EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

JRP-ENG09
Metrology for Biofuels

Paola Fisicaro

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MESURES & RÉFÉRENCES
Clés de la COMPÉTITIVITÉ et d'un MONDE PLUS SÛR

Laboratoire national de métrologie et d'essais

"Metrology for Biofuels" – context of the project

EURAMET
European Association of National Metrology Institutes

EMRP
European Metrology Research Programme
Programme of EURAMET

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About the EMRP

The European Metrology Research Programme (EMRP) is a metrology-focused European programme of coordinated R&D that facilitates closer integration of national research programmes. The EMRP is jointly supported by the European Commission and the participating countries within the European Association of National Metrology Institutes (EURAMET e.V.). The EMRP will ensure collaboration between National Measurement Institutes, reducing duplication and increasing impact. The overall goal of the EMRP is to accelerate innovation and competitiveness in Europe whilst continuing to provide essential support to underpin the quality of our lives.

The EMRP is a long-term programme for high quality joint R&D amongst the metrology community in Europe.

ENG09 BIOFUELS
Metrology for biofuels

From 01/06/2010

JRP-Coordinator
Paola Fisicaro
LNE

JRP partners

LNE – Le progrès, une passion à partager
BAM – Federal Institute for Materials Research and Testing
DFM
METROSERT
NPL – National Physical Laboratory
SP
VSL – Dutch Metrology Institute
iNRiM – Istituto Nazionale di Ricerca Metrologica
irmm – Institute for Reference Materials and Measurements
LGC – Setting standards in analytical science
nel – technology for life
PTB
TÜBİTAK UME
UNIVERSITÄT ROSTOCK

"Metrology for Biofuels" - Needs for the project / 1

WHITE PAPER

ON

INTERNATIONALLY COMPATIBLE BIOFUEL STANDARDS

*To **support the global trade of biofuels**, representatives of Brazil, the EU and the U.S. agreed to promote, whenever possible, the **compatibility** of biofuels-related standards in their respective regions. The objective of the Task Forces was to collect and analyse **existing standards** on pure bioethanol and biodiesel developed by ABNT, ASTM and CEN.*
*Since it was noted that many parameters were different, […] specific **recommendations to address the differences** were made.*

TRIPARTITE TASK FORCE
BRAZIL, EUROPEAN UNION &
UNITED STATES OF AMERICA

DECEMBER 31 2007

"Metrology for Biofuels" - Needs for the project / 2

VSL

BIOREMA

REference MAterials for BIOfuel specifications

Call:

- FP7 Cooperation Work Programme: Theme 5 / Energy
- Coordination and Support Action
- Grant agreement 219081

Duration: 24 months
Start date: 27 November 2008

BIOREMA

Dutch Metrology Institute

Page 1

Contact: abaldan@vsl.nl

VSL

BIOREMA Conclusions

BIOREMA

- Further research is needed for a number of other parameters, e.g., electrolytic conductivity and pHe in bio-ethanol and glycerides in biodiesel. Moving away from operationally defined measurands for these parameters, and therefore providing reliable property values which are traceable to the SI, is challenging. The best course of action for these measurands may be to establish robust standardised test methods with low sensitivity to variations in experimental parameters.

- The results of the ILCs show that, in general, the current practice in assessment of biofuels against required specifications by field laboratories is satisfactory. At the same time, the ILC results underpin the demand for certified reference materials in support of: method validation, quality control, and most importantly for improving the precision and trueness of results of test laboratories tasked with assessing fuel quality against specifications.

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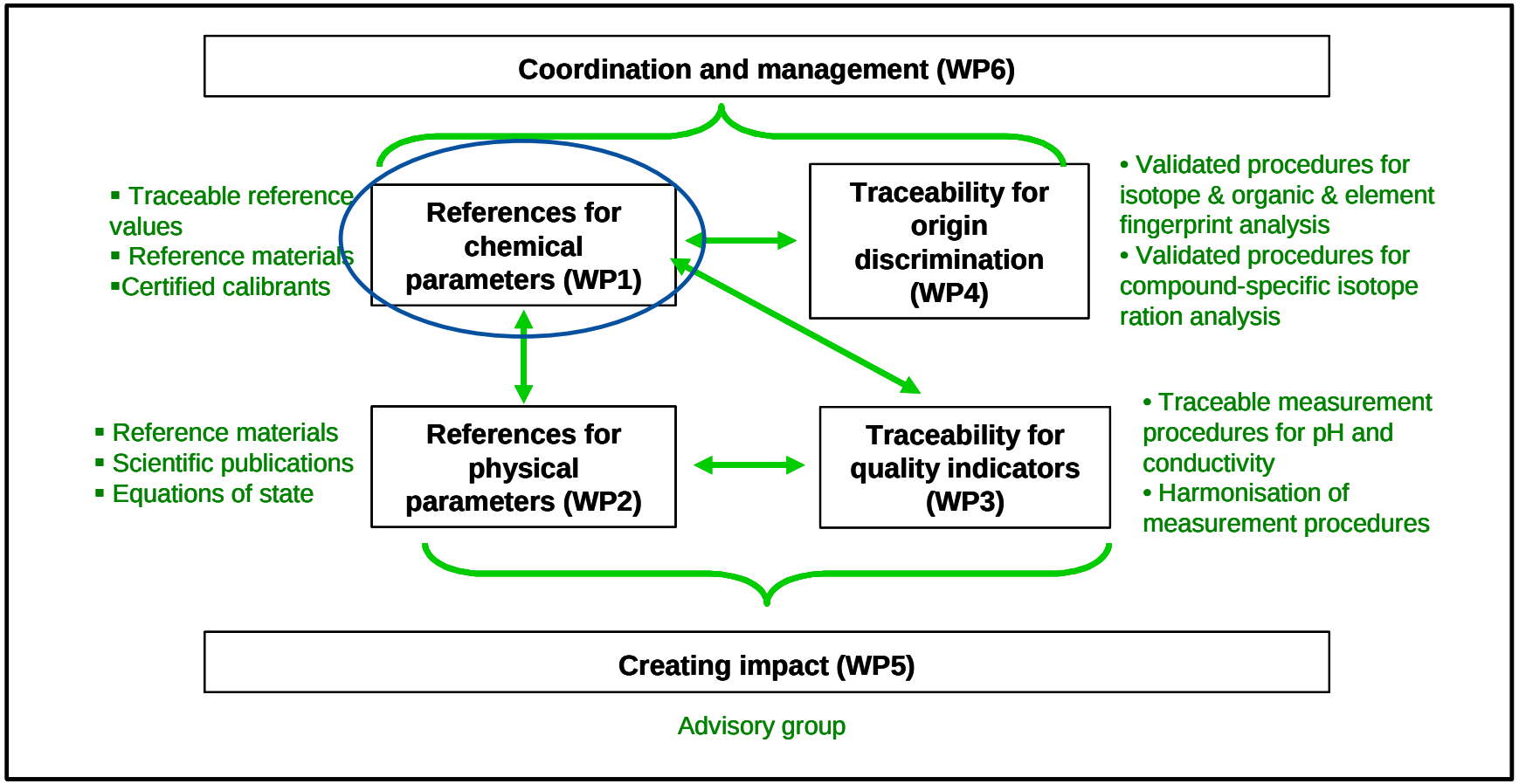
"Metrology for Biofuels" - Aims of the Project

