Analytical Issues – Do you understand your results?

K. Clive Thompson
Chief Scientist
ALcontrol Laboratories
clive.thompson@alcontrol.com

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NOTE: -

The authors of the revised BS 10175 circulated a first draft to the Steering Committee in April 2010. Over 90% of my approx 15 pages of comments on this first draft have been accepted and incorporated into the DPC by the authors. These comments were mainly relating to sampling and analysis.

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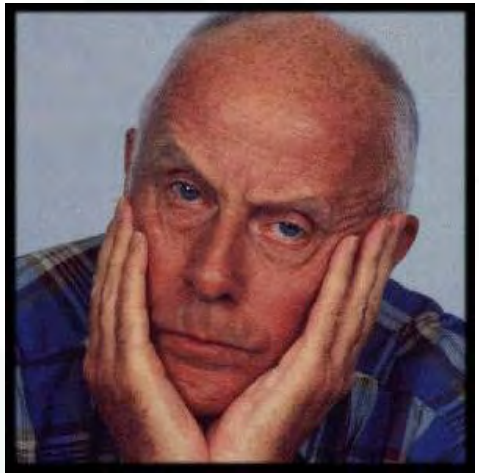
Disclaimer

The views and opinions expressed in this presentation are solely those of the author and not necessarily those of ALcontrol Laboratories

This “Victor Meldrew” short presentation will attempt to highlight the issues and problems with the analysis of samples associated with contaminated land investigations



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Benefits of MCERTS

- The introduction of MCERTS has vastly improved the quality of analysis associated with contaminated land analysis
- MCERTS was the result of liaison between the major contaminated land contract laboratories and the Environment Agency
- MCERTS accreditation is an add-on to ISO 17025 and competence to this standard is assessed by UKAS.
- Allows the use of any fit for purpose “total” analytical method that the user has fully validated and the on-going QC data demonstrates no significant deterioration in performance
- No requirement to use ISO/CEN/BS standard methods

Performance Requirements

The Environment agency has agreed with UKAS that when a laboratory requests accreditation of additional parameters not listed in Annex A of this standard, the following performance requirements (as per the existing listed parameters) shall be enforced:

Metals –	**7.5% precision and 10% bias**
Organometallics –	**15% precision and 30% bias;**
Inorganics –	**10% precision and 20% bias**
Organics –	**15% precision and 30% bias**

If a laboratory is unable to meet these requirements for additional parameters due to matrix effects or fitness for purpose issues it shall propose alternative performance characteristics and submit them to the Environment Agency via UKAS for assessment.

