Setting standards
in analytical science

Reference Materials for Environmental Performance Testing

Dr Steve Wood
Head of Regulatory and Legislative Services

ISPRA

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Outline

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- Background to LGC
- UK MCERTS scheme
- Reference materials production at LGC Teddington
- Case study
- Issues and Considerations

LGC Limited - Locations

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Activities at LGC Teddington

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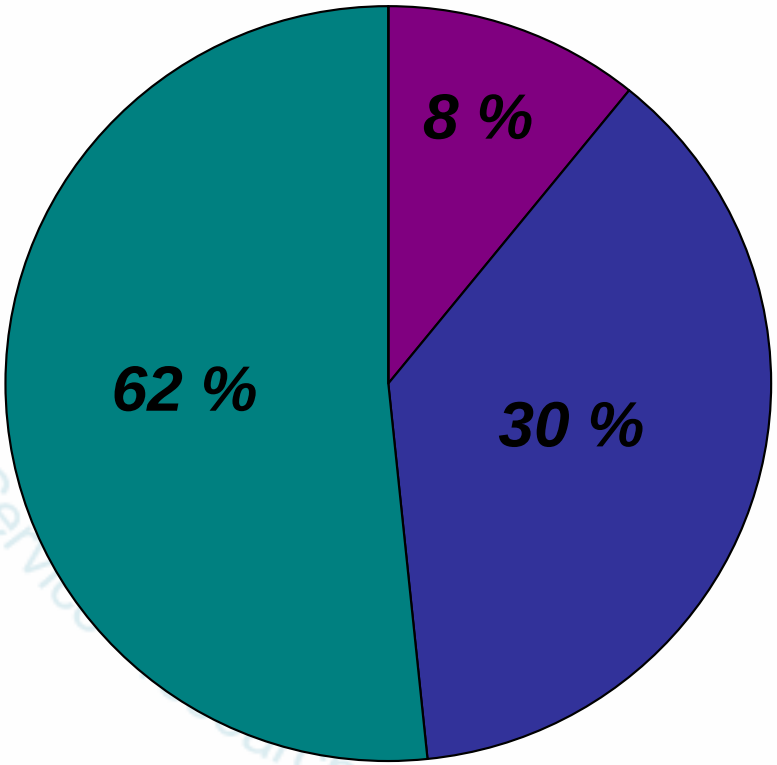
Analytical Services

- Forensic Science
- Food Safety
- Pharmaceutical
- Lifescience



Quality Services

- Reference Materials
- Proficiency Testing
- Training

~ 400 staff on Teddington site

Activities at LGC Teddington

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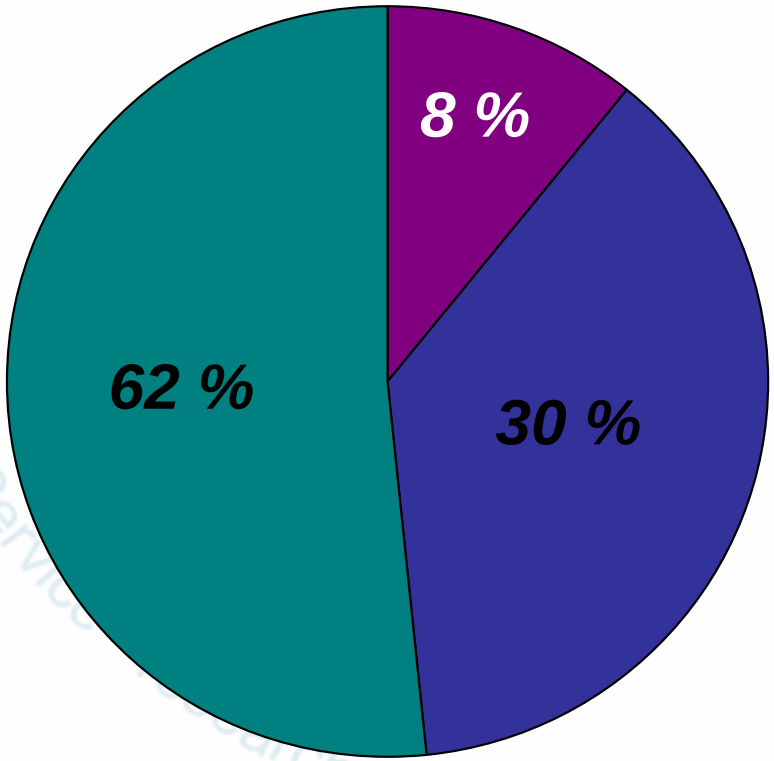