To provide validated and reliable methods with **clear traceability** of the measurement results for physical and chemical parameters of liquid biofuels, focusing on first generation materials.

To develop **reference materials** to be used as tools for method **validation** and instrument **calibration**, covering both chemical parameters and physical transport properties.

To promote the **harmonization of measurement and written standards** across borders, essential for confidence in international quality assurance, needed to facilitate global trade.

"Metrology for Biofuels" – structure of the project



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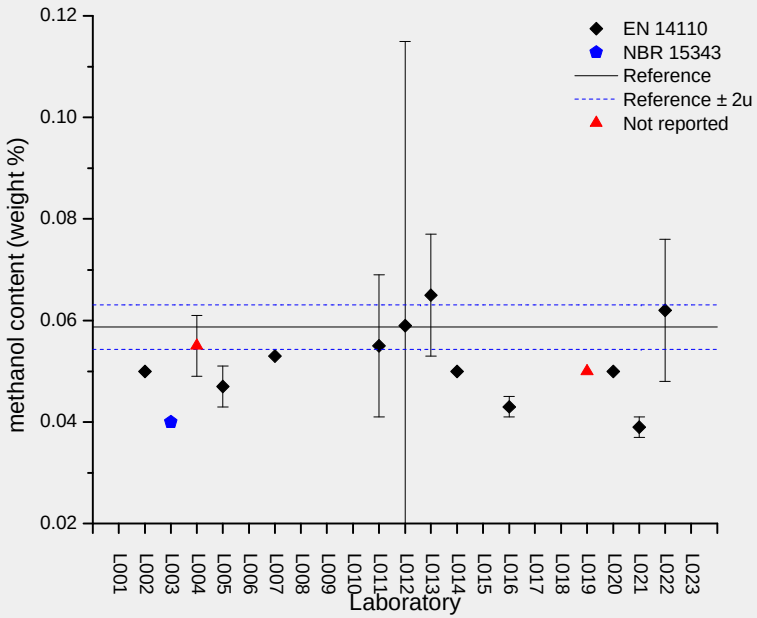
BIOREMA

Methanol content
Test material C (soybean CRM)

- p = 14 (11 used EN 14110), no dataset removed
- consensus value (CV) 0.051?10-2 g/g
- reference value (RV) 0.0587?10-2 g/g
- CV < RV

→ MeOH content in CRM << specification limit (0.2%m/m, EN 14214), but representative of real samples

→ Need to provide a reference system to cover methanol content specification limit



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EMRP Biofuels – MeOH content in FAME

- Objective:
  - Develop a reference method for Methanol content in biodiesel optimised for the specification limit of 0.20 % (m/m)
- Method:
  - Automated Head Space GC-FID (external calibration)
- Work:
  - EN14110 “Fat and oil derivatives – Fatty Acid Methyl Esters (FAME) – Determination of methanol content” as start approach
  - Validation study of the reference method