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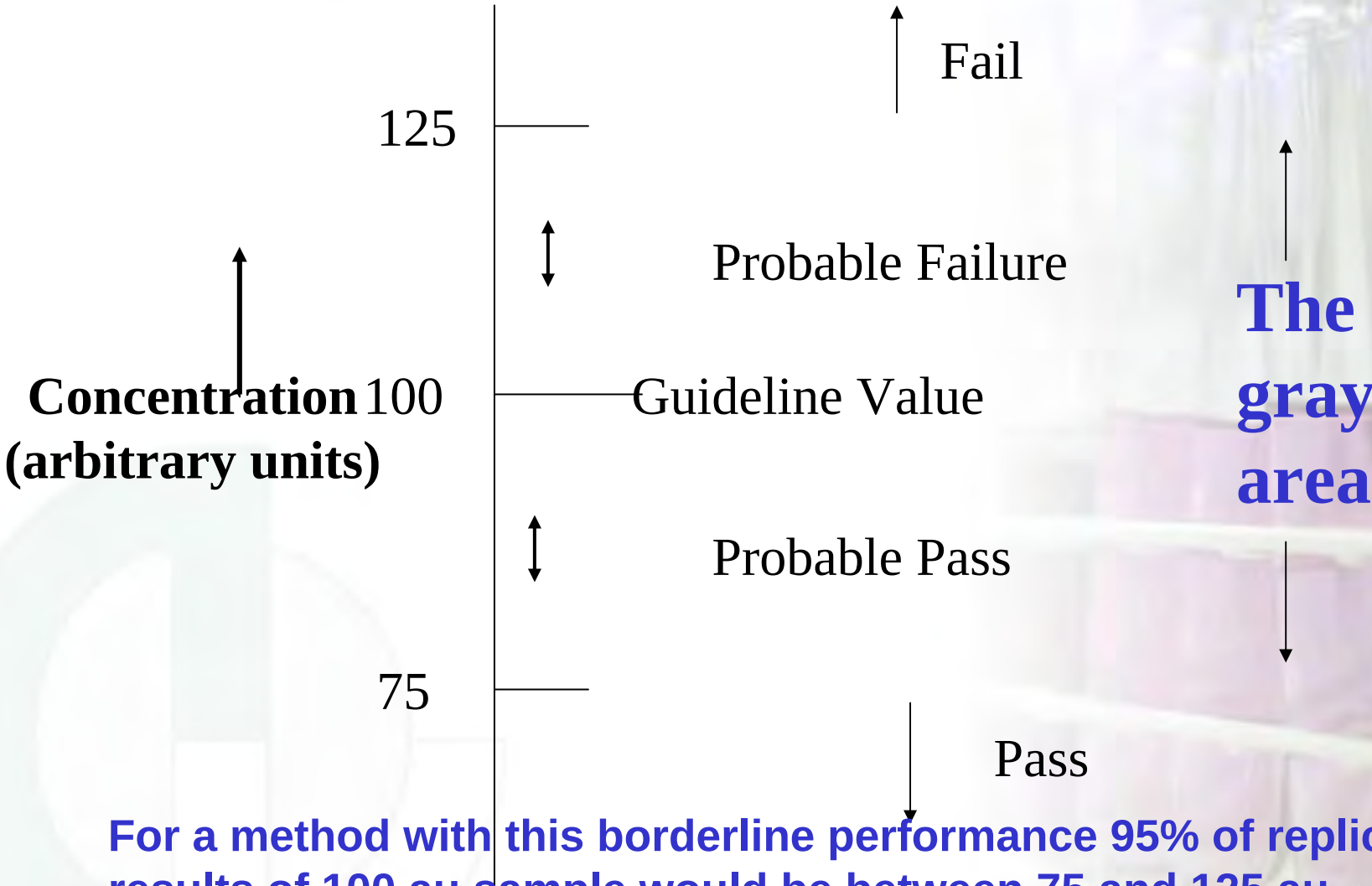
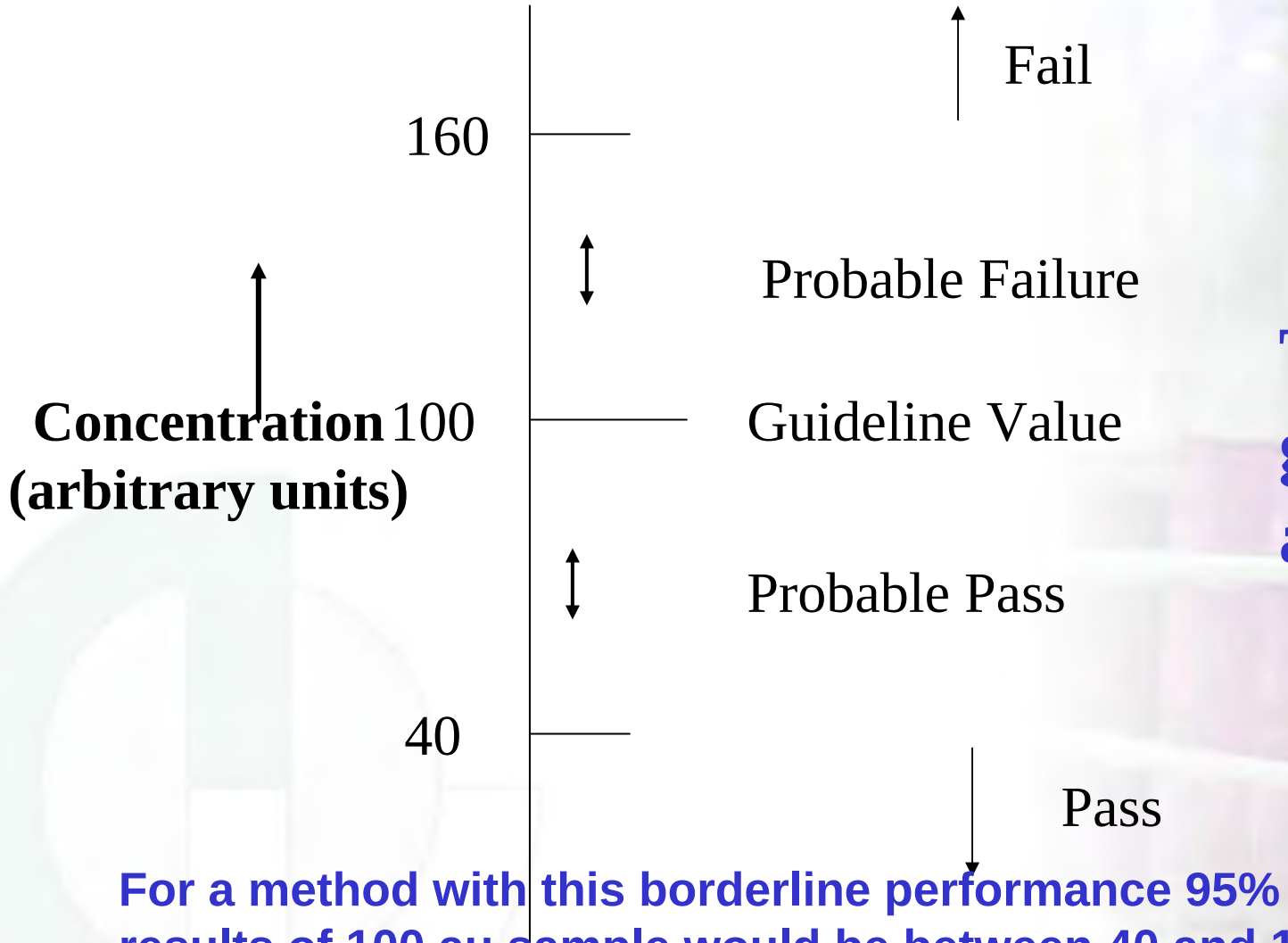
Importance of Result Confidence Limits (1)
(e.g. MCERTS for most toxic metals)



