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REPORT

VAM Workshop on Traceability in Analytical Measurements

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VALID ANALYTICAL MEASUREMENT

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VAM Workshop on Traceability in Analytical Measurements

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TRACEABILITY IN ANALYTICAL MEASUREMENT

by

D H Nettleton

EXECUTIVE SUMMARY

This report summarises a workshop held for Customers and Contractors of the DTI VAM Programme by NPL on 25th May 1999. Extended summaries have been prepared by the chairs of the five workshop sessions and some overall conclusions from the day's discussions are presented.

1. INTRODUCTION

This report is intended as a summary of the presentations and discussions which took place at the VAM Customer Contractor Workshop held at the National Physical Laboratory, Teddington on 25 May 1999.

The theme for this workshop was 'Traceability in Analytical Measurements'. the workshop began in the morning with presentations from various members of staff from NPL, LGC and AEA Technology. for the afternoon session, delegates were split into four working groups where different aspects of traceability were discussed.

2. MORNING SESSION

The morning session comprised nine plenary lectures:

Traceability of emission level gases through static gravimetry - *Paul Holland.*

Traceability of air quality measurements - *Bill Bell.*

The essential need for traceability in surface analysis - *Martin Seah.*

Traceability of reactive gas mixtures - *Nick Davies.*

Role of traceability in chemical measurements - *Mike Sargent.*

Development of IDMS as a primary technique - *Tim Catterick.*

Uncertainty in IDMS measurements - *Celine Briche.*

Cascading traceability to working laboratories - *Steve Ellison.*

Traceable aerosol standards and developments in the VAM programme - *Ian Marshall.*

3. REPORTS FROM WORKING GROUPS

3.1 REPORT FROM WORKING GROUP 1 - TRACEABILITY IN OUT OF LABORATORY MEASUREMENTS.

CHAIRMAN - PETER BEDSON (LGC)

Speakers:

Optical measurements of gas composition	Bill Bell
Traceability in open path monitoring	Brian Goody
Traceability in aerosol standards for field measurements	Mike Yeoman
Issues in establishing traceability for out of laboratory measurements	Peter Bedson (LGC)
Reference materials for field measurements	Andy Holmes

SUMMARY

- The syndicate provided a useful opportunity for LGC, NPL & AEAT to bring each other up-to-date on work being taken forward in their respective VAM projects.

- The syndicate assumed the role of a means to exchange information rather than to provoke debate / discussion of issues.

- An important common theme was the need for standards / certified reference materials to calibrate field or out-of-laboratory measurement processes.

- Many of the differences in approach, different problems encountered, arose as a result of issues or complications associated with the matrix.

- Some optical measurements of gases tended to be less dependent on the matrix - high resolution spectroscopy (in the mid- or near infrared) are highly selective and could be used to identify / quantify the target species irrespective of other gases present.

- Development of optical techniques might also lead to new approaches to calibration (e.g. by using traceable absorption cross-section measurements) which would remove the need for gas standards in some applications.

- Measurements of particulates in stacks, and analytes in liquid or solid samples presented more challenges, particularly in relation to the matrix. For these measurements it was harder to produce homogenous calibration standards / reference materials. Analytes might also be defined in terms of the method rather than in absolute terms.

- An important factor in establishing traceability was understanding how different factors (e.g. environmental conditions) affected and contributed to measurement uncertainty.

3.2 REPORT FROM WORKING GROUP 2 - WORKING TOWARDS TRACEABILITY TO SI FOR ANALYTICAL MEASUREMENTS

CHAIRMAN - MARTIN MILTON

Speakers:

Openness and completeness in specifying traceability	Peter Cumpson
Traceable measurements in Air Quality	Nick Davies
CCQM work on inorganic IDMS	Ben Fairman
Traceability to reference materials and methods	Ron Walker
CCQM - future plans	Martin Milton

SUMMARY

The strong increase in interest in traceability to the SI for analytical measurements was evident in all of the talks presented during the workshop. Two particular aspects were highlighted by the five speakers in this workshop:

- the requirements for traceability and the uncertainty in measurements should be "fit for purpose" in each application;

- there is a continuing demand for improved uncertainties to meet present and future requirements in many fields;

These two themes emerged from each of the presentations.

- Ron Walker showed how the selection of chemical reference materials for any application leads to a demand for them to have specific properties that are suited to that application. These might be stability, high accuracy or having a value assigned by a particular method. Most of these different properties are brought together in materials that have traceable values;

- A benchmarking study reported by Peter Cumpson illustrated how the cost and efforts devoted to maintaining traceability and related to the magnitude of the consequences of a "failure" in the end result. For example, the task of maintaining documented links between different versions of engineering plans is directly related to the complexity of the overall task;

- Nick Davies described how the requirements of comparability for air quality measurements throughout the European Union will be met through the use of secondary standard gas mixtures to calibrate monitoring stations. However, the level of comparability of these standards prepared at different laboratories dose not yet meet the requirement of 1%.