Quality Services

- Reference Materials
- Proficiency Testing
- Training

~ 400 staff on Teddington site

LGC's UK National Roles

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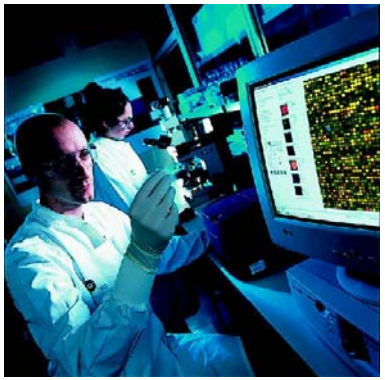
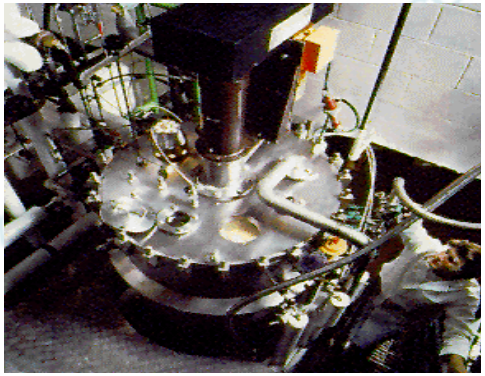
Government Chemist

- Referee Analyst (20 Acts of Parliament)
- Adviser to UK government & industry on regulations and scientific input



National Measurement Institute

- Delivers world-class measurement science & technology
- Provides traceable and increasingly accurate standards of measurement for use in trade, industry, academia and government



What is MCERTS?

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- UK Environment Agency's Monitoring Certification Scheme
  - for monitoring emissions to air, land and water .
  - provides the framework for businesses to meet the UK EA’s quality requirements.
  - compliance with MCERTS gives the authorities confidence in the monitoring of emissions to the environment.

- Monitoring emissions to land
  - **Chemical testing of soil.**

- Monitoring emissions to water
  - Equipment for continuous monitoring discharges to rivers, smaller watercourses and the sea.
  - Direct toxicity assessment of effluents.
  - Portable equipment for monitoring water.
  - **Sampling and chemical testing of water.**
  - Self monitoring of effluent flow.

Key requirements of MCERTS

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- Based on ISO/IEC 17025 with additions:
- Validation
  - Methods shall be validated for each parameter analysed on matrices likely to be analysed within the laboratory. This validation shall include at least *three different soil matrices*.
  - In the absence of suitable certified reference materials, recovery estimates relevant to the matrix and parameter under investigation shall be determined by the use of spiking experiments.
  - Where a suitable certified reference material becomes available after recovery estimates have been undertaken, it shall be used to check the bias is satisfactory.
  - Specific performance targets for bias and precision by analyte.

Soil types

Classified by particle-size and organic composition:

- Organic > 20 to 30 % organic matter.
- Mineral < 20 to 30 % organic matter (depending on clay content)
  - three particle-size groups according to the proportions of sand, silt and clay sized particles in the inorganic fraction <2mm:
    - Sandy
    - Clays
    - Loamy

RM Production at LGC Teddington

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- ISO Guide 34
  - General Requirements for the Competence of Reference Material Producers
- ISO/IEC 17025
  - General Requirements for the Competence of Calibration and Testing Laboratories
- ISO Guide to the Expression of Uncertainty in Measurement (GUM)

United Kingdom Accreditation Service

ACCREDITATION CERTIFICATE

UKAS
UNITED KINGDOM ACCREDITATION SERVICE

REFERENCE MATERIAL PRODUCER
No. 4005

LGC Ltd

is accredited in accordance with the recognised International Guide ISO Guide 34:2000 *General requirements for the competence of reference material producers* through assessment against this Guide and against ISO/IEC 17025:2005 as appropriate for the related laboratory activities.

This accreditation demonstrates technical competence for a defined scope as detailed in and at the locations specified in the schedule to this certificate.

The schedule to this certificate is an essential accreditation document and from time to time may be revised and reissued by the United Kingdom Accreditation Service. The most recent issue of the schedule of accreditation, which bears the same accreditation number as this certificate, is available from the UKAS website www.ukas.com.

This Accreditation is subject to continuing conformity with United Kingdom Accreditation Service requirements. The absence of a schedule on the UKAS website indicates that the accreditation is no longer in force.

