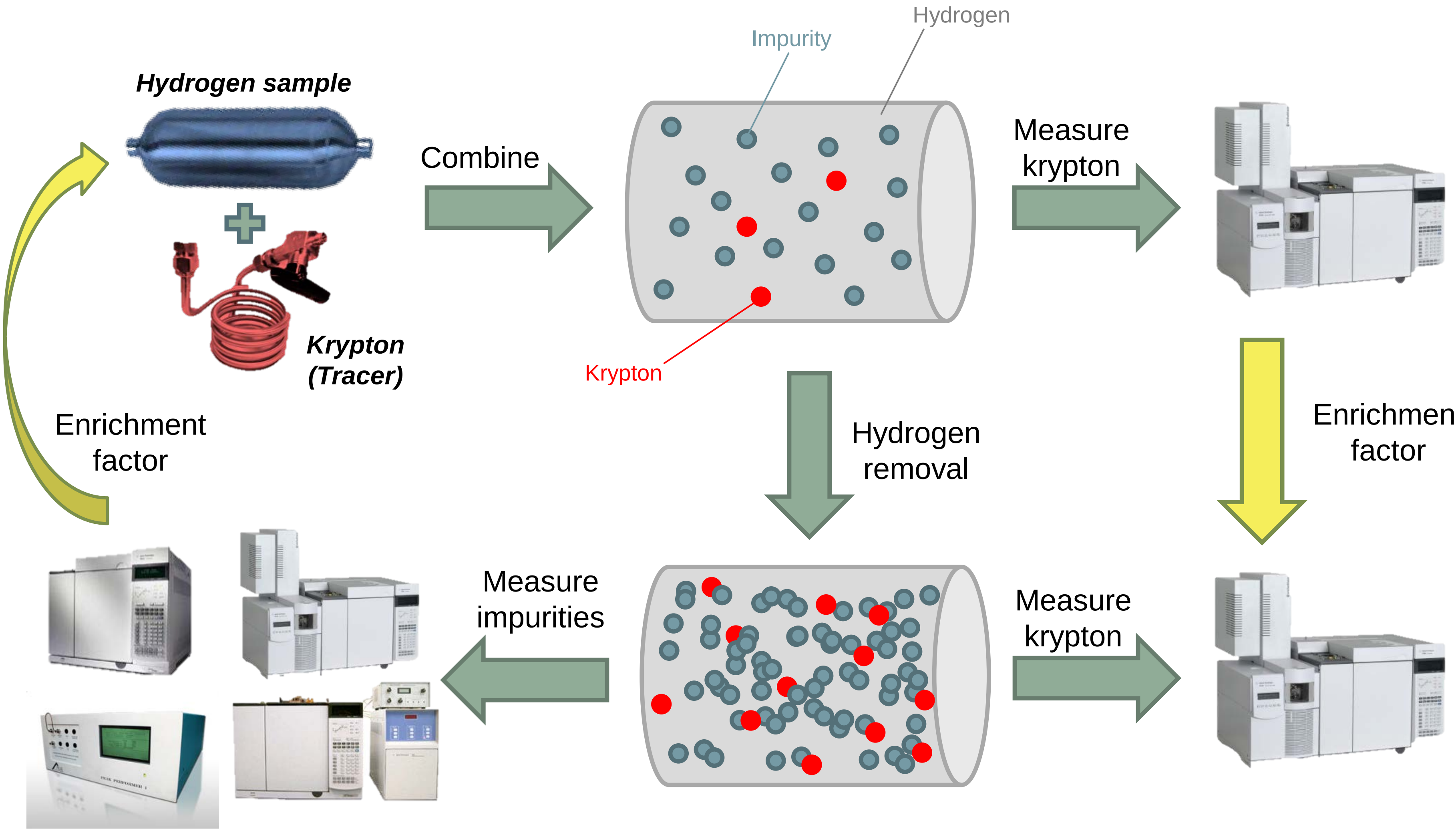
- Capital expenditure → <€200k total (using routine GC-MS)
- Small volumes of sample → No problems with low volume samples
- Limits of detection → GC-MS can be used for most impurities
- Time for analysis → Less time needed to use all instruments

Hydrogen Impurity Enrichment Device (HIED)

NPL's tracer enrichment method



Hydrogen sample

Krypton (Tracer)