- Ben Fairman reviewed the different studies of elemental analysis by IDMS carried out by members of the CCQM. Results in the first round were disappointing with comparability

in the range 2-6%. Subsequent improvements, including an emphasis on each laboratory preparing its own spike solutions have led to comparability in the range 0.2-2% in the third round.

- Martin Milton explained how the CCQM was undertaking a detailed review of the requirements for comparability in analytical measurement in order to plan future comparisons. Although the list of requirements is lengthy, the work of CCQM will be restricted to those areas where traceable measurements are feasible and useful.

3.3 REPORT FROM WORKING GROUP 3 - COMPARING VIEWS OF THE MEANING OF TRACEABILITY

CHAIRMAN - DAVID NETTLETON

Speakers:

Traceability - meanings and misunderstandings	Liz Prichard
Traceability in pH measurements	Robert Wielgosz
Traceability at the boundaries of physics and chemistry	Paul Quincey
Networks and traceability	Alan Woolley
Full traceability requirements for a physical CRM	Martin Seah
Physical traceability in biochemical measurements	Ginny Saunders
Traceability of biological materials to test bio-aerosol samplers	Alan Nichols

SUMMARY

Liz Prichard made the following points:

- The use of the word 'traceability' is not restricted to the metrological definition and sometimes refers only to an audit trail. A new term e.g. trackability has been suggested.

- The primary reference point for chemical measurements is not always clear. Even when it is the mole there can still be some ambiguity e.g. dimers, isomers, chirality

- Units for measurements can also cause problems, e.g. %, ppm, $mgkg^{-1}$, $molkg^{-1}$ are all used. Sometimes a quantity to be measured cannot be defined in terms of SI, e.g. fat content or polymer.

Robert Wielgosz described primary and other standards for pH measurement:

- Traceability is required to achieve comparability of measurements.

- Uncertainty requirement is relevant to the method used to obtain traceability.

- pH can be traceable to the SI, when the full uncertainty of each step is taken into account.

Paul Quincey sought to characterise differences between the physicist and chemists' use of the word traceability:

- Physicist - reference point is a primary standard established by measurement or definition under SI. This leads naturally to a calibration chain and an uncertainty budget. Biases, where they occur, are calibrated out.

- Chemist - reference is to a primary method. This leads to an interest in repeatability of the method and the importance of bias of the method.

- In the boundary between these two cases, primary standards and available but have high uncertainty associated with them.

- Different perceptions of phycisists and chemists can lead to misunderstandings as the same words have subtly different meanings.

Alan Woolley looked at traceability issues in air quality monitoring networks.

- He explained operation of automated data collection sites and their regular calibration. As calibrations are done in the field, training of LSO's (Local Site Operators) is important to achieve traceability (an unbroken chain of calibrations).

- Traceability is required for comparability and international acceptance of data.

- Ozone measurements are traceable to an agreed design of "primary" photometer. The data used to calculate ozone concentration from this photometer are accepted internationally. They may be traceable to the SI, but this has not been treated in detail.

Martin Seah's presentation was related to surface analysis.

- He described a CRM used to calibrate surface analysis machines.

- He brought out the benefits of characterising this CRM by a number of different methods.

- This approach minimised uncertainty and identified bias in particular methods.

Ginny Saunders gave a with particular emphasis measurements of the DNA molecule.

- This is a fast moving technology where concepts of traceability are not well developed.

- Markers for measuring the length of DNA molecules, an important measurement for PCR, are produced commercially and are improving as the technique evolves.

- Main issues of traceability are for more traditional, physical measurements, where sensitivity of methods to, for example, temperature are not always recognised.

Alan Nichols made the following points:

- Traceability is mainly used when referring to measurement procedures in this area.
- To make measurements requires a source of reference material, suitable handling arrangements and measurement procedures.
- Community is seeking to make progress through 'traceable' procedures, i.e. everyone makes measurements in the same way to give comparable results.

SUMMARY

- Physicists, chemists and biologists sometimes use words associated with traceability to mean slightly different things.
- Traceability to SI is often not easily achievable and a consensus, which at best approximates to SI, is often used for convenience.
- Physicists tend to use primary standard artefacts and can usually make good assessments of uncertainty.
- Chemists tend to use primary methods and are interested in repeatability and bias of methods.
- Traceability is a new concept to biologists, and is sometimes used to indicate a procedure agreed by consensus.
- Unbroken chains for traceability require trained personnel to carry out the calibrations.