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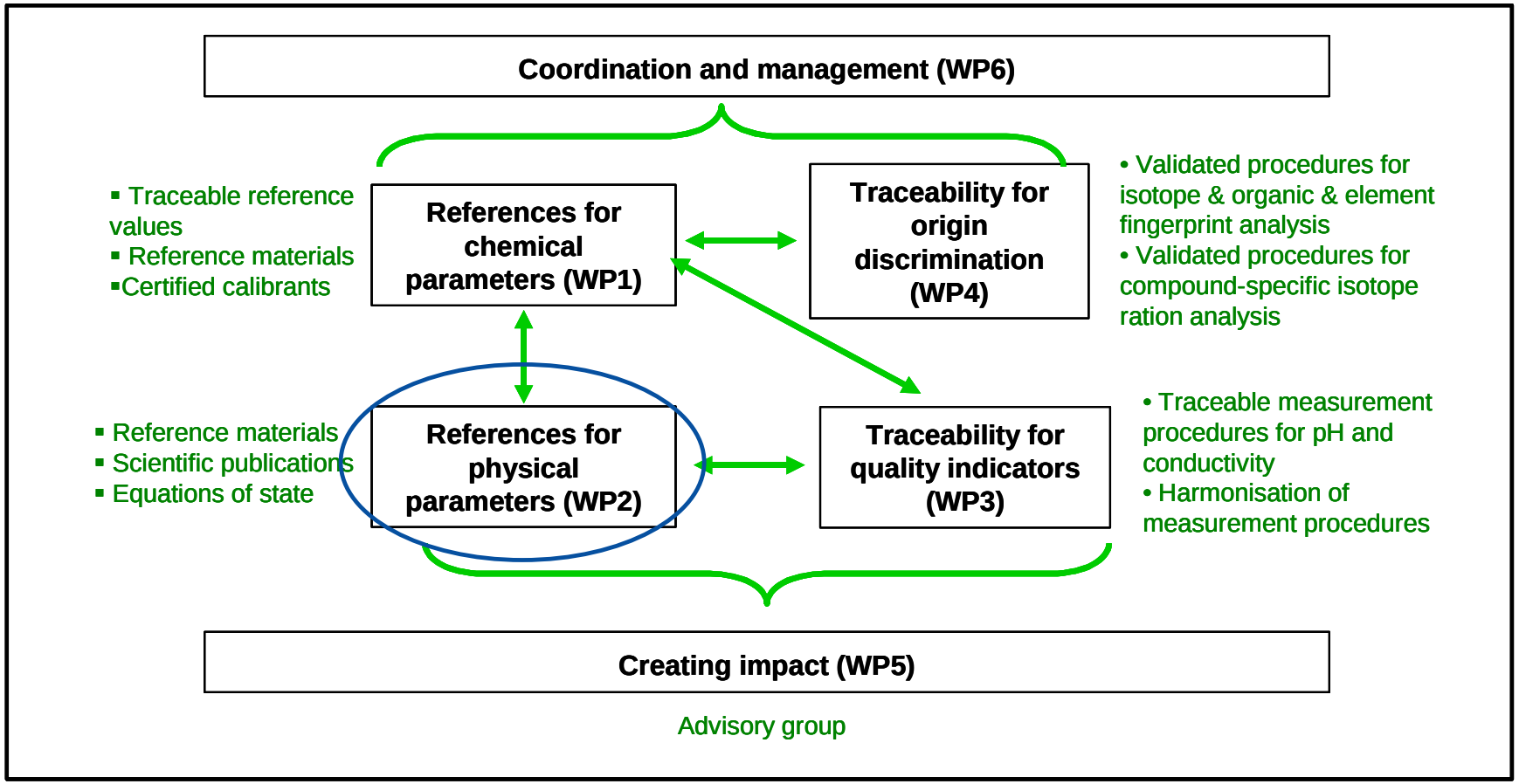
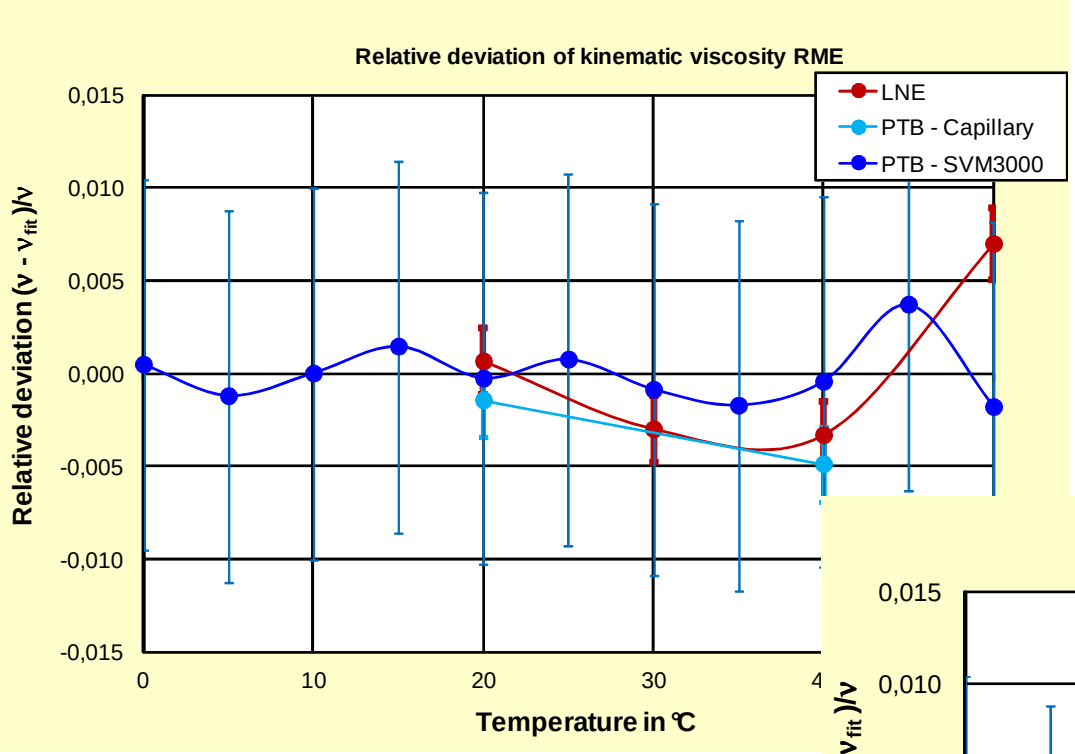
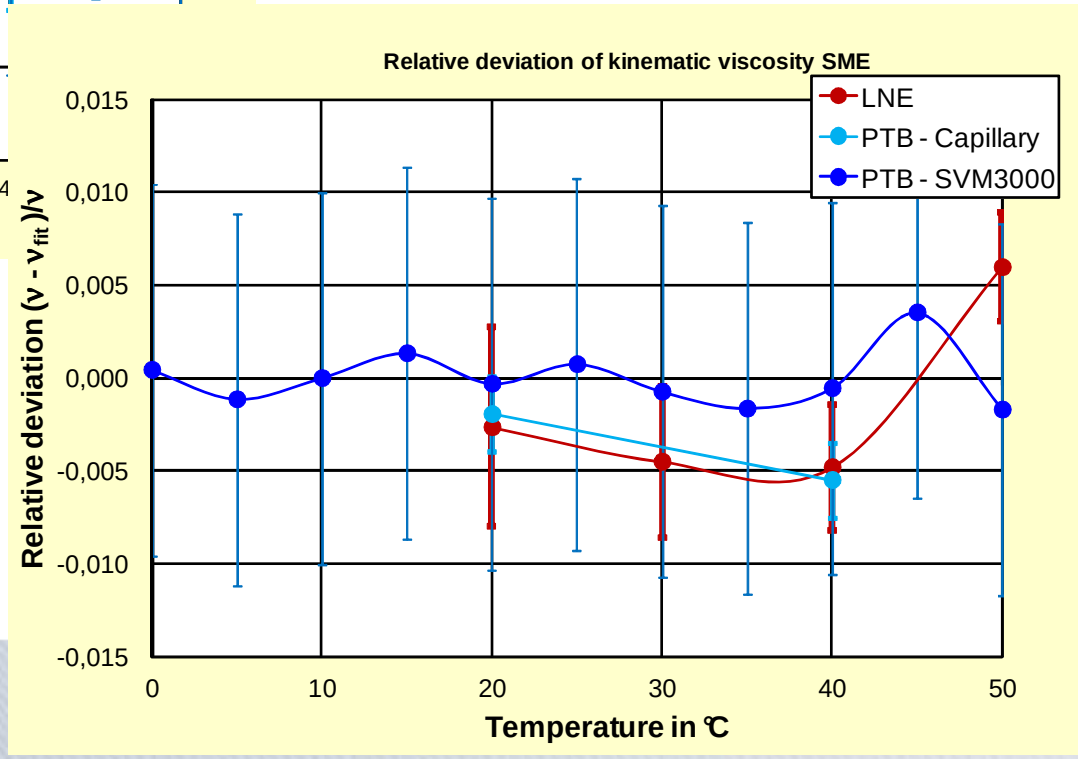
Contact: abaldan@vsl.nl


