Instituto Português da Qualidade

IPQ Gas Standard Activities in Support of the Environment and Clean Air

Florbela Dias

Reference Gas Laboratory

LNM – IPQ

www.ipq.pt

Reference Gas Laboratory Main Objectives

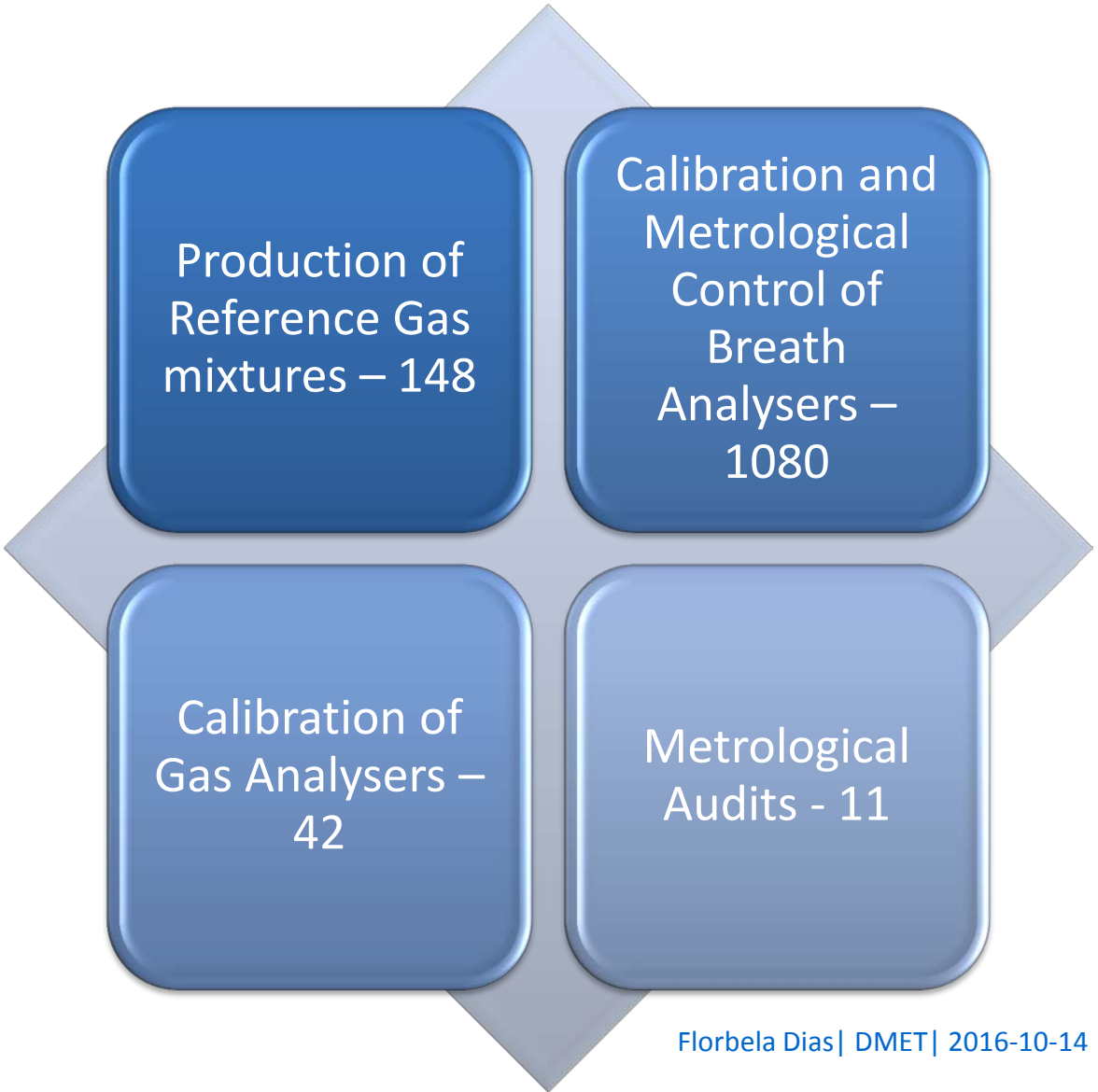
Production, maintenance and development of National Primary Gas Standards;

To supply reference standards to the State agencies, industry, companies, laboratories and research centres;

To support the entities responsible for fulfilment and monitoring of EU Directives, namely through the supply of reference gas standards;

To assure national and international recognition of the calibration and measurement capabilities (CMC).