3.4 REPORT FROM WORKING GROUP 4 - TRACEABILITY ACROSS NATIONAL BORDERS

CHAIRMAN: MIKE SARGENT

Speakers:

Harmonisation of air quality measurements in Europe (HAMAQ)	Clare Paton Walsh
The role of international intercomparisons and accreditation in ensuring the accuracy of routine measurements	Peter Woods
Achieving equivalence in chemical measurements	Mike Sargent
The problems of organising CCQM intercomparisons	Ken Webb
Comparability of air quality measurements (aerosols) across national borders	Mike Woodfield

SUMMARY

The Working Group structured its discussion around the example of gas analysis which has established a precedent for international traceability in the field of chemical analysis. Lessons which can be drawn from this example are:

- An appropriate structure was already in place at national (NMI), regional (Euromet, EU) and international (ad hoc, CCQM) levels

- The need for international traceability had been driven by regulation, for example in Europe an EU Directive sets uncertainty specifications for measurements by field laboratories

- Initial intercomparisons (HAMAQ) had shown that not all NMI's were up to speed and some had needed guidance

- Even this relatively simple model highlighted problems in achieving uncertainties at NMI level which are sufficiently lower than those required of field laboratories (eg SO_2/NO_2).

Problems in applying the gas model more widely include:

- The national traceability chain for gases is very short, a longer chain in other chemical measurement fields poses even greater demands for uncertainty levels achieved by NMI's
- Many of these national chains do not yet exist

- The great difficulty of estimating uncertainty reliably for many applications

- The number of international intercomparisons which are required

- The cost and difficulty of each such intercomparison.

A number of general conclusions were drawn:

- International traceability chains are difficult and expensive to implement

- The goal is valid and worthy but will take a long time to achieve

- In view of this it is important to demonstrate gains along the way eg through improvements to current standards and methods

- There is wide agreement that regulation is the driving force for traceability but, in turn, good measurements lead to better regulations.

The Working Group recommended three approaches by which those striving to achieve international chemical traceability could ensure progress:

- Adapt and augment current structures wherever possible

- Make an input to policy and regulatory development to ensure the appropriate drivers for adoption of traceability concepts

- Achieve and demonstrate real gains which are of early benefit to industry and commerce.

Finally, the Working Group noted that the resource needed to achieve international chemical traceability would only be made available if NMI's could demonstrate how better measurements and better measurement technology can be applied to good effect in areas such as commerce, manufacturing, health, agriculture and environmental protection.

4. OVERALL CONCLUSIONS

Many of the participants made it clear that the workshop was a useful opportunity to exchange viewpoints and experience between the contractors working on the VAM Programme. It was observed that as the series of VAM Customer/Contractor Workshops has proceeded, they have become more useful, and this one has been the most effective with its combination of plenary presentations and workshop discussion.

Previous workshops have tended to highlight the difference in approach between practitioners in the different areas that the VAM Programme covers. The discussion has often appeared to be dominated by issues arising from differences in the way terms are understood and applied. At this workshop it has been very encouraging to observe that discussions are beginning to highlight areas of agreement and that there is a strong trend towards agreement on important underlying principles. These include:

- the benefits of being measurements on traceability to the SI, where this is cost-effective and achievable.

- the necessity of stating the reference point to which claims for "traceability" refer.

- the need to support claims for traceability with calculations of the associated uncertainty.

Although there agreement is now emerging on these basic issues, there continue to be significant differences between their implementation in the different areas covered by the VAM Programme. These differences are often sector specific, for example:

- particular sectors, including contaminated land and food have continuing requirements for CRM's to support matrix dependant measurement methods.

- valid and repeatable sampling is an important issue in some sectors (for example, contaminated land, environmental and stack gases).

- the word "traceability" is largely understood in biology to apply to specified measurement methods and not standards or reference materials.

Although such issues will continue to arise in many sectors, the workshop provided strong evidence that the emphasis of the VAM Programme on generic issues including traceability and uncertainty have contributed to the recent changes in thinking amongst the physicists, chemists and biologists involved. This change seems to reflect a similar change amongst those commissioning, performing and interpreting analytical measurements in the UK as a whole.

5. APPENDIX

5.1 WORKSHOP PROGRAMME

10:00 Registration and coffee

10:30 Start of morning session, chairman - David Nettleton.