Coordination and management (WP6)
References for chemical parameters (WP1)
Traceability for origin discrimination (WP4)
References for physical parameters (WP2)
Traceability for quality indicators (WP3)
Creating impact (WP5)
Advisory group
▪ Traceable reference values
▪ Reference materials
▪Certified calibrants
• Validated procedures for isotope & organic & element fingerprint analysis
• Validated procedures for compound-specific isotope ration analysis
▪ Reference materials
▪ Scientific publications
▪ Equations of state
• Traceable measurement procedures for pH and conductivity
• Harmonisation of measurement procedures

Physical parameters – an example: viscosity measurements

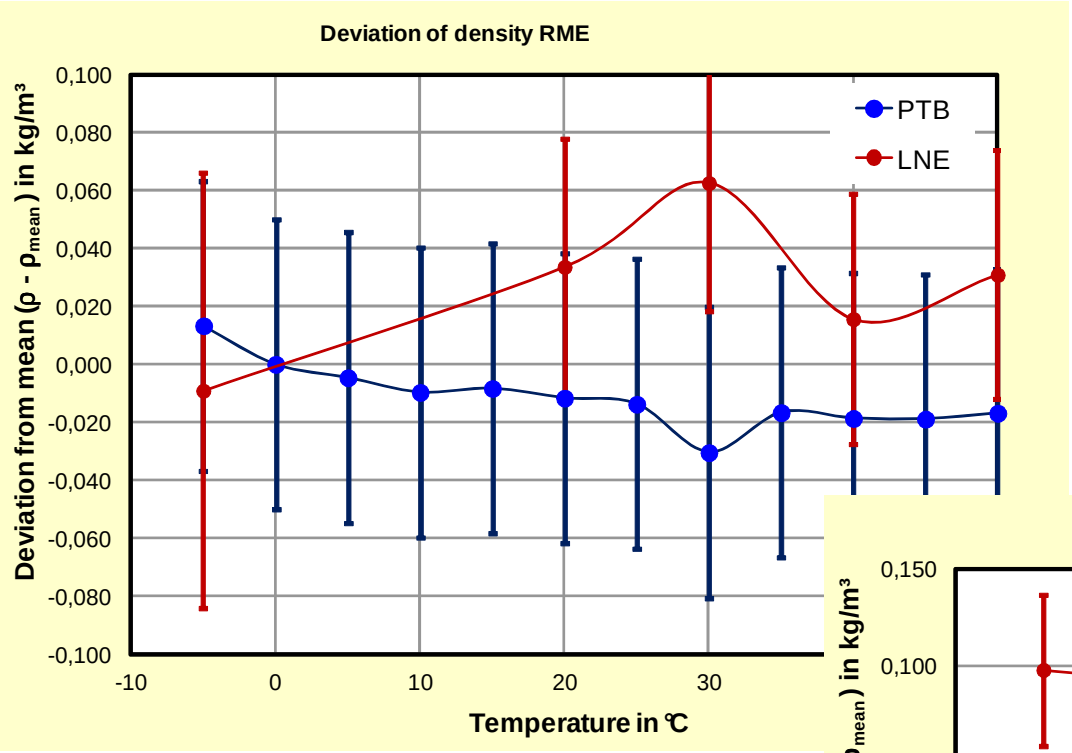


Very good matching!

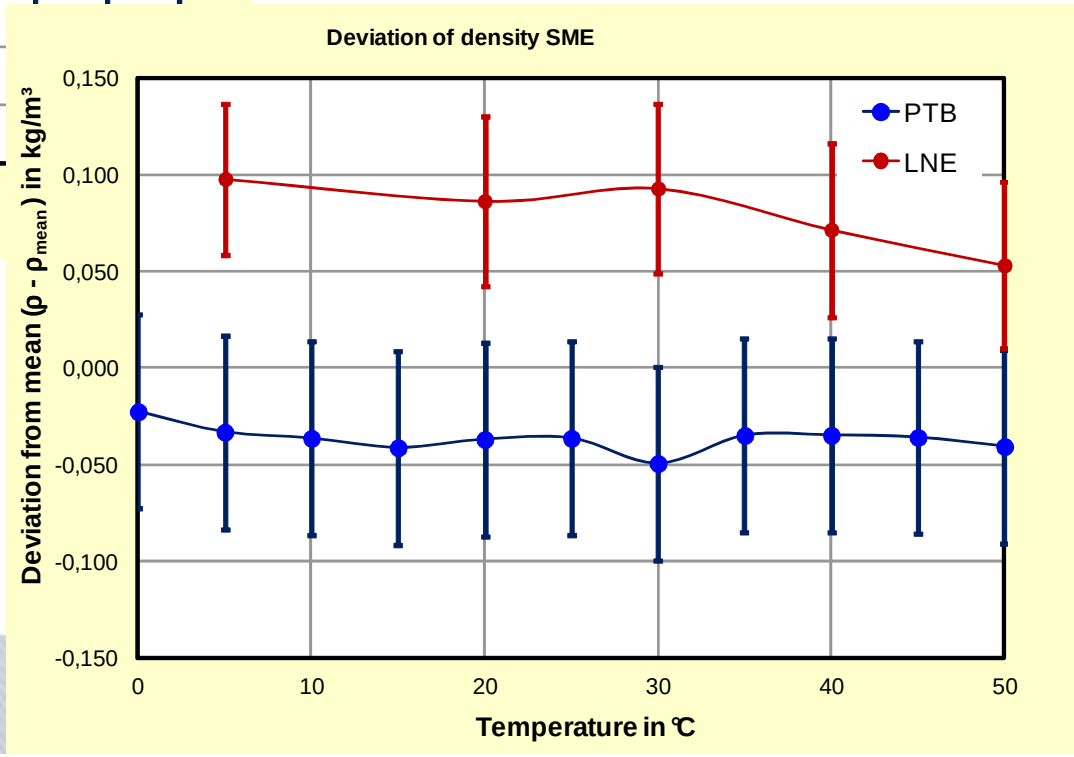


Contact: henning.wolf@ptb.de

Physical parameters – an example: density measurements



Not in any case
very good matching!