Accreditation Manager, United Kingdom Accreditation Service

Initial Accreditation date
30 June 2006

This certificate issued on
30 June 2006

The Department of Trade and Industry (DTI) has entered into a memorandum of understanding with the United Kingdom Accreditation Service (UKAS) through which UKAS is recognised as the national body responsible for assessing and accrediting the competence of organisations in the fields of calibration, testing, inspection and certification of systems, products and persons

RM Production

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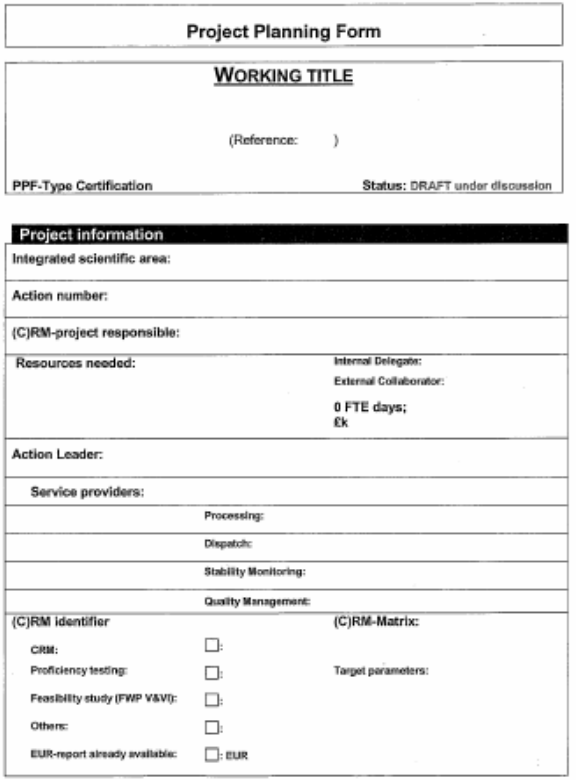
Written project plan for production of every reference material

- Production Steps
  - Material specification
  - Sourcing, preparation and sub-division
  - Homogeneity assessment
  - Stability assessment
  - Characterisation of the assigned value(s)
  - Calculation of the assigned value and its uncertainty
  - Documentation and storage of the material
  - Sales and storage and distribution
    - LGC Standards



Project Planning Form

WORKING TITLE

(Reference:)

PPF-Type Certification — Status: DRAFT under discussion

Project information		
Integrated scientific area:		
Action number:		
(C)RM-project responsible:		
Resources needed:		Internal Delegate: External Collaborator: 0 FTE days; €k
Action Leader:		
Service providers:		
	Processing:	
	Dispatch:	
	Stability Monitoring:	
	Quality Management:	
(C)RM identifier		(C)RM-Matrix:
CRM:	☐:	
Proficiency testing:	☐:	Target parameters:
Feasibility study (FWP V&VI):	☐:	
Others:	☐:	
EUR-report already available:	☐: EUR	

Material Certification

- Certification Panel
  - In house group
  - Project team members
  - Independent experts (e.g. statistics)
  - Quality Team representative
  - Review; examine; approve and authorise

- European Reference Materials Co-operation
  - Technical review by experts from German (BAM) and European (IRMM) metrology and reference material organisations
  - ERM Panel approval
  - www.erm-crm.org

Certificate (ISO Guide 31)

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CERTIFICATE OF ANALYSIS

ERM® - AC020a

***trans*-5,6-Dihydro-4-methoxy-6-(2-phenylethenyl)-2H-pyran-2-one (Kavain)**		
Parameter	Certified value [1] (mass %)	Uncertainty [2] (mass %)
Purity	99.8	0.2

1) The certified value is traceable to the analytical methods and standards used in the characterisation study and described in the certificate.

2) The quoted uncertainty is the half-width of the expanded uncertainty calculated using a coverage factor (k) of 2.45, which gives a level of confidence of approximately 95 %.

This certificate is valid for 12 months from the date of shipment provided the sample is stored under the recommended conditions.

The minimum amount of sample to be used is 2 mg.

NOTE

European Reference Material ERM® - AC020a was produced and certified under the responsibility of LGC according to the principles laid down in the Technical Guidelines of the European Reference Materials® co-operation agreement between BAM-LGC-IRMM. Information on these guidelines is available on the Internet (http://www.erm-crm.org).

Accepted as an ERM®, Teddington, August 2006.