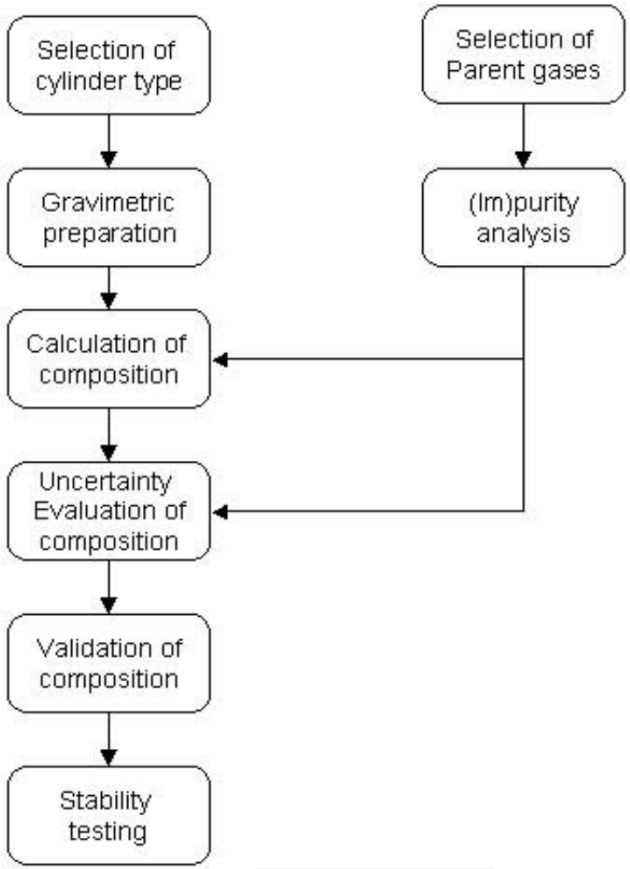
Reference Gas Laboratory in Numbers (2015)



Gravimetric Preparation of Reference Gas Mixtures

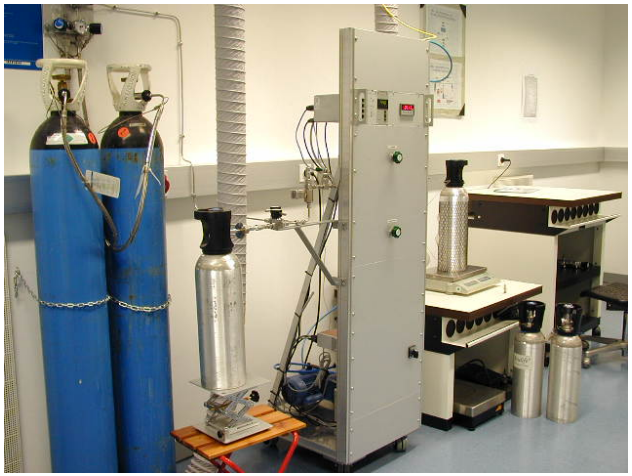
The preparation of gas standards is carried out in accordance with an harmonised procedure, based on the international standard ISO 6142.

These primary mixtures are prepared at highest level of accuracy by gravimetric blending methods.



Outline of the preparation process

Gravimetric Preparation of Reference Gas Mixtures



In a previously evacuated and passivated cylinder, each component is added through a filling station, where all equipment (pipes, valves etc.) are electro polished and free of oil.

The mass of each component is determined using a mass comparator balance.

The mixture is prepared by gravimetric addition of each component.

Gravimetric Preparation of Reference Gas Mixtures

The mole fractions of the components in the final mixtures are calculated using the following equation

$$x_i = \frac{\sum_{A=1}^{P} \left(\frac{x_{i,A} . m_A}{\sum_{i=1}^{n} x_{i,A} . M_i} \right)}{\sum_{A=1}^{P} \left(\frac{m_A}{\sum_{i=1}^{n} x_{i,A} . M_i} \right)}$$

Where

x_i is the mole fraction of the component *i* in the final mixture, *i*= 1,….,*n;*

P is the total number of the parent gases;

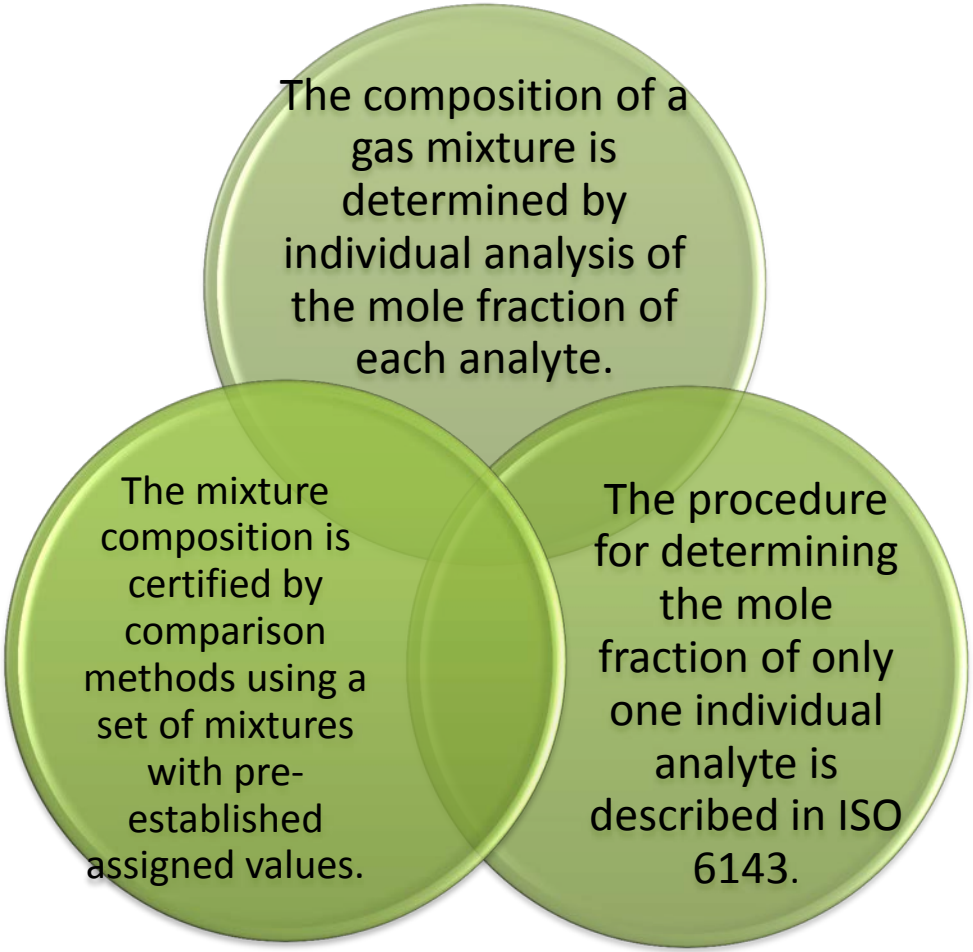
n is the total number of the components in the final mixture;