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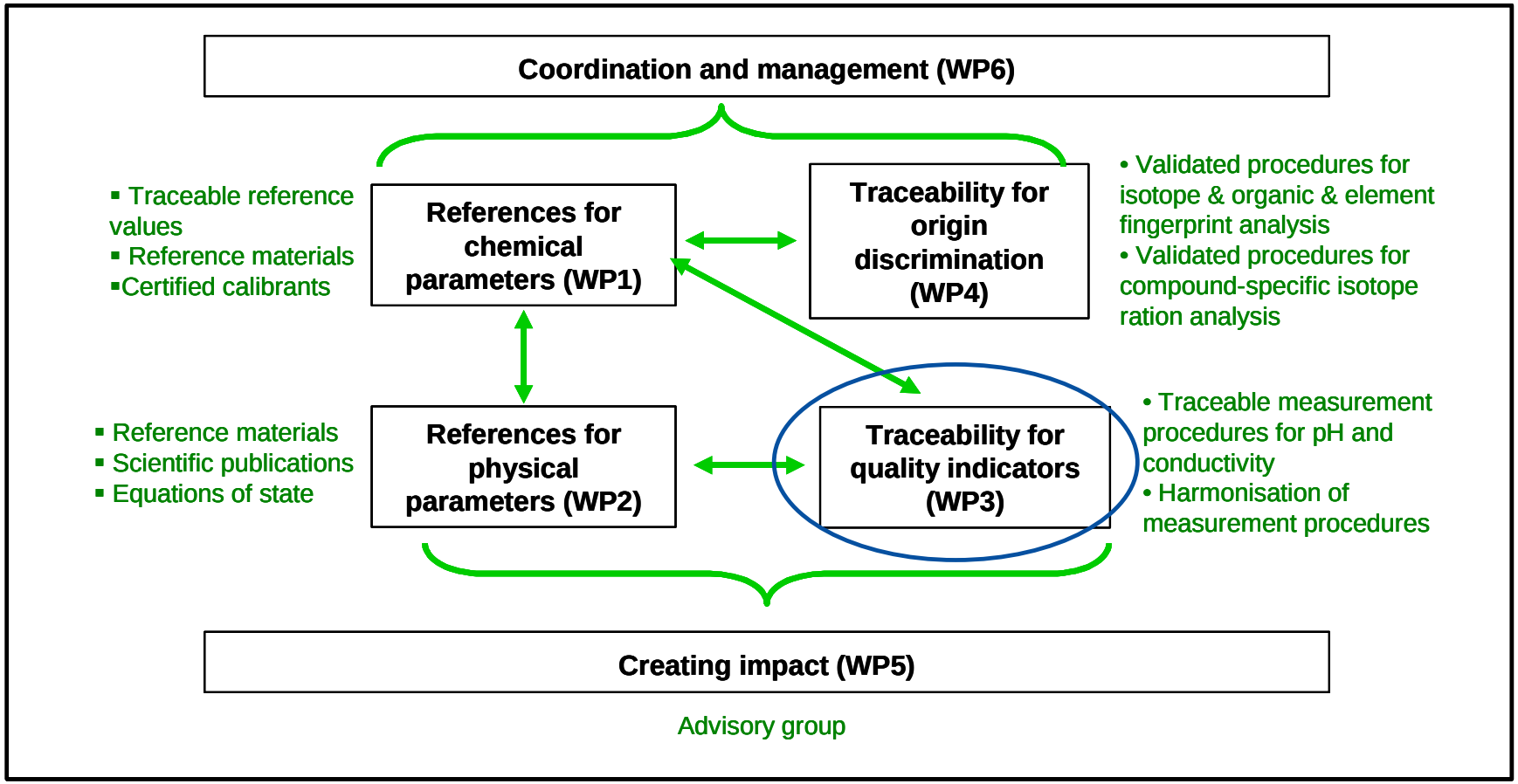
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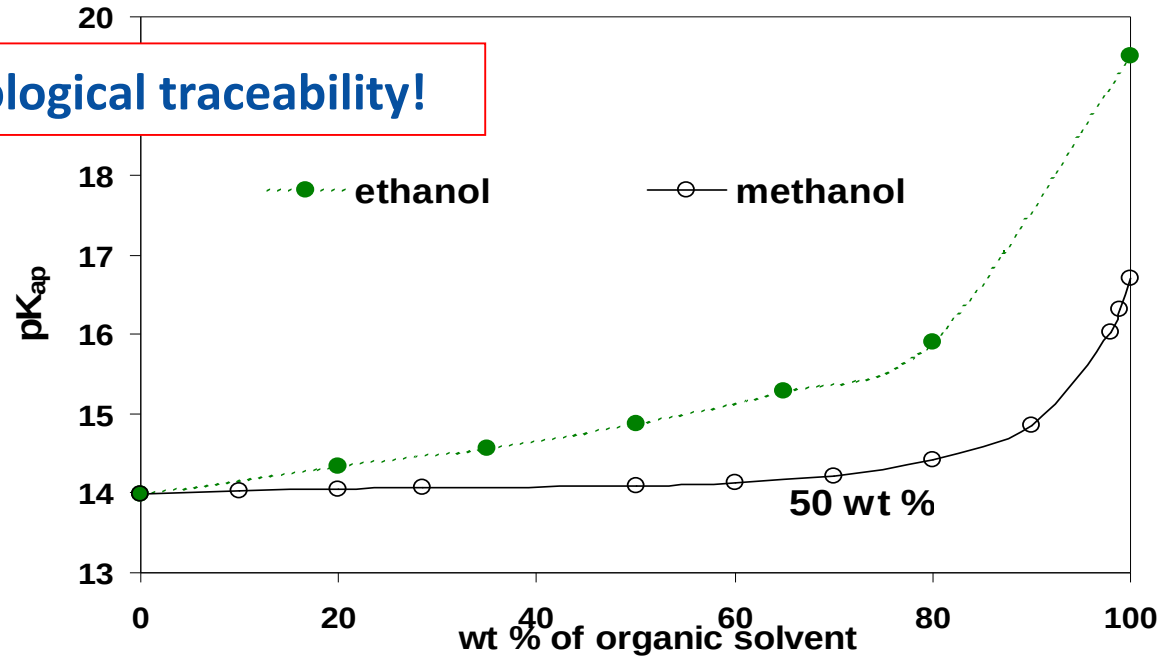
Quality parameters – reference method for pHe

The acidity measurement is a good indicator of corrosion potential of ethanol.