Signed: _____

Dr John Marriott, UK Government Chemist
LGC Limited
Queens Road
Teddington
Middlesex
TW11 0LY, UK

4006

DESCRIPTION OF THE SAMPLE

A batch of D,L-kavain obtained from a commercial supplier of chemical reagents was mixed and dispensed as 10 mg units into screw-capped amber glass vials.

The material was considered to be homogeneous on the basis of High Performance Liquid Chromatography with UV detection (HPLC-UV) measurements on 10 randomly selected 2 mg portions, which showed no significant variation in purity value.

The identity of the material was confirmed by 250 MHz ^{1}H-NMR spectroscopy and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS/MS) utilising accurate mass measurement for determination of elemental formulae in combination with product ion MS.

The material contains a mixture of D and L kavain; the proportion of these isomers in the material is not necessarily the same as that found in nature.

INTENDED USE

The primary use of this reference material is for the calibration of methods for the determination of kavain in herbal products, foodstuffs and other relevant matrices

ANALYTICAL METHOD USED FOR CERTIFICATION

<u>High Performance Liquid Chromatography with UV Detection (HPLC-UV)</u>

The purity of the material was determined by HPLC-UV using a reversed phase column (150 × 2 mm, Phenomenex Luna C18 (2), 5 µm), with an isocratic mobile phase consisting of 55 % water and 45 % acetonitrile and a flow rate of 0.2 mL/min. Solutions of kavain in acetonitrile (0.01mass %) were prepared from 9 units of the material. The purity of the material was quantified by peak area normalisation using UV detection at λ=246 nm.

<u>Differential Scanning Calorimetry</u>

A Polymer Labs STA 625 differential scanning calorimeter was used, with a sample size of approximately 2 mg in aluminium pans and a heating rate of 1.3 °C/min. The instrument was calibrated using a high purity indium certified reference material (LGC2601). A total of 6 determinations were carried out.

<u>Gas Chromatography Flame Ionisation Detection (GC-FID)</u>

The purity of the material was determined by GC-FID using a DB-1 column (60 m × 0.25 mm id, df = 0.25 µm) with a constant flow of helium as the carrier gas (1 mL/min) and column temperature programme of 30 °C for 1 minute, ramp @ 10 °C to 40 °C, ramp @ 5 °C to 200 °C for 1 minute, ramp @ 1 °C to 270 °C for 20 minutes with the Flame Ionisation Detector (FID) at a temperature of 280 °C. Solutions of kavain in dichloromethane (0.1 mass %) were prepared from 10 portions of the material. Each solution was analysed by cold on-column injection of 1 µL. The purity of the material was quantified by peak area normalisation.

The data from these three techniques is shown in Table 1.

In addition to the above, moisture and inorganic material was also determined:

<u>Moisture</u>

Moisture was determined by coulometric Karl Fischer titration and the value subtracted from the purity determined by HPLC-UV and GC-FID.

<u>Inorganic Content</u>

The percentage of inorganic material was assessed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), and confirmed by ash determination at 550 °C. The value was subtracted from the purity value determined by HPLC-UV and GC-FID. The percentage inorganic content was not subtracted from the DSC purity value as this technique allows for the presence of inorganics in the sample.

Characterisation Approaches

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- Single Primary (Definitive) Method
  - cost effective if methodology and equipment is readily available
- Accurate Gravimetric Preparation
  - valid and effective where analyte(s) can be added to the matrix homogeneously
- Two or More Independent Methods
  - preferable to have validation information available for methods (precision and accuracy)
- Inter-laboratory Study

Inter-laboratory Studies

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- Qualified participants
- QC material supplied with candidate material
- Detailed protocol provided to participants
- Safety data sheets prepared and supplied
- Conventional or robust statistical data processing

- Number and availability of participants

Uncertainty

- A CRM has one or more property values each with an uncertainty:

- Uncertainty has 3 components:
  - characterisation
  - homogeneity
  - stability

$$u_{CRM} = \sqrt{u_{char}^2 + u_{\text{hom}}^2 + u_{lts}^2}$$

$$U_{CRM} = k \times u_{CRM}$$

LGC Contaminated Land RMs

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SOIL MATERIALS

- ERM-CC135 Brick Works Soil – Extractable Metals
- LGC6115 Contaminated Soil – PCBs and PAHs
- LGC6141 Contaminated Soil with Clinker Ash
- LGC6145 Contaminated Soil – Extractable Metals, PAHs and Inorganics
- LGCQC3004 Clay Soil 1
- LGCQC3005 Loamy Sand Soil 1
- LGCQC3006 Sandy Loam Soil 1