Combine

Measure krypton

Enrichment factor

Hydrogen removal

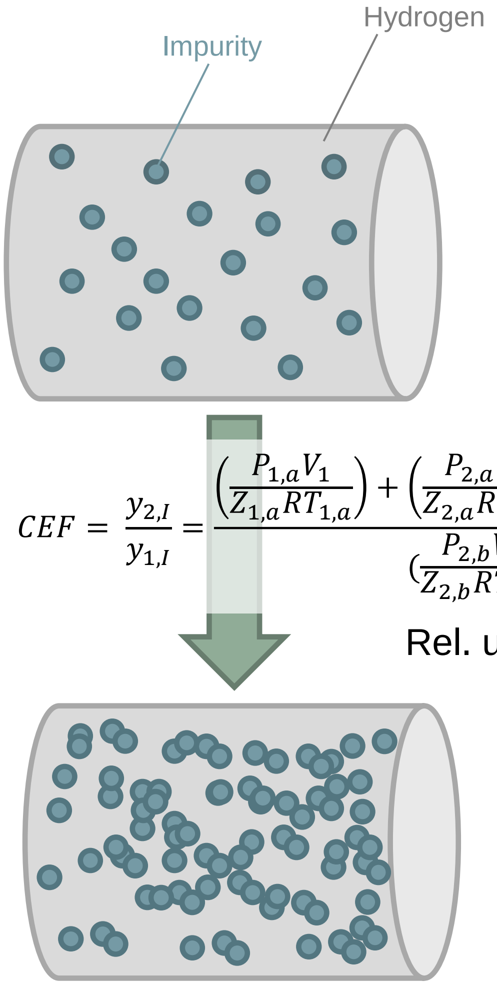
Measure krypton

Measure impurities

Enrichment factor

Calculating enrichment factors

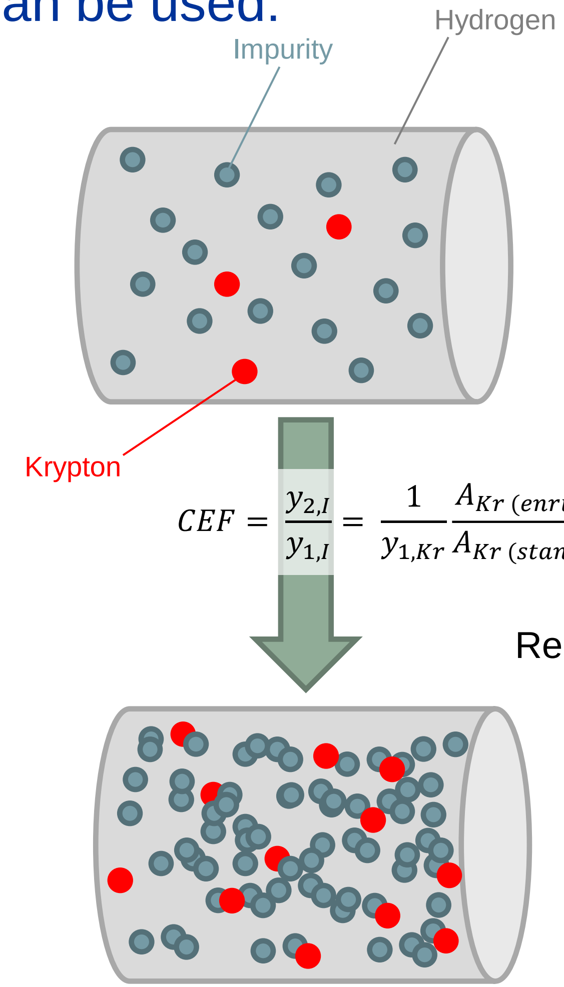
Two methods can be used:



$$CEF = \frac{y_{2,I}}{y_{1,I}} = \frac{\left(\frac{P_{1,a}V_1}{Z_{1,a}RT_{1,a}}\right) + \left(\frac{P_{2,a}V_2}{Z_{2,a}RT_{2,a}}\right) - \left(\frac{P_{1,b}V_1}{Z_{1,b}RT_{1,b}}\right)}{\left(\frac{P_{2,b}V_2}{Z_{2,b}RT_{2,b}}\right)}$$

Rel. u/c = ~10% (*k*=2)

Ideal gas law method



$$CEF = \frac{y_{2,I}}{y_{1,I}} = \frac{1}{y_{1,Kr}} \frac{A_{Kr\ (enriched)}}{A_{Kr\ (standard)}} y_{Kr\ (standard)}$$

Rel. u/c = ~2.5% (*k*=2)

Krypton tracer method

Results – Test 1

CO is lower
CH_4 is slightly higher

Reaction taking place?