For a method with this borderline performance 95% of replicate results of 100 au sample would be between 75 and 125 au

Importance of Result Confidence Limits (2)
(e.g. MCERTS for all organic parameters)



The gray area

For a method with this borderline performance 95% of replicate results of 100 au sample would be between 40 and 160 au

Uncertainty

Need to aware of potential uncertainty due to both sampling and analysis. For key regulatory parameters it is important to aware of the uncertainty of the results

A result cited on an analysis printout as 95.95 mg/kg is better expressed as 96 ± 40 mg/kg, if this is the associated sampling and analysis uncertainty

Contractors should always liaise with their laboratories as stressed throughout the BS 10175 standard

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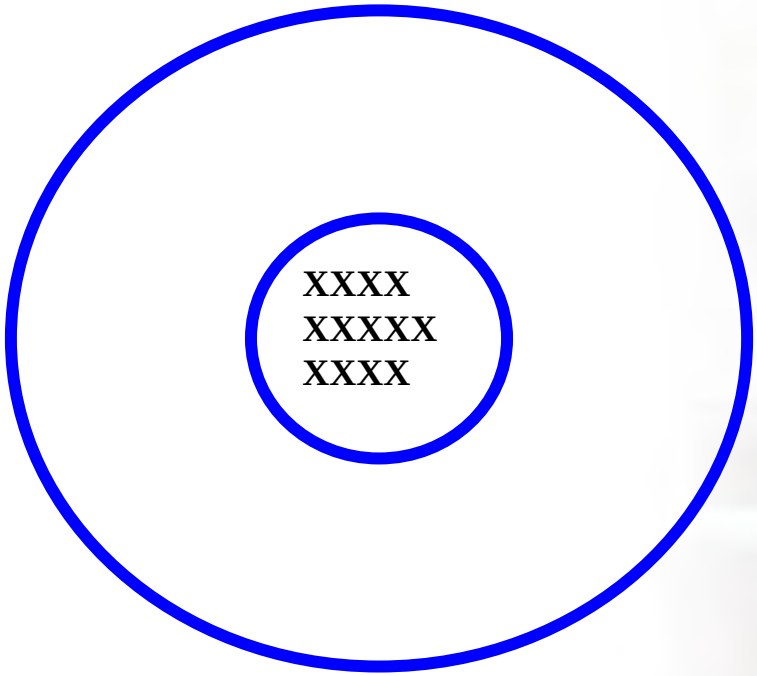
GOOD PRECISION, NEGLIGIBLE BIAS