SEDIMENT MATERIALS

- **Freshwater Sediment Materials**
  - LGC6187 River Sediment – Extractable Metals
  - LGC6188 River Sediment – PAHs
  - LGC6189 River Sediment – Extractable Metals

- **Marine Sediment Materials**
  - LGC6137 Estuarine Sediment – Extractable Metals

SEWAGE SLUDGE MATERIALS

- ERM-CC136a Sewage Sludge – Metals
- LGC6181 Sewage Sludge – Leachable Metals
- LGC6182 Sewage Sludge – PAHs
- LGC6184 Sewage Sludge – PCBs

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CASE STUDY
LGC6115 – Soil Characterised for PAHs and PCBs

Production summary

- Soil sourced from the Czech republic
- Blended from 3 soils
  - 1 blank soil
  - 1 PCB contaminated soil
  - 1 PAH contaminated soil
- Soil typed
- Ground to specific particle size
- Homogenised
- Sub-sampled and bottled
- Irradiated
- Isotope dilution mass spectrometry for PAHs and PCBs
- Submitted as a PT scheme round

Analytes

- PAH
  - Naphthalene
  - Acenaphthylene
  - Acenaphthene
  - Fluorene
  - **Phenanthrene**
  - Anthracene
  - **Fluoranthene**
  - Pyrene
  - **Benz[a]anthracene**
  - Chrysene
  - Benzo[b]fluoranthene
  - Benzo[k]fluoranthene
  - **Benzo[a]pyrene**
  - Indeno[123cd]pyrene
  - Dibenzo[ah]anthracene
  - **Benzo[ghi]perylene**

- **PCB**
  - **PCB101**
  - **PCB118**
  - **PCB138**
  - **PCB153**
  - **PCB180**

PCB Homogeneity

- Measured as ratios. No absolute values assigned
- RSD calculated for ratios and then the absolute value was determined based on the characterised value from IDMS measurements

Analytes	Mean Value (as ratio)	U_h (as ratio)	%RSD	Homogeneous @95%	Homogeneous @99%
PCB101	0.866	0.022	2.54	No	No
PCB118	0.865	0.009	1.04	Yes	Yes
PCB138	0.826	0.048	5.81	Yes	Yes
PCB153	0.769	0.05	6.5	Yes	Yes
PCB180	1.031	0.131	12.71	Yes	Yes

PCB values and uncertainties

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Analyte	Certified value (mg/kg)	u_{char} (mg/kg)	u_h (mg/kg)	u_{lts} (mg/kg)	u_{crm} (mg/kg)	k	U_{crm} (mg/kg)	RSD
PCB101	91.70	0.97	2.33	2.33	3.43	2	6.87	7.5%
PCB118	114.70	0.89	1.19	1.19	1.91	2	3.82	3.3%
PCB138	15.40	0.37	0.89	0.89	1.32	2	2.64	17.1%
PCB153	19.22	0.16	1.25	1.25	1.77	2	3.55	18.5%
PCB180	9.52	0.32	1.21	1.21	1.74	2	3.48	36.6%

MCERTS performance characteristics:

Precision = 15 % RSD

Bias = 30 %

PAH values and uncertainties

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Analyte	Certified Value (mg/kg)	u_{char} (mg/kg)	u_h (mg/kg)	u_{lts} (mg/kg)	u_{crm} (mg/kg)	k	U_{crm} (mg/kg)	RSD
Phenanthrene	176.01	2.02	3.70	3.70	5.61	2	11.21	6%
Fluoranthene	308.21	2.54	1.25	1.25	3.09	2	6.17	2%
Benzo[a]anthracene	35.24	0.17	0.25	0.25	0.38	2	0.77	2%
Benzo[a]pyrene	0.13	0.0040	0.0058	0.0058	0.01	2	0.02	14%
Benzo[g,h,i]perylene	0.32	0.0135	0.0198	0.0198	0.03	2	0.06	19%

MCERTS performance characteristics:

Precision = 15 % RSD

Bias = 30 %

Issues and challenges

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- Contaminated soil
- Specialised processing facilities
- Soil types
  - Soils versus sediments
- Incurred versus spiked materials
- Number of willing participants in inter-laboratory studies
- Transport of samples

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- Mark Pettengell
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- Chris Hopley and David Carter

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  - Chemical and Biological Metrology Knowledge Base Programme
  - www.nmschembio.org.uk

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Further information:

Gill.Holcombe@lgc.co.uk