CH_4 = 2.008 ppm
CO = 1.896 ppm
N_2 = 2.023 ppm
H_2 balance

Enrichment
x 60

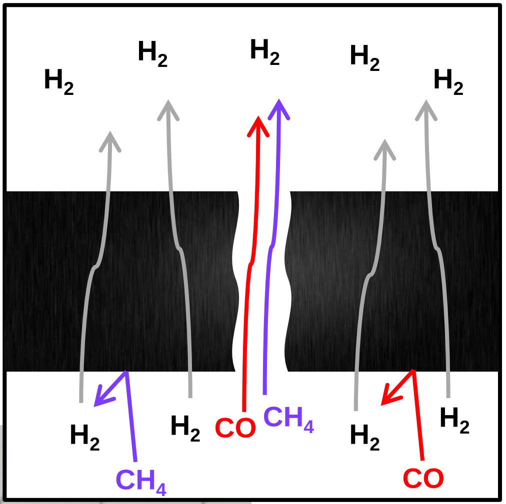
CH_4 = 2.027 ppm (+1.0%)
CO = 1.697 ppm (-10.5%)
N_2 = 2.123 ppm (+4.9%)
H_2 balance

Ideal gas law method

CH_4 = 2.027 ppm (+3.1%)
CO = 1.749 ppm (-7.8%)
N_2 = 2.189 ppm (+8.2%)
H_2 balance

Krypton tracer method

Results – Test 2



CH_4 = 2.008 ppm
CO = 1.896 ppm
N_2 = 2.023 ppm
H_2 balance

Enrichment
x 60

CH_4 = 0.106ppm (-94.7%)
CO = 0.075 ppm (-96.0%)
N_2 = 0.134 ppm (-93.4%)
H_2 balance

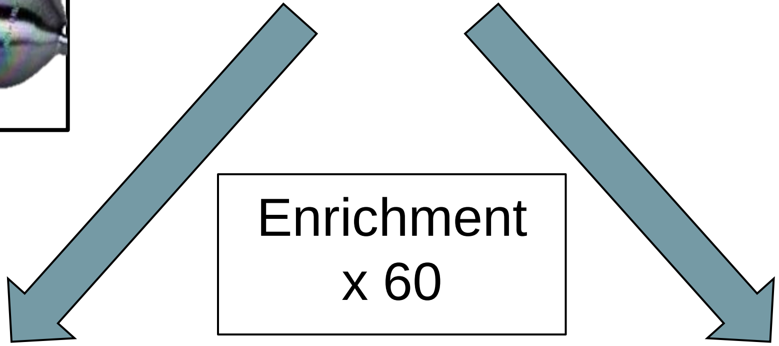
CH_4 = 2.069 ppm (+3.1%)
CO = 1.458 ppm (-23.1%)
N_2 = 2.598 ppm (+28.4%)
H_2 balance

Ideal gas law method

Krypton tracer method

Results – Test 3

CH_4 = 1.506 ppm
CO = 1.422 ppm
N_2 = 1.537 ppm
H_2 balance



Enrichment
x 60

CH_4 = 0.972 ppm (-35.5%)
CO = 0.949 ppm (-33.3%)
N_2 = 1.576 ppm (+2.5%)
H_2 balance

CH_4 = 1.603 ppm (+1.6%)
CO = 1.565 ppm (+10.0%)
N_2 = 2.599 ppm (+69.1%)
H_2 balance