m_A is the mass of parent gas A determined by weighing, *A*= 1,……, *P;*

M_i is the molar mass of the component *i;*

$x_{i,A}$ is the mole fraction of the component *i*.

Certification of Reference Gas Mixtures



Certification of Reference Gas Mixtures

The traceability of these measurements is guaranteed by links to national and international primary gas standards.

In order to establish the relationship between equipment response and the composition of the series of calibration mixtures, the following aspects must be considered:

- Analytical method
- Calibration range
- Measuring conditions
- Number and sequence of replicate measurements

Results are expressed together with their measurement uncertainty, according to GUM.

The composition of gas mixtures is certified by analytical methods such as Gas Chromatography (GC), Non Dispersive Infrared Spectroscopy (NDIR), Non Dispersive Ultra Violet Spectroscopy (NDUV) and Paramagnetic .

Certified Reference Materials (CRM)

Reference Material (RM) material, sufficiently homogeneous and stable with reference to specified properties, which has been established to be fit for its intended use in measurement or in examination of nominal properties.

Certified Reference Material is a RM, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures.

Certified Reference Materials (CRM)

Certified Reference Materials (CRM) of gas mixtures are prepared according to ISO Guide 34:2009 and are used for the purpose of equipment calibration and verification.

Certified Reference Materials (CRM)

Certified Gas Mixtures

Environmental and pollutants gases; Exhaust gases; Gaseous fuels; Forensic

CO, CO_2, CH_4, C_3H_8,O_2, NO, NO_2, SO_2, H_2S, C_2H_5OH in nitrogen and Natural Gas

Target institutions:
Metrology laboratories; Metrological verification bodies; Accredited laboratories; Security forces; Gas manufacturers; Representatives of equipment.

Installed Metrological Capability

Component	Range
CO in N_2	(0 to 5) $\times 10^{-2}$ mol/mol
CO_2 in N_2	(0 to 20) $\times 10^{-2}$ mol/mol
C_3H_8 in N_2	(0 to 2,5) $\times 10^{-2}$ mol/mol
C_2H_5OH in N_2	(50 to 1000) $\times 10^{-6}$ mol/mol
$CO + CO_2 + C_3H_8 + O_2$	Typical range
Natural Gas	Typical range
O_2 in N_2	(1 to 30) $\times 10^{-2}$ mol/mol
NO in N_2	(25 to 1000) $\times 10^{-6}$ mol/mol
NO_2 in N_2	(50 to 1000) $\times 10^{-6}$ mol/mol
SO_2 in N_2	(25 to 1000) $\times 10^{-6}$ mol/mol
H_2S in N_2	(25 to 200) $\times 10^{-6}$ mol/mol
CH_4 in N_2	(2,5 to 4,5) $\times 10^{-2}$ mol/mol

Traceability Chain

mass prototype nº 69

Amount of Substance,mol (SI)
$n = m/M$

Avogadro constant, N_A (2002 CODATA)

Molar mass (IUPAC)

mass, kg nº 69

mass, kg (SI)

Gravimetric Method (ISO 6142)
Determinig and checking the composition(ISO 6143)

PSM (Primary Standard gas Mixture)

PRM (Primary Reference Mixture)

CCQM key comparison

CRM (Certified Reference Material)