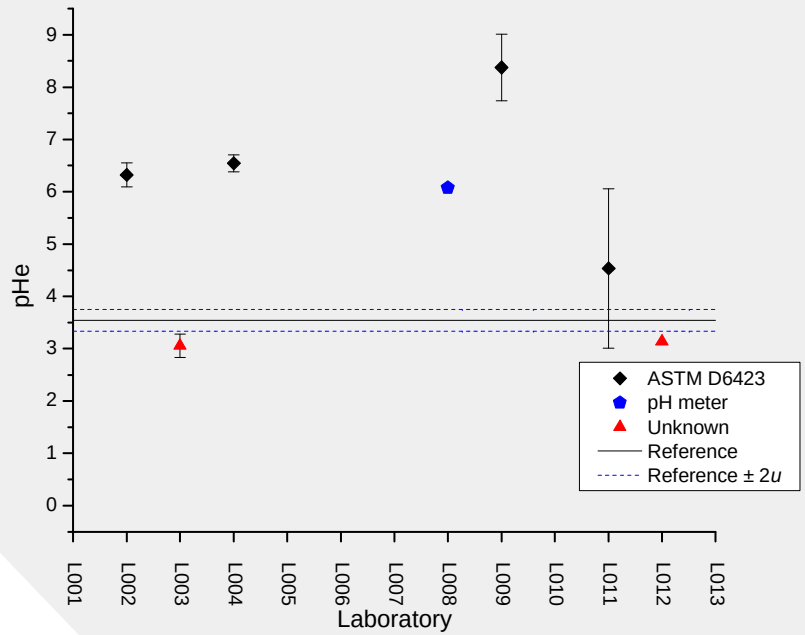
The measure of acidity is preferable to the total acidity since this one can over-estimate the contribution of weak acids (eg CO2) and/or underestimate the corrosion potential of low concentrations of strong acids (eg H2SO4)

BUT: Lack of metrological traceability!



S. Rondinini, P. Longhi, P.R. Musssini, T. Mussini, Pure&Appl. Chem, 59(12), 1693-1702, (1987)

pHe results
Test material A (bioethanol)



•Seven of the thirteen laboratories have reported results. The visual representation includes the reference value which was obtained using the ASTM D6423 method.

•The consensus value is 5.709, based on 7 measurement results.

•There is a large gap between the consensus value and reference value (3.543 ± 0.207)

•This effect could be explained by the difficulty in following closely the requirements of the ASTM method. The presence of non-aqueous reference materials for this parameter would facilitate the improvement of the quality of the results.

•It should be noted that pHe shall have a value around 6.5 according to specifications (fiscal reasons). Considering the reference value, the material should have been flagged as "non-compliant" by the field labs. However, some of the laboratories would have identified the material as compliant.

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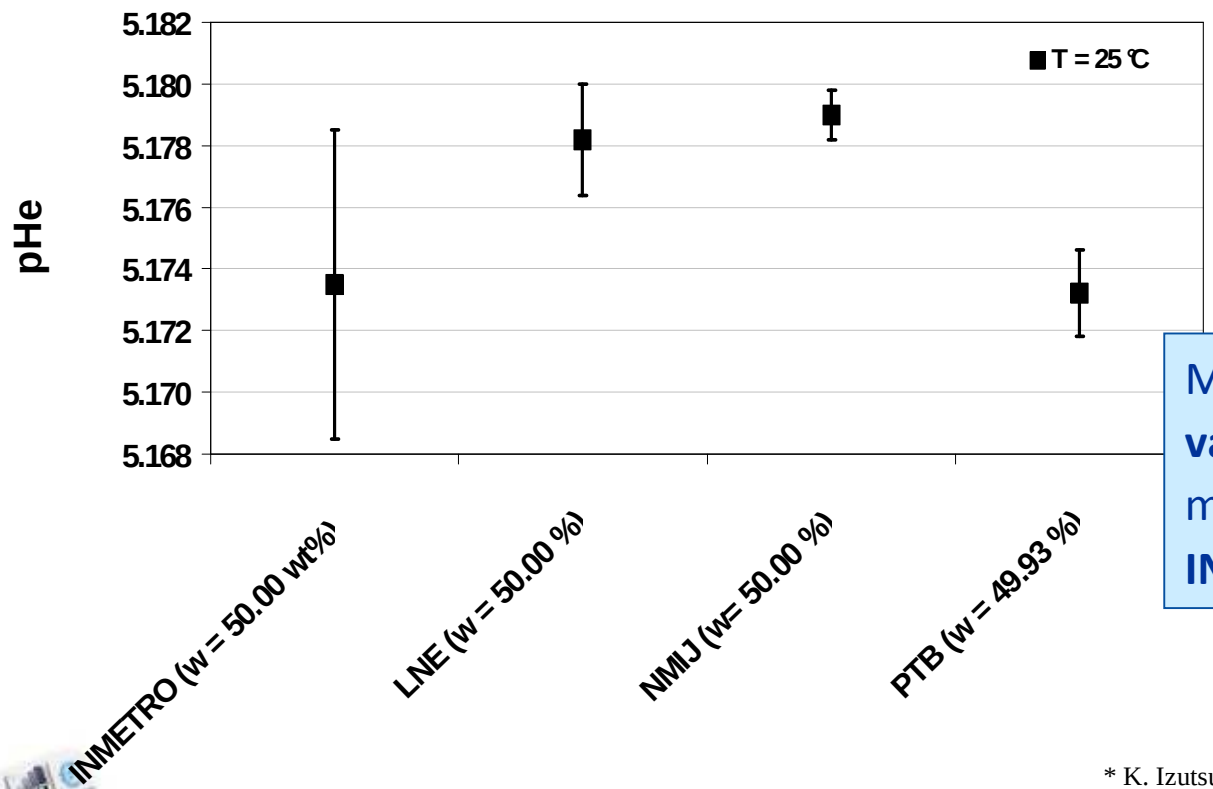
Primary measurements of pHe