Ideal gas law method

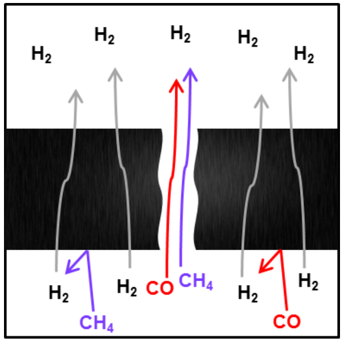
Krypton tracer method

Conclusions

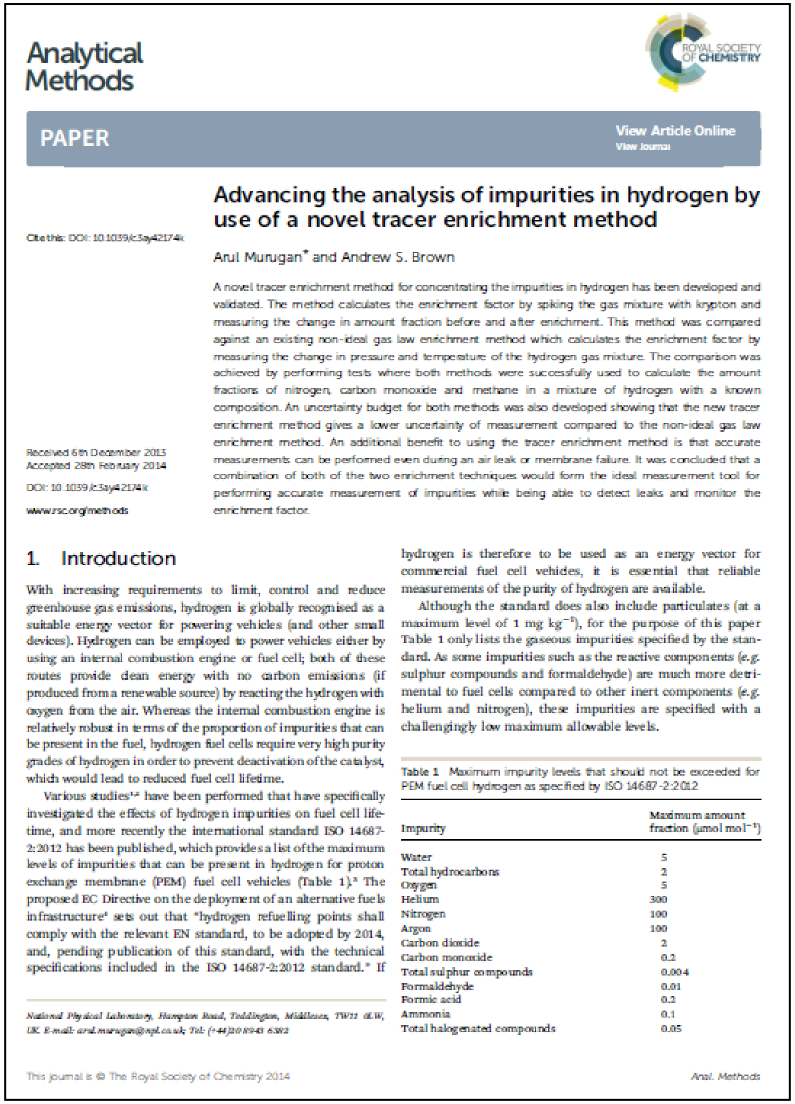
Use krypton tracer method to calculate enrichment factor

AND…

Use ideal gas law method to check for membrane failure or air leak



Further reading



Analytical Methods

PAPER

View Article Online
View Journal

Advancing the analysis of impurities in hydrogen by use of a novel tracer enrichment method

Cite this: DOI: 10.1039/c3ay42174k

Arul Murugan* and Andrew S. Brown

A novel tracer enrichment method for concentrating the impurities in hydrogen has been developed and validated. The method calculates the enrichment factor by spiking the gas mixture with krypton and measuring the change in amount fraction before and after enrichment. This method was compared against an existing non-ideal gas law enrichment method which calculates the enrichment factor by measuring the change in pressure and temperature of the hydrogen gas mixture. The comparison was achieved by performing tests where both methods were successfully used to calculate the amount fractions of nitrogen, carbon monoxide and methane in a mixture of hydrogen with a known composition. An uncertainty budget for both methods was also developed showing that the new tracer enrichment method gives a lower uncertainty of measurement compared to the non-ideal gas law enrichment method. An additional benefit to using the tracer enrichment method is that accurate measurements can be performed even during an air leak or membrane failure. It was concluded that a combination of both of the two enrichment techniques would form the ideal measurement tool for performing accurate measurement of impurities while being able to detect leaks and monitor the enrichment factor.

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www.rsc.org/methods

1. Introduction

With increasing requirements to limit, control and reduce greenhouse gas emissions, hydrogen is globally recognised as a suitable energy vector for powering vehicles (and other small devices). Hydrogen can be employed to power vehicles either by using an internal combustion engine or fuel cell; both of these routes provide clean energy with no carbon emissions (if produced from a renewable source) by reacting the hydrogen with oxygen from the air. Whereas the internal combustion engine is relatively robust in terms of the proportion of impurities that can be present in the fuel, hydrogen fuel cells require very high purity grades of hydrogen in order to prevent deactivation of the catalyst, which would lead to reduced fuel cell lifetime.

Various studies[1,2] have been performed that have specifically investigated the effects of hydrogen impurities on fuel cell lifetime, and more recently the international standard ISO 14687-2:2012 has been published, which provides a list of the maximum levels of impurities that can be present in hydrogen for proton exchange membrane (PEM) fuel cell vehicles (Table 1).[3] The proposed EC Directive on the deployment of an alternative fuels infrastructure[4] sets out that "hydrogen refuelling points shall comply with the relevant EN standard, to be adopted by 2014, and, pending publication of this standard, with the technical specifications included in the ISO 14687-2:2012 standard."[5] If hydrogen is therefore to be used as an energy vector for commercial fuel cell vehicles, it is essential that reliable measurements of the purity of hydrogen are available.