OIML R 126
Portaria nº 1556/2007

Screening Device Calibration

Evidential Breath Analysers Metrological Control

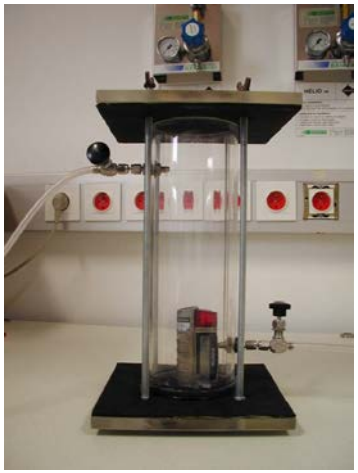
Certified Gas Standards

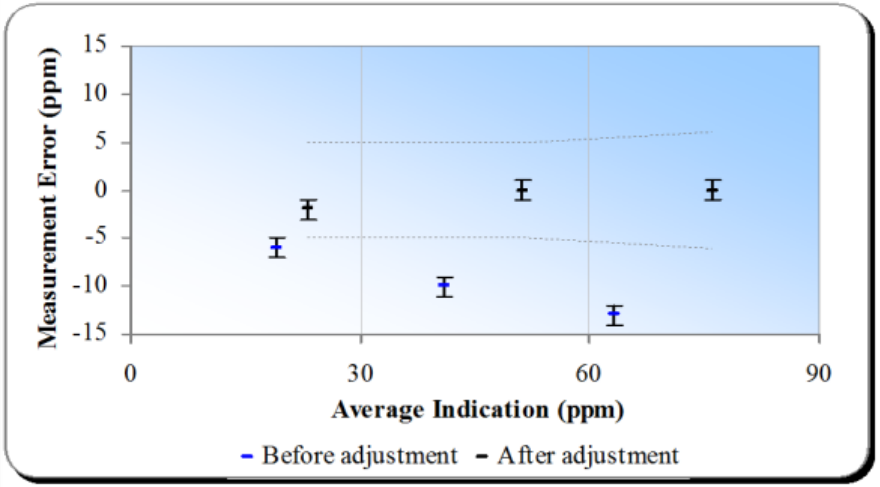
Calibration of Carbon Monoxide Gas Analysers

Carbon monoxide analyzers are used in network gas inspections.

Generally these analyzers do not allow a direct admission of the gas so the calibration is performed in a camera.

The calibration begins by the choice of the standards. Since the limit is 50 ppm, the calibration is done with three certified reference material concentrations with a lower concentration, a 50 ppm one and a higher concentration.





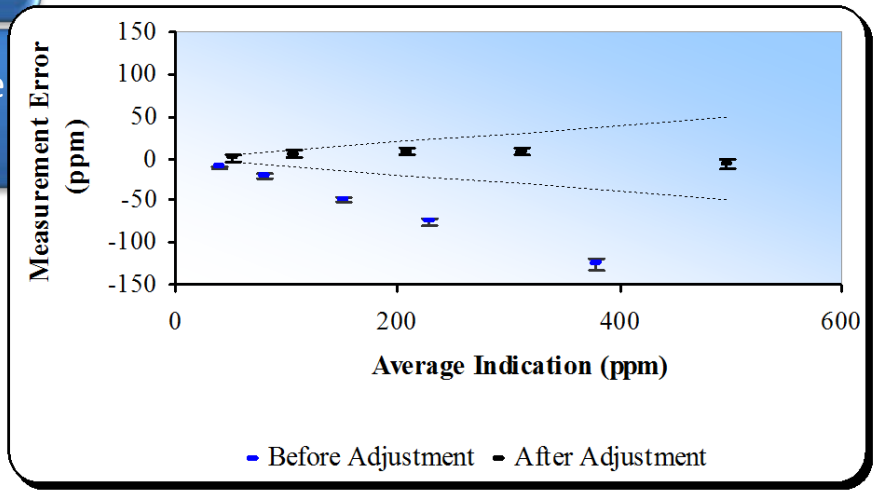
Calibration of Ambient and Pollutant Gas Analysers

Pollutant gas analysers are used by entities that make the gas emissions monitoring in industry.

For this type of analysis the calibration is done with five certified reference mixtures to cover the work range.

Acceptance criterion: error less than or equal to 10 %.

If the criterion is not met an adjustment is made to the sensor.



Calibration of Breath Alcohol Detector

The calibration is done using the comparison method and measurements are performed in the range 0 g/l to 3 g/l of BAC, with one to five concentrations, depending on the instrument application and the customer choice.

Certified reference binary gas mixtures (ethanol in nitrogen) are used. These mixtures are traceable to IPQ primary standards.

The results must meet the errors specified by the manufacturer. If the criterion is not achieved, an adjustment is made to the breath analyser.

Metrological Verification of Breath Alcohol Detector

The metrological control of breath analysers falls within the legal metrology, since these instruments are used by entities with legal competence as GNR and PSP. The legal metrology is to defend the interests of citizens.

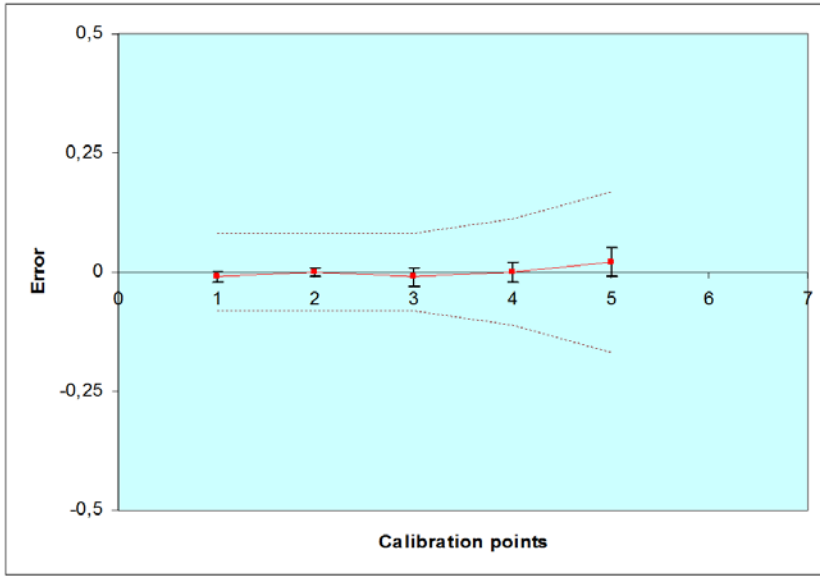
The evidential breath analysers in particular, must meet the requirements within the Decree law 1556/2007 of 10th December and the characteristics and technical specifications defined by recommendation OIML R126.