Desired Analysis Results

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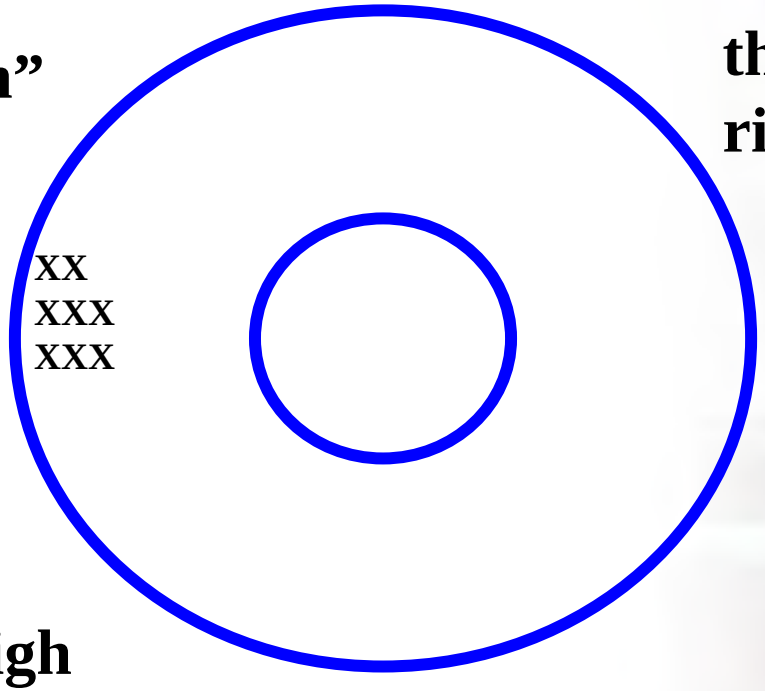
GOOD PRECISION, SIGNIFICANT BIAS

"The repeat analysis result is the same therefore it must be right!!!"

WRONG!

"Precise Rubbish"



Do not equate high precision with accuracy

The more complex the sample matrix, the larger the likely bias

Effect of Method Bias

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Empirical versus Total Measurements

1. **Total measurements can be carried out by any fit for purpose method.**
   E.g. manganese in groundwater can be competently analysed using FAAS; ETA-AAS; ICP-OES; ICP-MS techniques to obtain equivalent results

2. **The results from an empirical method critically depend upon the method used. (e.g. BOD; COD; leaching tests). Often, empirical methods represent a partial extraction/measurement of the analyte from the sample matrix. These needs very prescriptive unambiguous methods**

3. **For many leaching tests significantly less than 1% of the total analyte concentration is extracted**

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QUESTION?

If I am using a CEN/ISO international standard method, my results must therefore be fit for purpose?

ANSWER

NOT NECESSARILY

I DO NOT BELIEVE IT!!!