Although the standard does also include particulates (at a maximum level of 1 mg kg^{-1}), for the purpose of this paper Table 1 only lists the gaseous impurities specified by the standard. As some impurities such as the reactive components (*e.g.* sulphur compounds and formaldehyde) are much more detrimental to fuel cells compared to other inert components (*e.g.* helium and nitrogen), these impurities are specified with a challengingly low maximum allowable levels.

Table 1 Maximum impurity levels that should not be exceeded for PEM fuel cell hydrogen as specified by ISO 14687-2:2012

Impurity	Maximum amount fraction (μmol mol^{-1})
Water	5
Total hydrocarbons	2
Oxygen	5
Helium	300
Nitrogen	100
Argon	100
Carbon dioxide	2
Carbon monoxide	0.2
Total sulphur compounds	0.004
Formaldehyde	0.01
Formic acid	0.2
Ammonia	0.1
Total halogenated compounds	0.05

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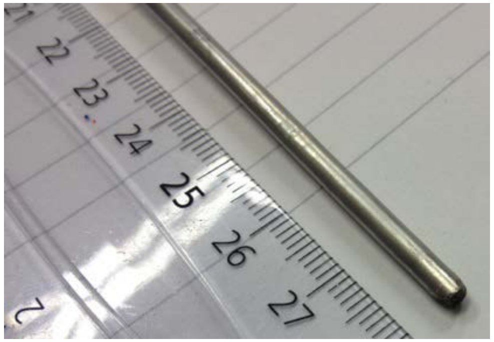
Advancing the analysis of impurities in hydrogen by use of a novel tracer enrichment method

A. Murugan & A. S. Brown (2014)

HOT ARTICLE

Next steps…



Currently using Pd-Ag coated with Pd-Cu

4 year Industrial Case PhD between NPL and Imperial College London to:

- Develop improved membranes
- Other types rather than palladium (possibly graphene)
- Investigate optimal enrichment conditions (to prevent reactions)

Marc Plunkett
(PhD student)

Prof. Kang Li
(Academic)

Dr. Arul Murugan
(Industrial)

Thank You!

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National Physical Laboratory