Aiming at characterising suitable calibrants: EtOH-H2O mixture (50% m/m)

0.05 mol/kg **potassium hydrogen phthalate (KHPh)** is a primary pH standard in aqueous solution

KHPh conserves its buffer capacity in protic solvents* ➔ suitable as standard in water-ethanol mixtures



Measurement procedure was **validated by a comparison** measurement between **INMETRO, LNE, PTB, NMIJ**

* K. Izutsu, H. Yamamoto, Talanta, Vol. 47, pp. 1157-1163, (1998)

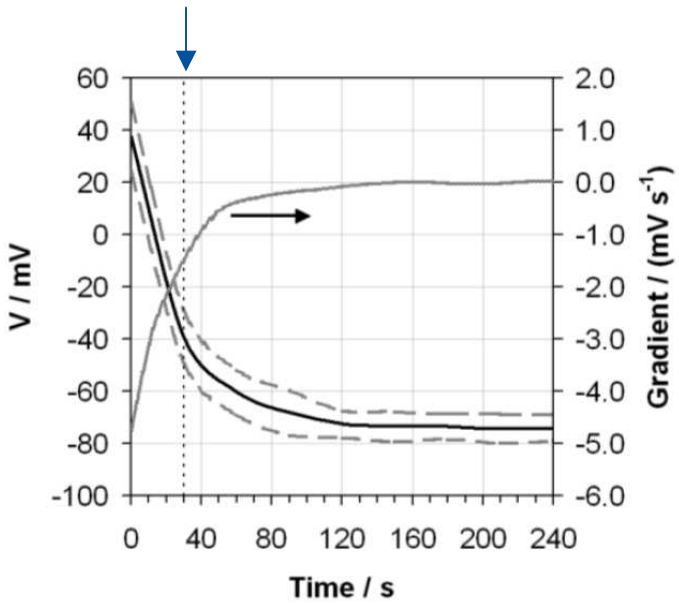
Secondary measurements of pHe

Voltage exhibited by the glass electrode as a function of time when measuring ethanol containing 0.02 g/g of water

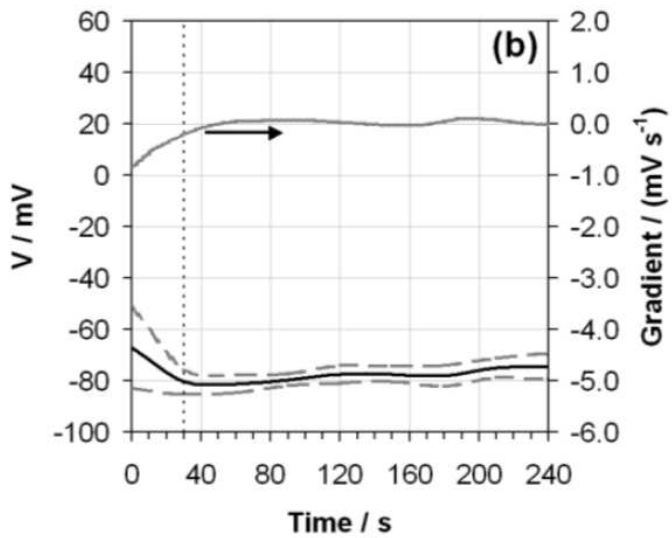
Using the current D6423 ASTM method

Washing the glass electrode with ethanol prior to measurement

Standards requires measurement after 30 s.

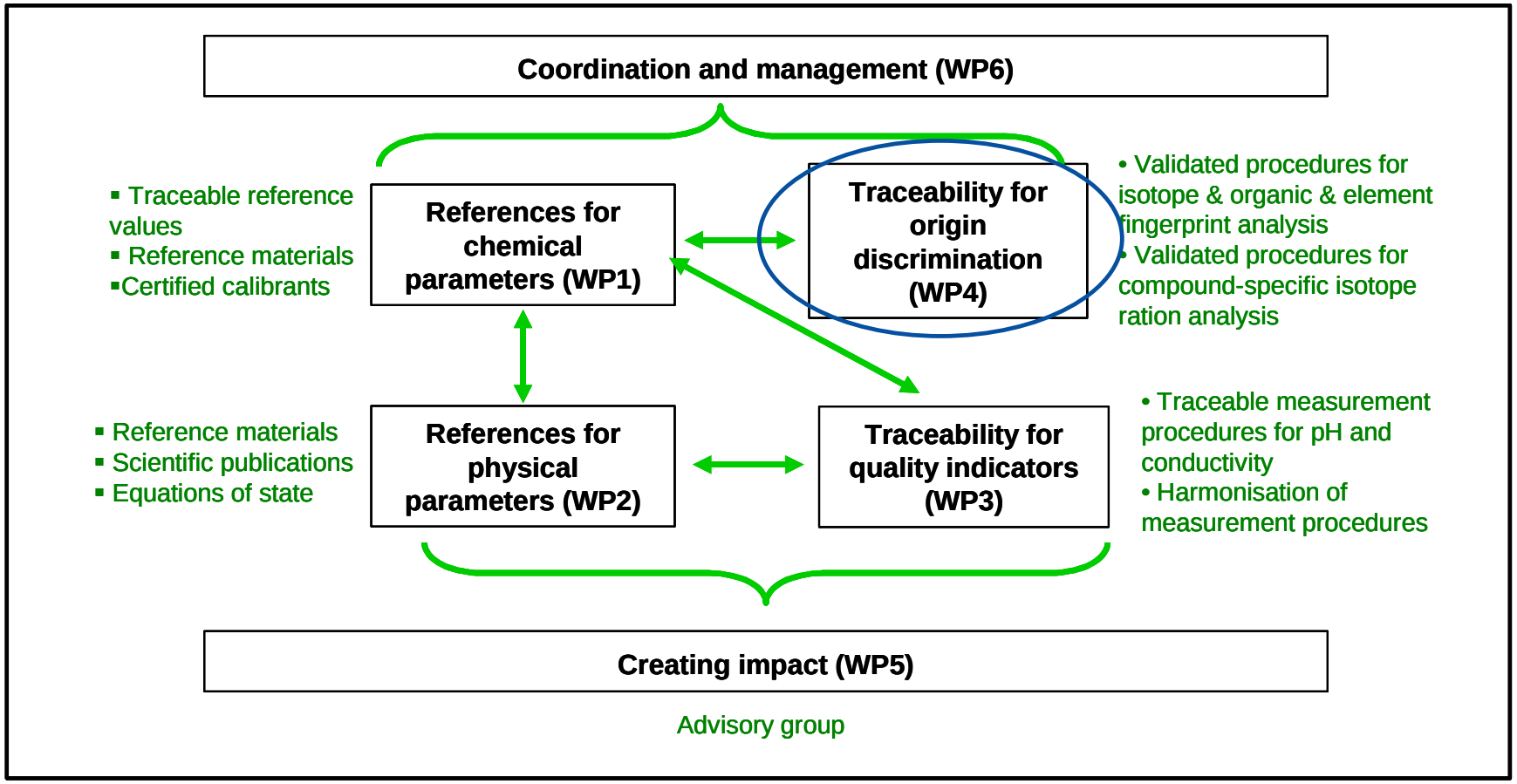


Standards requires measurement after 30 s.