The metrological control involves several operations, including type approval, initial verification, periodic and extraordinary verification.

Metrological Verification of Breath Alcohol Detector

The gases are reference mixtures of ethanol in nitrogen, certified and traceable to IPQ primary standards.

The metrological control is done with five mixtures with different concentrations of ethanol in nitrogen covering the verification range of the equipment, 0 g/l to 2 g/l BAC.



Graphical representation of the breath analyser verification results in g/l BAC. The red line represents the errors for each equipment indication. The error is the difference between the average indication of equipment and the reference value. The dotted line represents permissible maximum errors.

International Recognition

IPQ is in the **CIPM Mutual Recognition Arrangement** (CIPM MRA) which is the framework through which National Metrology Institutes demonstrate the international equivalence of their measurement standards and the calibration and measurement certificates they issue. The outcomes of the Arrangement are the internationally recognized (peer-reviewed and approved) Calibration and Measurements Capabilities of the participating institutes. Approved CMCs and supporting technical data are publicly available from the CIPM MRA database (KCDB).

The Technical Committee for Quality (TC-Q) is EURAMET's operational instrument to share and develop knowledge on ISO/IEC 17025 and on its implementation in the National Metrology Institutes (NMIs). This TC has become the EURAMET way of doing Quality System review by peers. IPQ is participating in this committee as expert and also as peer reviewed.

Peer review in 2011 in frame of EURAMET Project 1123.