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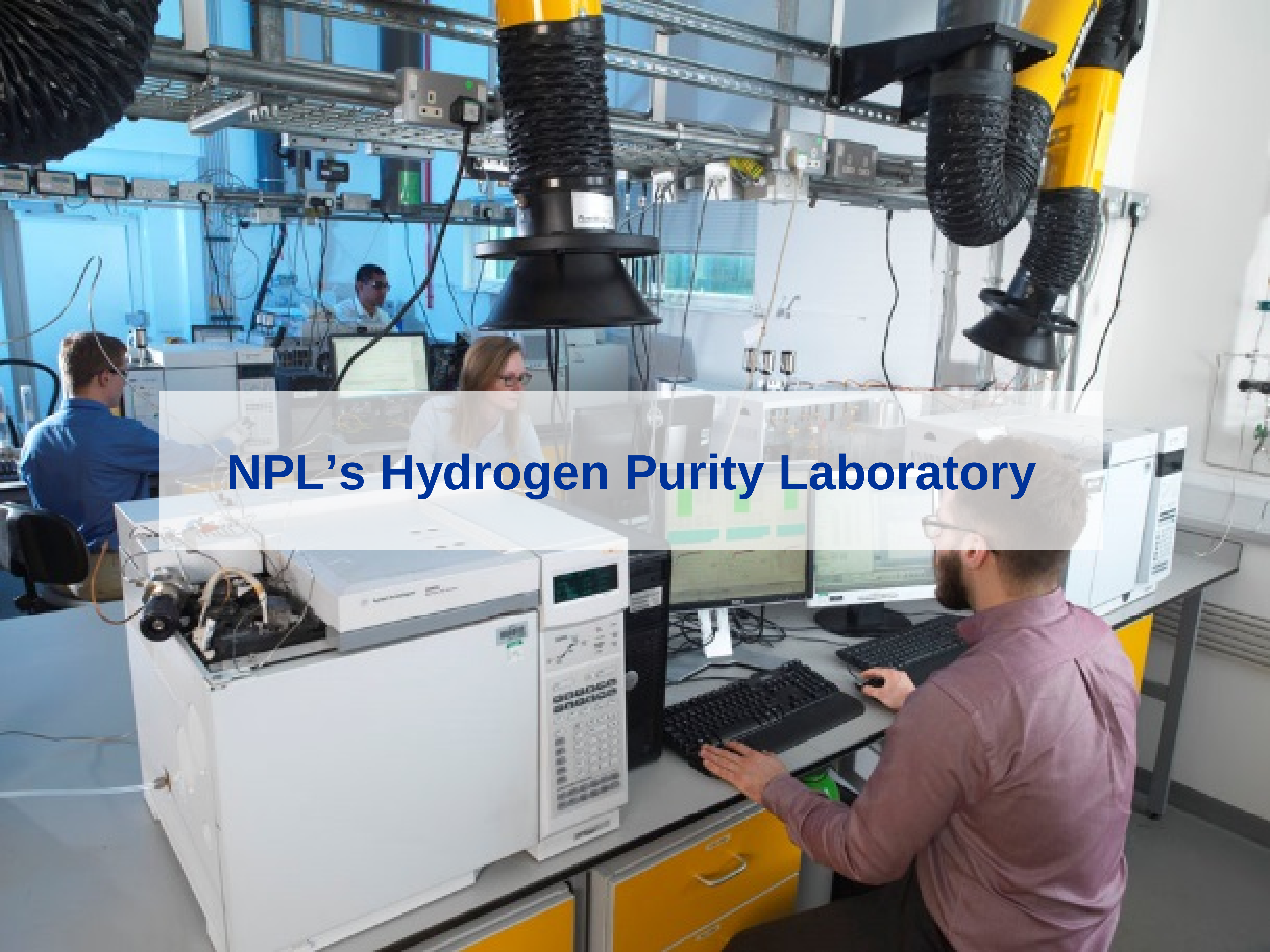
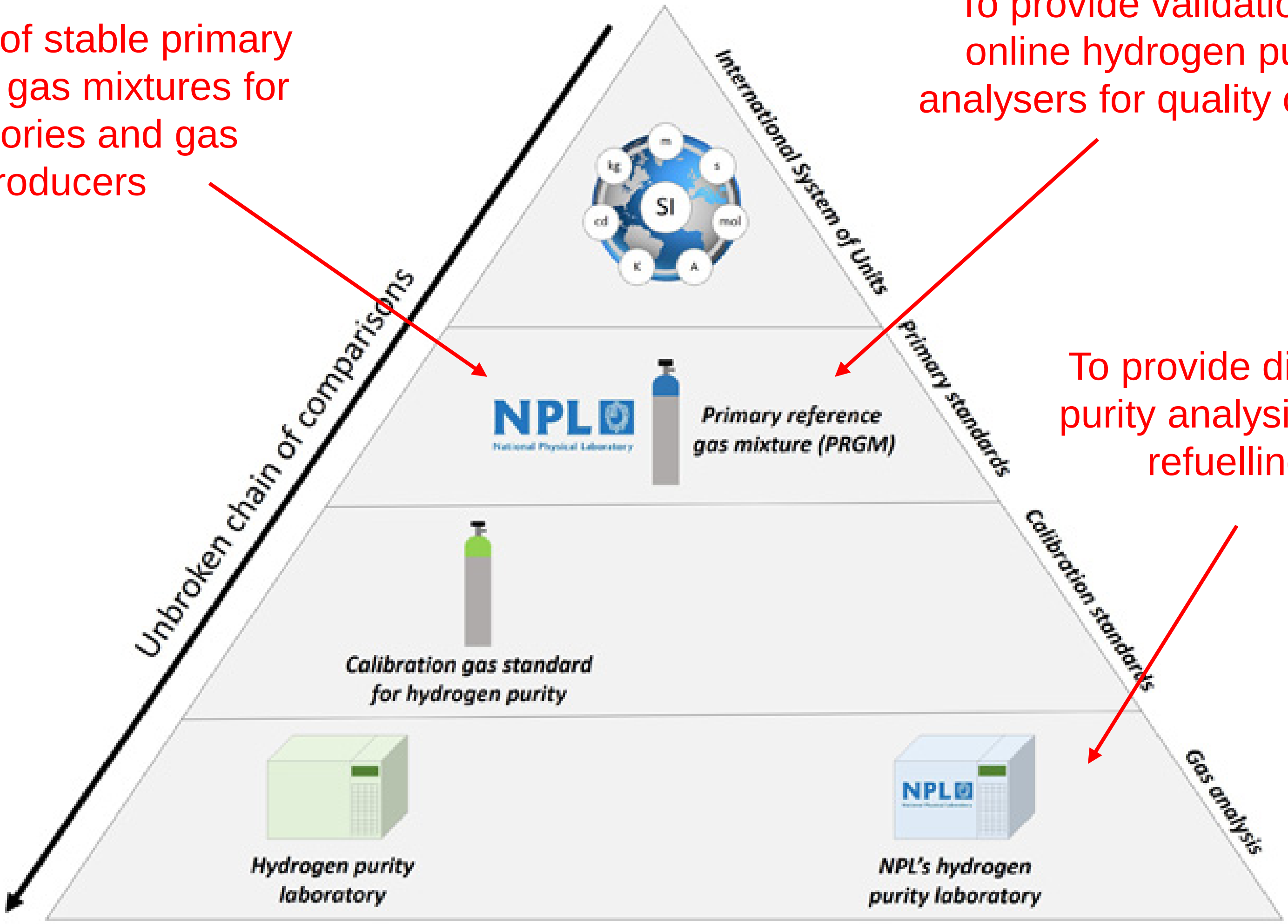
NPL’s Hydrogen Purity Laboratory