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Problems of CEN/ISO/BS Standards (1)

1. Relatively easy to produce simple prescriptive methods such as BOD; COD; colour, electrical conductivity etc

2. Very difficult for complex techniques that require high tech equipment (e.g. GC-MS^n; LC-MS^n; ICP-OES; ICP-MS; ETA-AAS. This is overcome by allowing a a large number of options. E.g the phrase "follow the manufacturers instructions" Normally there are not any documented detailed instructions in the standard. This effectively means that the standard is only a guideline standard

3. Tend to compromise and include all participating countries preferred options.

Problems of CEN/ISO/BS Standards (2)

1. Lack of adequate method validation owing to lack of funding and often also due to the lack of volunteer labs.
2. Lack of suitable validation samples and impossible to validate all method options
3. If a revolutionary new technique becomes available, it can take up to ten years to introduce a new standard.
4. Many standards for the more complex methods are really only technical guidance with numerous potential options rather than a “prescribed” standard

Example of the Draft Horizontal CEN Mercury Standard Validation Data

The individual mean accepted lab results for one of the two sludge samples (across the 5 accepted participating labs) were: -

0.89; 0.90; 1.07; 1.31; 1.44 mg/kg.

There were two outlier labs. Thus the data from 2 out of 7 (29%) participating labs were outliers. The mean was 1.2 mg/kg. This was the only sample with a mean mercury level above 1 mg/kg

There were 48 method options

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Three Example of Prescriptive Standards

ISO 6060:1989 Water quality -- Determination of the chemical oxygen demand

ISO 5815-1:2003 Water quality -- Determination of biochemical oxygen demand after n days (BODn) -- Part 1: Dilution and seeding method with allylthiourea addition

BS EN 12457-3:2002
Characterisation of waste — Leaching —Compliance test for leaching of granular waste materials and sludges — Part 3: Two stage batch test at a liquid to solid ratio of 2 l/kg and 8 l/kg for materials with a high solid content and with a particle size below 4 mm (without or with size reduction)

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Round 69 Contest Proficiency Scheme Leaching Results Summary

C18: Air-dried soil ground to pass a 200µm sieve. This sample was prepared by air drying (to approximately 5% moisture), grinding (to less than 200µm particle size) and homogenising. The soil was then divided into portions. The soil sample for this round consisted of a black clayey, ashy sand with some gravel.

This should be regarded as a "best case" sample

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BS 12457-3 Sample Prep Specification

4.3.2 Particle size reduction

The tests shall be made on material with a grain size of at least 95 % (mass) less than 4 mm. Therefore the laboratory sample shall be sieved (4.2.6). If oversized material exceeds 5 % (mass) the entire oversized fraction shall be crushed with a crushing equipment (4.2.5). On no account shall the material be finely ground. Non-crushable material (e.g. metallic parts such as nuts, bolts, scrap) in the sample shall be separated and the weight and nature of the material shall be recorded. The method of size-reduction applied shall be documented and recorded in the test report. Irrespective of any necessary size reduction, the separate fractions with the exception of the non-crushable material and the material that may be used according to note under 5.4, shall be mixed to constitute the test sample. If the laboratory sample cannot be crushed or sieved because of its moisture content, it is allowed, only in this case, to dry the laboratory sample. The drying temperature shall not exceed 40 °C.

Summary of Results for CONTEST Round 69 Leaching Test (1)

Parameter	Median result (mg/litre)	Low (mg/litre)	High (mg/litre)	Standard Deviation (mg/litre)
Chromium (total)	44.6	17.7	70.2	8.7
Chromium (VI)	43.9	17.2	65.2	10.8
Potassium	16.0	11.7	79.4	13.7
Sodium	10.8	6.5	35.0	5.35
Sulphate	319	183	3226	558
Chloride	82.5	42.0	716	123
Nitrate	118	17.5	1661	368
Ammonia	1.83	0.79	12.7	3.37
Phenol Index	2.04	0	51.9	22.5
Conductivity (us/cm)	1244	827	7057	1073
TOC	19.5	11.3	46.4	7.5
Note: - Typically 22 - 27 results for each parameter				

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Summary of Results for CONTEST Round 69 Leaching Test (2)