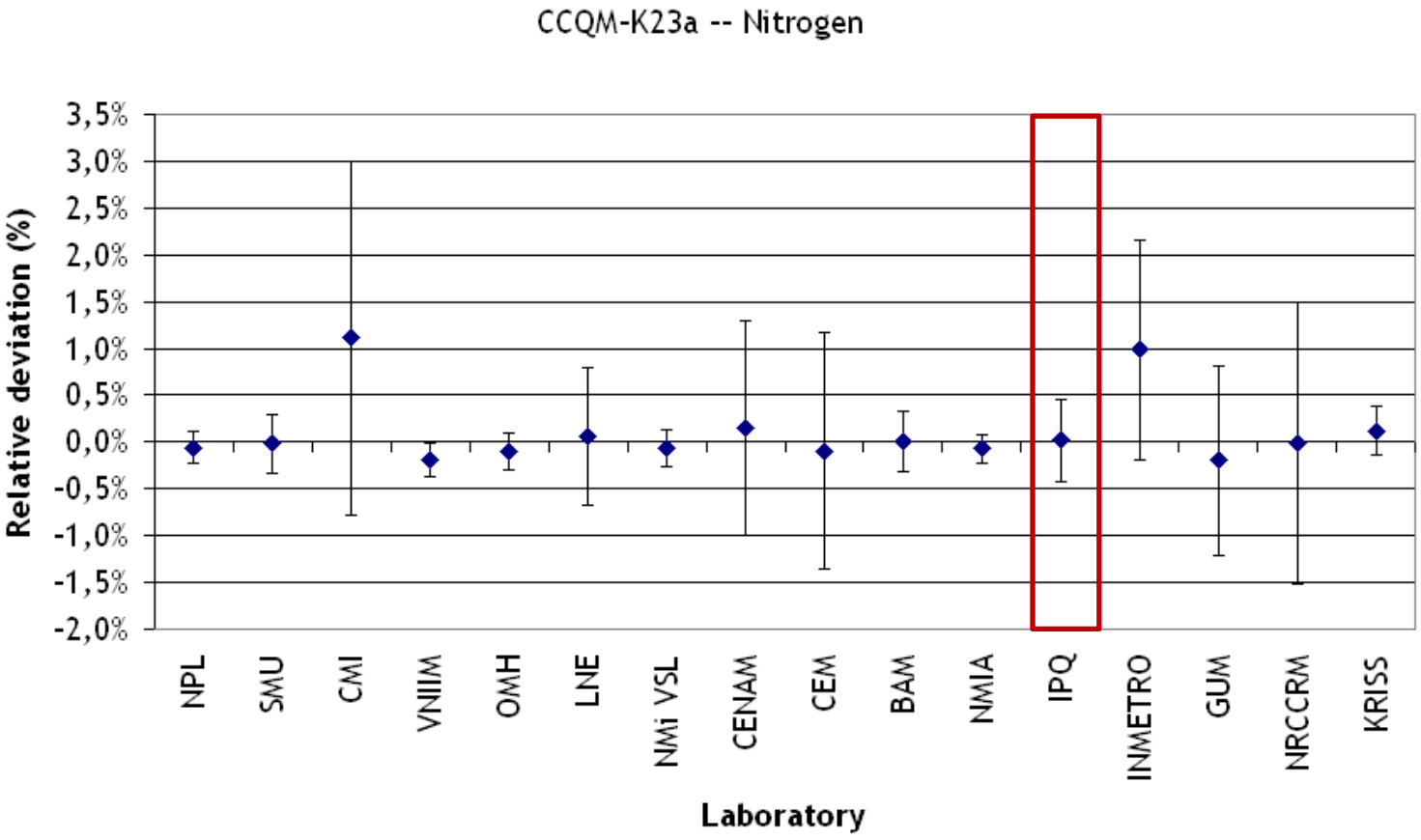
International Comparison

A key element in our activities is to provide measurement traceability, by means of links to the national standards of mass, pressure, temperature and primary gas mixtures.

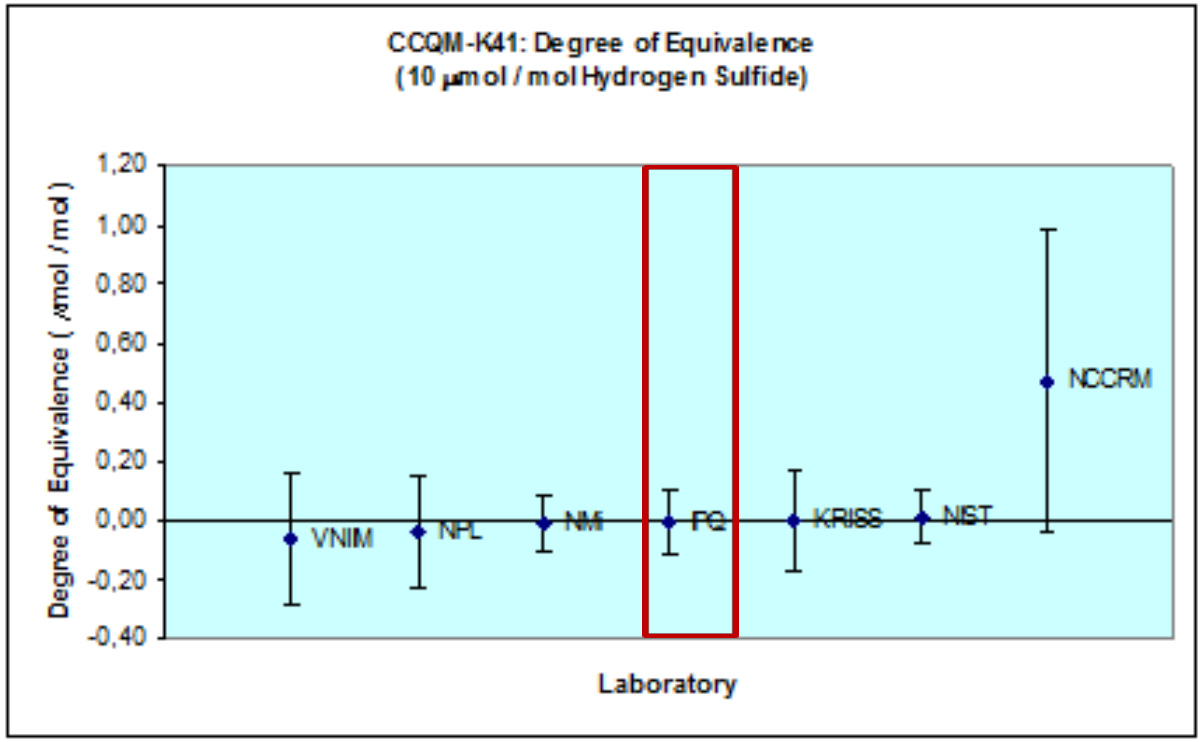
Under this assumption, traceability to international standards is guaranteed through the use of well defined and internationally agreed methods for the preparation and certification of gas mixtures.

The participation in international comparisons provides the demonstration of accurate measurements and evidence of the quality of our work.