Traceability of emission level gases through static gravimetry - *Paul Holland.*

10:45 Traceability of air quality measurements - *Bill Bell.*

11:00 The essential need for traceability in surface analysis - *Martin Seah.*

11:15 Traceability of reactive gas mixtures - *Nick Davies.*

11:30 Role of traceability in chemical measurements - *Mike Sargent.*

11:45 Development of IDMS as a primary technique - *Tim Catterick.*

12:00 Uncertainty in IDMS measurements - *Celine Briche.*

12:15 Cascading traceability to working laboratories - *Steve Ellison.*

12:30 Traceable aerosol standards and developments in the VAM programme - *Ian Marshall.*

12:45 LUNCH

13:45 Start of afternoon session

Working group 1, chairman - Peter Bedson
Exhibition Room -'Traceability in out of laboratory measurements'

◊ Optical measurements of gas composition - Bill Bell.
◊ Traceability in open path monitoring - Brian Goody.
◊ Traceability of aerosol standards for field measurements - Mike Yeoman.
◊ Issues in establishing traceability of out of laboratory measurements' - Peter Bedson.
◊ Reference materials for field measurements - Andy Holmes.

Working group 2, chairman - Martin Milton
Globe Room -'Working towards traceability to SI for analytical measurements'

◊ Traceability of national air quality monitoring networks - Nick Davies.
◊ The role of CCQM - Martin Milton.
◊ CCQM work on the purity of primary organic standards - Nicola Maidwell.
◊ CCQM work on inorganic IDMS - Ben Fairman.
◊ Traceability to reference materials and methods - Ron Walker.
◊ Openness and completeness in specifying traceability - Peter Cumpson.

Working group 3, chairman - David Nettleton
Historical Museum -'Comparing views of the meaning of "traceability" from the physicist, chemist and biologist'

◊ Traceability: Meanings and misunderstandings - Liz Prichard.
◊ Traceability in pH measurements - Robert Wielgosz.
◊ Traceability at the boundaries of physics and chemistry - Paul Quincey.
◊ Networks and traceability - Alan Woolley.
◊ Full traceability requirements for a physical CRM". - Martin Seah.
◊ Physical traceability in biochemical measurements - Ginny Saunders.
◊ Traceability of biological materials to test bio-aerosol samplers - Alan Nichols.

Working group 4, chairman - Mike Sargent
Conference Room -'Traceability across national borders'

◊ Harmonisation of air quality measurements in Europe (HAMAQ) - Clare Paton-Walsh.
◊ The role of international intercomparisons and accreditation in ensuring the accuracy of routine measurements - Peter Woods, NPL.
◊ Achieving equivalence in chemical measurements - Mike Sargent, LGC.
◊ The problems of organising CCQM intercomparisons - Ken Webb, LGC.
◊ Comparability of air quality measurements (aerosols) across national boundaries - Mike Woodfield, AEAT.

Feedback Session, chairman - Peter Woods

14:45 The chairman of Working Group 1 will give a brief summary of their working group followed by a discussion.

15:00 The chairman of Working Group 2 will give a brief summary of their working group followed by a discussion.

15:15 The chairman of Working Group 3 will give a brief summary of their working group followed by a discussion.

15:30 The chairman of Working Group 4 will give a brief summary of their working group followed by a discussion.

15:45 Round up

16:00 Close.

5.2 LIST OF DELEGATES

NPL	LGC	AEA Technology	NMSPU	VAM Working Group Members
Des Alphonso	Vicki Barwick	Ian Marshall	Roy Crouch	Hugh Berridge
Bill Bell	Peter Bedson	Alan Nichols	Joan Cocksedge	Peter Carter
Chris Brookes	Lyndsey Birch	Mike Woodfield	Alistair Hooley	Chris Cowper
Peter Cumpson	Celine Briche	Mike Yeoman	Graham Reed	Les Ebdon
Nick Davies	Brian Brookman		Lee Vousden	Mike Ford
Hansa D'Souza	Tim Catterick			John Green
Ian Gilmore	Johanne Cornett			Ernie Newman
Brian Goody	Mike Cullen			David Sykes
Paul Holland	Steve Ellison			David Westwood
Sarah Horrocks	Ben Fairman			
James Johnstone	Andy Holmes			
Nick Martin	Steve Kippin			
Martin Milton	Nicola Maidwell			
David Nettleton	John Marriott			
Clare Paton-Walsh	Liz Prichard			
Paul Quincey	Mike Sargent			
Rod Robinson	Ginny Saunders			
Martin Seah	Ron Walker			
Ian Uprichard	Ken Webb			
Rob Wielgosz				
Peter Woods				
Alan Woolley				