Parameter	Median result (mg/litre)	Lower satis 2z limit	Upper satis 2z Limit	% Satisfactory results Z = 0 - 2	% Unsatisfactory results Z <3 or >3
Chromium (total)	44.6	36.4	54.6	85.2	7.4
Chromium (VI)	43.9	35.1	52.7	72.2	22.2
Potassium	16.0	12.8	19.2	86.4	9.1
Sodium	10.8	8.6	13.0	78.3	13.0
Sulphate	319	255	382	76.7	13.3
Chloride	82.5	66.0	99.0	59.3	29.6
Nitrate	118	94.5	142	57.7	38.5
Ammonia	1.83	1.46	2.20	57.9	31.6
Phenol Index	2.04	1.63	2.45	20.0	80.0
Conductivity (us/cm)	1244	995	1493	93.3	6.7
TOC	19.5	15.6	23.4	76.0	16.0
pH	10.52	8.42	12.62	93.5	6.5
					Greater than 20%

Notes: -

Best case dried and ground homogeneous sample
Most highly toxic substances close to LOD. Therefore not shown above
Except for chromium, only simple parameters with levels well above LOD shown above

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Comparison of Five Different Bioaccessibility Methods (Environ. Sci. Technol., 2002, (36), 3326 – 3334)

	Soil 1	Soil 2	Soil 3
Arsenic	6 - 95%	1 - 19%	10 - 59%
Cadmium	7 - 92%	5 - 92%	6 - 99%
Lead	4 - 91%	1 - 56%	3 - 90%

This slide illustrates the problems with empirical methods where the method protocol defines the result.

"The application of bioaccessibility can only be justified by the provision of a significant body of supporting evidence that the methodology was scientific, robust and reproducible, and that the uncertainties were taken into account in any conclusions. Given the current uncertainties associated with bioaccessibility testing, we consider its application to be limited at this time"

http://www.environment-agency.gov.uk/static/documents/3-science_update_02_1793841.pdf

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Conclusions (1)

1. **ISO 17025 alone is not sufficient accreditation for fit for purpose environmental analysis**
2. **For “total” methods the UK MCERTS accreditation approach is recommended where laboratories can employ any fit for purpose method after demonstrating initial validation across all matrices and then demonstrating ongoing QA/QC compliance to retain accreditation**
3. **For all empirical methods a single prescribed method must be used for the relevant step(s)**
4. **MCERTS has vastly improved the quality of analysis associated with contaminated land site investigations**
5. **Clients should regularly liaise with their laboratory**

Conclusions (2)

6. **The post A level teaching of environmental analytical chemistry needs to be improved. The Open University distance learning approach with their completely new Analytical Science Foundation Degree is to be commended.**
   Effectively an Apprenticeship Scheme

There is a seminar at RSC Chemistry Centre on Thurs 11th Nov entitled: -
The Open University Foundation Degree in Analytical Science: Year 1 Review and the Way Forward

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Conclusions (3)

7. The RSC Register of Analytical Chemists is to close: -

Existing RSC Website wording from early 1990s: -

"The high standards of professional conduct and the importance of the role of specialists in the field of analytical chemistry has been recognised throughout our industrialised history. In response to this demand the Royal Society of Chemistry has published the Register of Analytical Chemists. The aim of the register is to publish the names of competent analytical chemists, for the benefit of employers, enforcement agencies and the general public. This register contains the names and addresses of those members of the Royal Society of Chemistry who have demonstrated a general knowledge of the subject of Analytical Chemistry, and established specific knowledge and experience in the principles and practice applicable to their own specialist field"

Conclusions (4)

9th June 2010

Dear Professor Thompson,

Re: Closure of the Register of Analytical Chemists

I am writing to let you know that the RSC will be closing the Register of Analytical Chemists from 31st December 2013.

The main reasons for closing the register are:

1.The benefits to members are not as great as was anticipated when the register was introduced in the early 1990s.

2.Legislation, envisaged at the time, has not been forthcoming and therefore being on the register is not a requirement or licence to practice.

3.Numbers on the register have been diminishing for several years and now stand at less than 80 of which only 14% are evidencing their continuing professional development.

4.The main assessment route to the register (i.e. NVQ level 5 in analytical chemistry) is being withdrawn due to lack of demand.

The cost of administering the register has to be considered in respect of giving value to our members.

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The bitter end!!!

Thank you for bearing with it.

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