***R. J. C. Brown, A. C. Keates and P. J. Brewer**
***Sensors* 2010, *10*, 9982-9993.**

NPL National Physical Laboratory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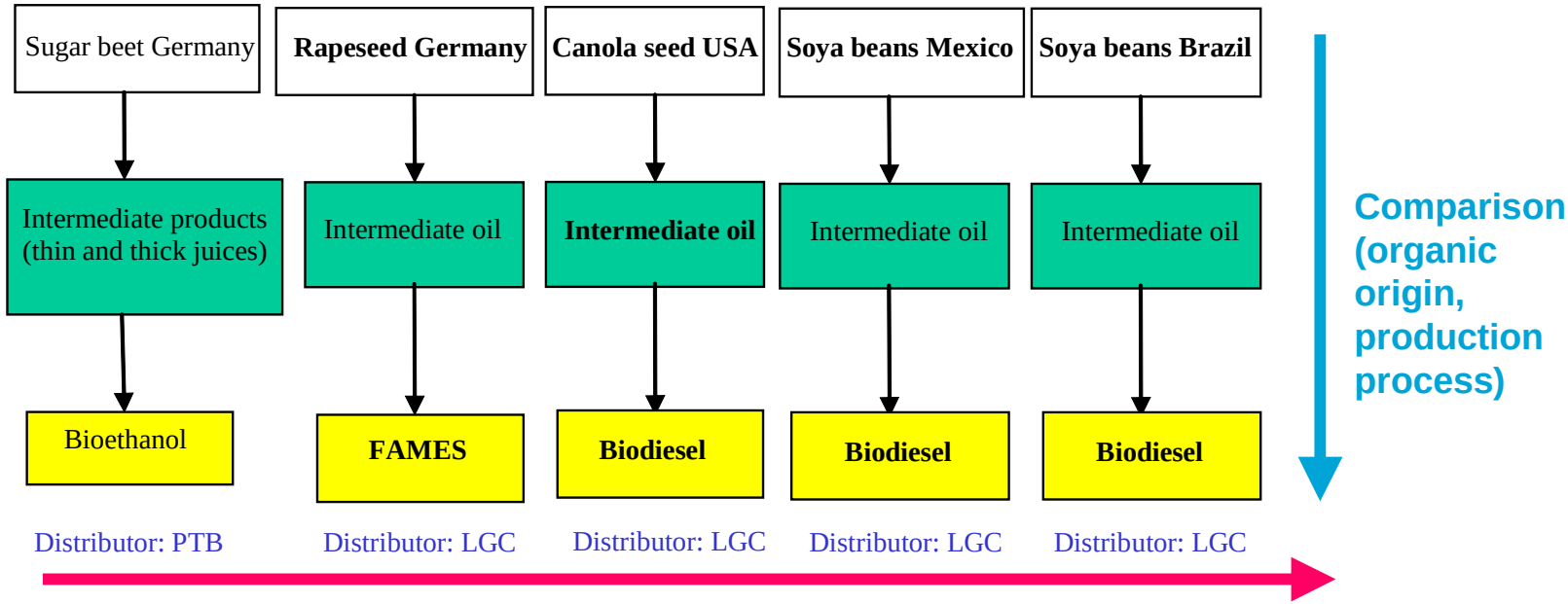
Traceability for origin discrimination



Elemental IR, light isotopes/compound specific IR, organic impurities for origin discrimination?

Type of raw material	Country of origin
> Soy bean (+ oil + biodiesel)	a) Mexico, MO, USA b) Brazil
> Rapeseed (+oil + biodiesel)	a) Velva, ND, USA (canola species) b) Europe

Contact: Heidi.Goenaga-Infante@LGCGroup.com

Isotope and fingerprint analysis

Bulk δ^2H, $\delta^{13}C$, $\delta^{18}O$

Preliminary results have shown that, unlike $\delta^{13}C$ measurements, **both δ^2H and $\delta^{18}O$ measurements have great potential** to **differenciate** between oils and biodiesel of different types of raw material and geographical origin

Generally, $\delta^{13}C$ and δ^2H values for the oil and corresponding biodiesel agreed well but significant differences were observed between the $\delta^{18}O$ values of the same pair of samples

Fingerprint analysis of inorganic elements

Identification of possible biomarkers of origin discrimination by using elemental mass fraction ratios obtained for the comparison between different four raw materials:

> A **direct correlation** was observed between ratios of mass fractions found for samples from the **same kind of raw material**

> An **anti-correlation** was observed between **different raw materials** (e.g. SB from Brazil and CS from USA).

Conclusions and highlights

The project will end in May 2013

Fruitful collaboration between the partners ➔ good outcomes of the project:

- ✓ Some methods already validated, some others under validation
- ✓ 4 peer-reviewed papers already published
- ✓ Some results presented at relevant French Standardisation committees

LNE
Sharing a passion for progress

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Workshop on biofuels characterization

The role of metrology in technical and economic development of biofuels

30-31 May 2013

(Definitive program to come !)

You are all welcome!

Acknowledgements

The European Union

on the basis of Decision No. 912/2009/EC, in the frame of the EMRP Project ENG09 "Metrology for Biofuels".

The Workpackage leaders

Andrea Held *(IRMM)*, ***Henning Wolf*** *(PTB)*, ***Richard Brown*** *(NPL)*, ***Heidi Goenaga-Infante*** *(LGC)*

All the JRP-partners

Thank you for you attention!