Aims of the laboratory

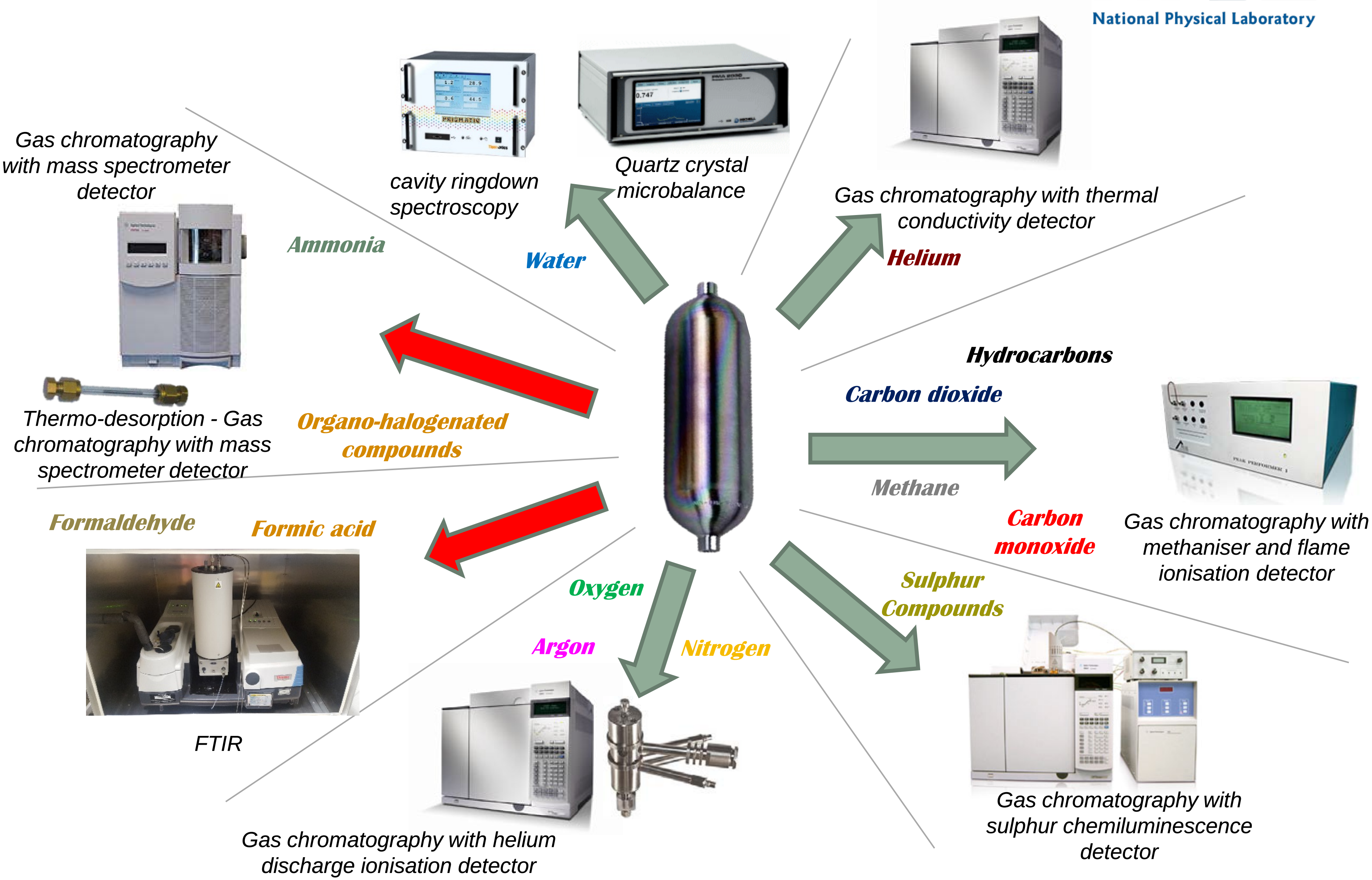
Provision of stable primary reference gas mixtures for laboratories and gas producers