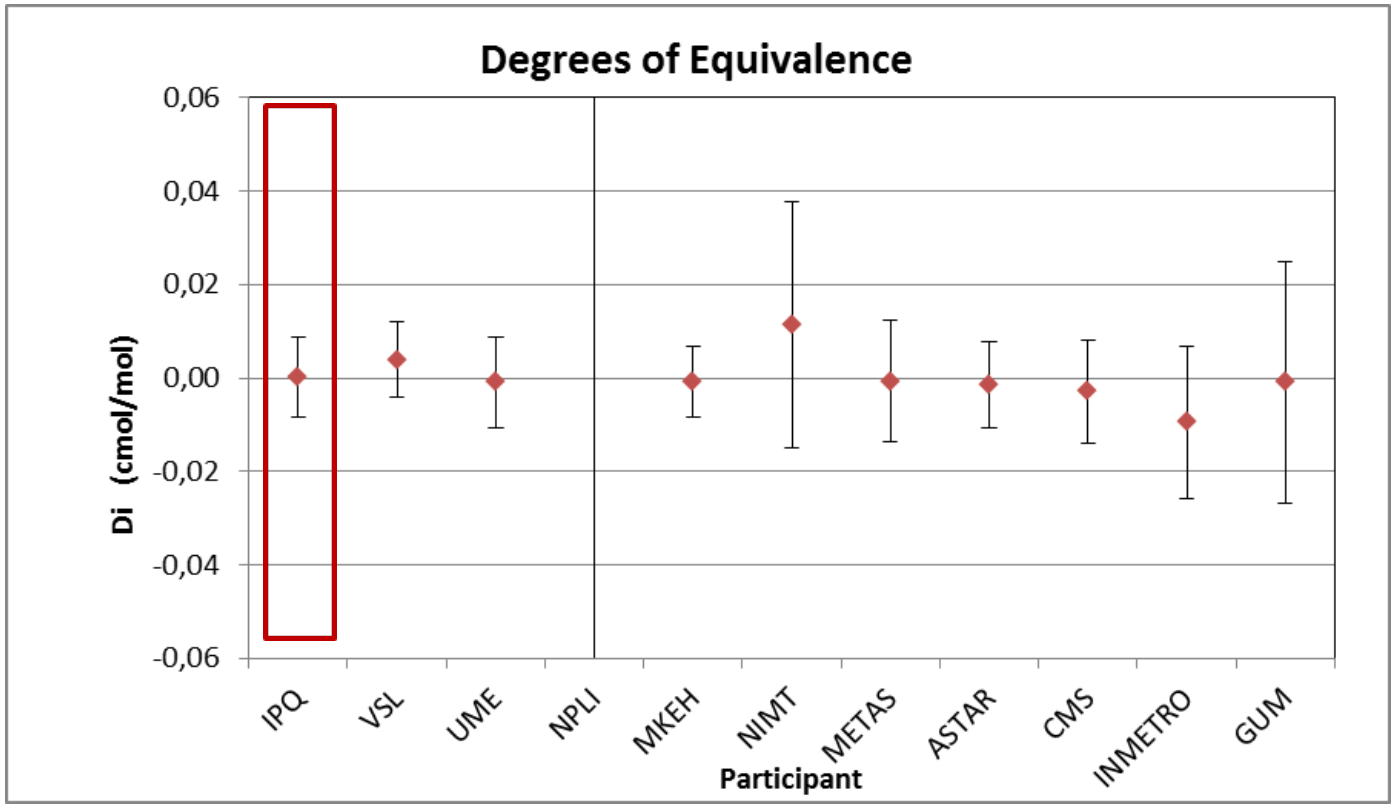
CCQM K23a (Gás Natural)



CCQM K41 (Hydrogen Sulfide)



EURO.QM-S5 / 1166: Carbon Dioxide Mixtures in Nitrogen ($3{,}0 \times 10^{-2}$ mol/mol)



Degree of equivalence (*D*) and associated expanded uncertainties (*U (D)*)
EURO.QM-S5 / 1166: Carbon Dioxide Mixtures in Nitrogen.

Calibration and Measurement Capabilities (CMC)

Calibration and Measurement Capabilities

Amount of substance, Gases, Portugal, IPQ (Instituto Portugues da Qualidade)

KCDB

The expanded uncertainty range is expressed as the uncertainty of the smallest value of the quantity to the uncertainty of the largest value of the quantity.
The expanded uncertainties correspond to $k = 2$ (level of confidence 95%)