To provide validation of online hydrogen purity analysers for quality control



To provide direct hydrogen purity analysis for hydrogen refuelling stations

NPL's capabilities



Gas chromatography with mass spectrometer detector

Ammonia

cavity ringdown spectroscopy

Quartz crystal microbalance

Water

Gas chromatography with thermal conductivity detector

Helium

Hydrocarbons

Carbon dioxide

Methane

Carbon monoxide

Gas chromatography with methaniser and flame ionisation detector

Sulphur Compounds

Gas chromatography with sulphur chemiluminescence detector

Oxygen

Argon

Nitrogen

Gas chromatography with helium discharge ionisation detector

Formaldehyde

Formic acid

FTIR

Organo-halogenated compounds

Thermo-desorption - Gas chromatography with mass spectrometer detector

Missing capabilities

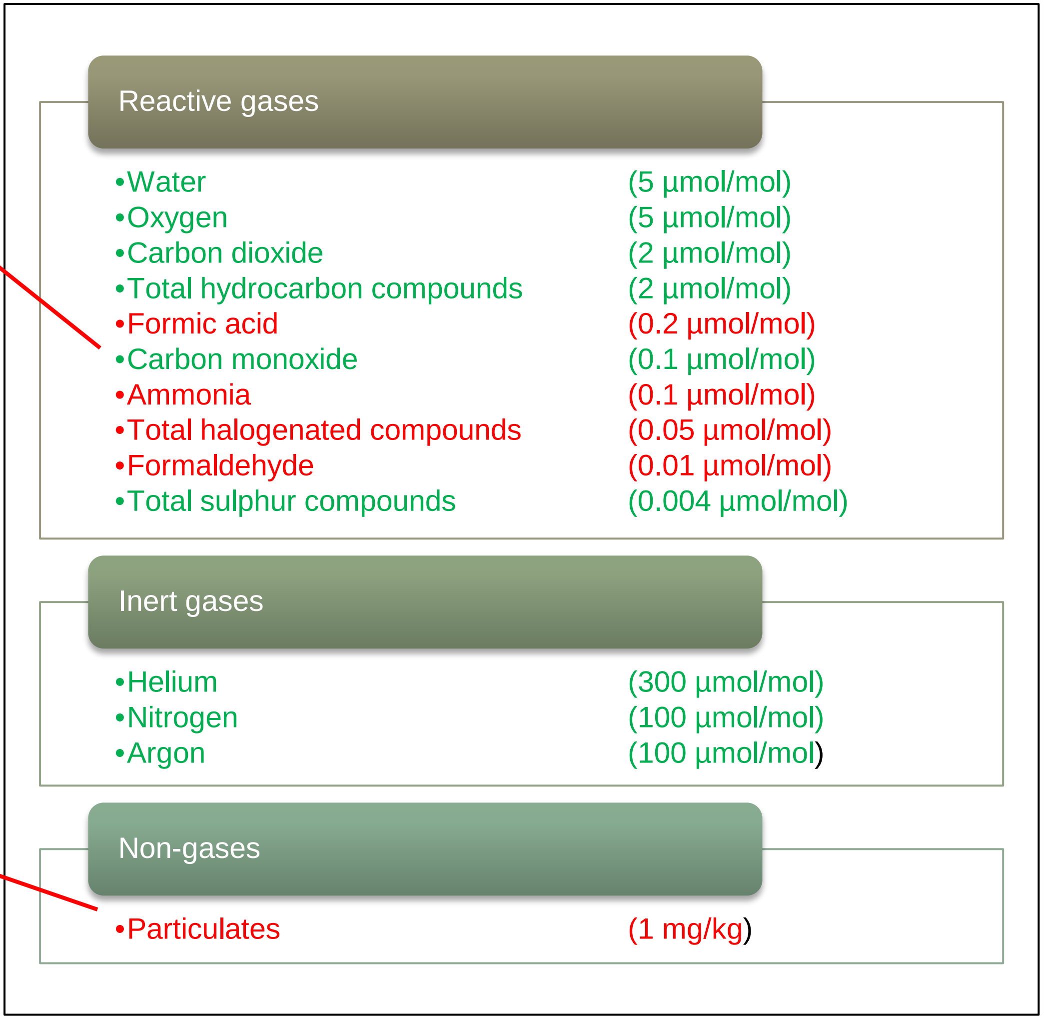
Our limits of detection are not low enough to reach these specifications

1) Use alternative spectroscopic methods (even though more sample is needed per analysis…)

2) Develop a method for concentrating impurities in hydrogen…

Particulates in hydrogen methods have not been developed yet

We will develop this method next year



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•Formaldehyde	(0.01 µmol/mol)
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Non-gases

•Particulates	(1 mg/kg)