NMI Service Identifier	Measurement Service Sub-Category	Matrix	Measurand		Dissemination Range of Measurement Capability			Range of Expanded Uncertainties as Disseminated				Range of Certified Values in Reference Materials			Range of Expanded Uncertainties for Certified Value				Mechanism(s) for Measurement Service Delivery	Comments
			Analyte or Component	Quantity	From	To	Unit	From	To	Unit	Is the expanded uncertainty a relative one?	From	To	Unit	From	To	Unit	Is the expanded uncertainty a relative one?		
702.01a	Environmental	nitrogen	carbon monoxide	Amount-of-substance fraction	100	4000	µmol/mol	0.6	0.5	%	Yes	100	4000	µmol/mol	0.6	0.5	%	Yes	Calibration, CRM, 702.01a	Approved on 19 July 2010
702.01b	Environmental	nitrogen	carbon monoxide	Amount-of-substance fraction	5	50	mmol/mol	0.5	0.5	%	Yes	5	50	mmol/mol	0.5	0.5	%	Yes	Calibration, CRM, 702.01b	Approved on 19 July 2010
702.01c	Environmental	nitrogen	carbon monoxide	Amount-of-substance fraction	5	100	µmol/mol	1.6	0.6	%	Yes	5	100	µmol/mol	1.6	0.6	%	Yes	Calibration, CRM, 702.01c	Approved on 19 July 2010
702.11	Environmental	nitrogen	hydrogen sulfide	Amount-of-substance fraction	5	250	µmol/mol	0.9	0.7	%	Yes	5	250	µmol/mol	0.9	0.7	%	Yes	Calibration, custom CRMs	Approved on 02 November 2006
702.05	Environmental	nitrogen	sulfur dioxide	Amount-of-substance fraction	20	500	µmol/mol	1.6	0.5	%	Yes	20	500	µmol/mol	1.6	0.5	%	Yes	Calibration, CRM, 702.05	Approved on 27 March 2013
702.08a	Environmental	nitrogen	propane	Amount-of-substance fraction	50	1000	µmol/mol	1.0	0.6	%	Yes	50	1000	µmol/mol	1.0	0.6	%	Yes	Calibration, CRM, 702.08a	Approved on 27 March 2013
702.08b	Environmental	nitrogen	propane	Amount-of-substance fraction	1	4	mmol/mol	0.6	0.5	%	Yes	1	4	mmol/mol	0.6	0.5	%	Yes	Calibration, CRM, 702.08b	Approved on 27 March 2013
702.03	Environmental	nitrogen	carbon monoxide	Amount-of-substance fraction	5	50	mmol/mol	0.6	0.6	%	Yes	5	50	mmol/mol	0.6	0.6	%	Yes	Calibration, CRM, 702.03	Approved on 8 July 2015
			carbon dioxide	Amount-of-substance fraction	60	140	mmol/mol	0.2	0.2	%	yes	60	140	mmol/mol	0.2	0.2	%	Yes		Approved on 8 July 2015
			propane	Amount-of-substance fraction	0.1	2	mmol/mol	0.8	0.5	%	Yes	0.1	2	mmol/mol	0.8	0.5	%	Yes		Approved on 8 July 2015
702.06	Environmental	nitrogen	nitrogen monoxide	Amount-of-substance fraction	40	150	µmol/mol	1.5	0.5	%	Yes	40	150	µmol/mol	1.5	0.5	%	Yes	Calibration, CRM	Approved on 27 March 2013
702.06a	Environmental	nitrogen	nitrogen monoxide	Amount-of-substance fraction	150	1000	µmol/mol	0,5	0,4	%	Yes	150	1000	µmol/mol	0,5	0,4	%	Yes	Calibration, CRM	Approved on 27 March 2013
702.02	Environmental	nitrogen	carbon dioxide	Amount-of-substance fraction	10	200	mmol/mol	0.3	0.2	%	yes	10	200	mmol/mol	0.3	0.2	%	Yes	Calibration, CRM, 702.02	Approved on 8 July 2015

The BIPM key comparison database, August 2015

1/2

Calibration and Measurement Capabilities (CMC)

Calibration and Measurement Capabilities

Amount of substance, Gases, Portugal, IPQ (Instituto Portugues da Qualidade)

KCDB

The expanded uncertainty range is expressed as the uncertainty of the smallest value of the quantity to the uncertainty of the largest value of the quantity.
The expanded uncertainties correspond to $k = 2$ (level of confidence 95%)

NMI Service Identifier	Measurement Service Sub-Category	Matrix	Measurand		Dissemination Range of Measurement Capability			Range of Expanded Uncertainties as Disseminated				Range of Certified Values in Reference Materials			Range of Expanded Uncertainties for Certified Value				Mechanism(s) for Measurement Service Delivery	Comments
			Analyte or Component	Quantity	From	To	Unit	From	To	Unit	Is the expanded uncertainty a relative one?	From	To	Unit	From	To	Unit	Is the expanded uncertainty a relative one?		
702.04	Forensic	nitrogen	ethanol	Amount-of-substance fraction	50	500	µmol/mol	1.3	0.7	%	Yes	50	500	µmol/mol	1.3	0.7	%	Yes	Calibration, CRM, 702.04	Approved on 8 July 2015
702.07	Fuel	synthetic natural gas	methane	Amount-of-substance fraction	700	900	mmol/mol	0.4	0.3	%	Yes	700	900	mmol/mol	0.4	0.3	%	Yes	Calibration, CRM, 702.07	Approved on 8 July 2015
			ethane		7	110	mmol/mol	0.5	0.5	%	Yes	7	110	mmol/mol	0.5	0.5	%	Yes		
			propane		3	45	mmol/mol	0.7	0.4	%	Yes	3	45	mmol/mol	0.7	0.4	%	Yes		
			n-butane		1	7	mmol/mol	1.4	0.8	%	Yes	1	7	mmol/mol	1.4	0.8	%	Yes		
			i-butane		1	7	mmol/mol	1.5	0.7	%	Yes	1	7	mmol/mol	1.5	0.7	%	Yes		
			nitrogen		12	140	mmol/mol	0.5	0.4	%	Yes	12	140	mmol/mol	0.5	0.4	%	Yes		
			carbon dioxide		2	40	mmol/mol	1.8	1.2	%	Yes	2	40	mmol/mol	1.8	1.2	%	Yes		

http://kcdb.bipm.org/appendixC/default.asp

The BIPM key comparison database, August 2015 2/2

RESEARCH STRATEGY FOR METROLOGY IN EUROPE

EURAMET

iMERA – ***Implementing Metrology in the European Research Area***

EMRP - ***European Metrology Research Programme***

EMPIR - ***European Metrology Programme for Innovation and Research***

European Commission

RESEARCH & INNOVATION

RESEARCH STRATEGY FOR METROLOGY IN PORTUGAL

National Participation

EURAMET-iMERA
2 Projects

EURAMET – EMRP
10 Projects

EURAMET – EMPIR
5 Projects

IPQ

Instituto Português da Qualidade

thank you!