



## **Codex Methods of Analysis: What, When, Why, How to Use?**

**IAM/MoniQA FST Workshop, Sunday, 7 March 2010**

### **Compliance and measurement uncertainty in analysis - where we are and what the Codex Commodity Committees need to appreciate**

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## **MEASUREMENT UNCERTAINTY – ANALYSIS and now SAMPLING**

Measurement uncertainty has been a contentious issue for analytical chemists for many years. It has been considered in a number of papers. In the majority of cases these papers have concentrated on how measurement uncertainty is to be estimated.

It is only recently that there have been discussions on how measurement uncertainty is to be used.



*Problems that we now face*

**CODEX COMMITTEE ON METHODS OF ANALYSIS  
AND SAMPLING: Thirty-first Session  
Budapest, Hungary, 8 – 12 March 2010**

**CX/MAS 10/31/4: PROPOSED DRAFT REVISED  
GUIDELINES ON MEASUREMENT UNCERTAINTY**

Emphasis is on what we do with MU, not how we measure it.



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OF SAMPLING**

Emphasis is on whether we should think about sampling uncertainty or take a “pragmatic” approach.



Method performance criteria are well defined –  
emphasis on collaborative trials for their validation

Laboratory quality is well defined – emphasis on  
accreditation



**GUIDELINES FOR THE ASSESSMENT OF THE  
COMPETENCE OF TESTING LABORATORIES  
INVOLVED IN THE IMPORT AND EXPORT CONTROL  
OF FOOD**

Adopted by the Commission at Step 8 in June 1997



### **What do these mean?**

- Accreditation
- Proficiency Testing
- Internal quality control
- Method validation

### ***Others not mentioned in Guidelines:***

- Recovery
- Single laboratory validation



## **CODEX GUIDELINES ON MEASUREMENT UNCERTAINTY**

**(CAC/GL 54-2004)**

### **Introduction**

It is important and required by ISO/IEC 17025:1999 that analysts are aware of the uncertainty associated with each analytical result and estimates that uncertainty. The measurement uncertainty may be derived by a number of procedures. Food analysis laboratories are required, for Codex purposes, to be in control, use collaboratively tested or validated methods when available, and verify their application before taking them into routine use. Such Laboratories therefore have available to them a range of analytical data which can be used to estimate their measurement uncertainty.



These guidelines only apply to quantitative analysis.

Most quantitative analytical results take the form of

“ $a \pm 2u$  or  $a \pm U$ ”

where “ $a$ ” is the best estimate of the true value of the concentration of the measurand (the analytical result) and “ $u$ ” is the standard uncertainty and “ $U$ ” (equal to  $2u$ ) is the expanded uncertainty. The range “ $a \pm 2u$ ” represents a 95% level of confidence where the true value would be found. The value of “ $U$ ” or “ $2u$ ” is the value which is normally used and reported by analysts and is hereafter referred to as “measurement uncertainty” and may be estimated in a number of different ways.



## Terminology

**Measurement uncertainty:** Non-negative parameter characterizing the dispersion of the values being attributed to a measurand, based on the information used.

### Notes:

Measurement uncertainty includes components arising from systematic effects, such as components associated with corrections and the assigned values of measurement standards, as well as the definitional uncertainty. Sometimes estimated systematic effects are not corrected for but, instead associated measurement uncertainty components are incorporated.

The parameter may be, for example, a standard deviation called standard measurement uncertainty (or a given multiple of it), or the half-width of interval having a stated coverage probability.



Measurement uncertainty comprises, in general many components. Some of these components may be evaluated by Type A evaluation of measurement uncertainty from the statistical distribution of the values from a series of measurements and can be characterized by experimental standard deviations. The other components which may be evaluated by Type B evaluation of measurement uncertainty can also be characterized by standard deviations, evaluated from assumed probability distributions based on experience or other information.



In general, for a given set of information, it is understood that the measurement uncertainty is associated with a stated quality value attributed to the measurand. A modification of this value results in a modification of the associated uncertainty.

Reference:

VIM, International Vocabulary of Metrology – Basic and general concepts and associated terms, 3<sup>rd</sup> edition, JCGM 200: 2008



## Recommendations

1. The measurement uncertainty associated with all analytical results is to be estimated.



2. The measurement uncertainty of an analytical result may be estimated by a number of procedures, notably those described by ISO (1) and EURACHEM (2). These documents recommend procedures based on a component-by-component approach, method validation data, internal quality control data and proficiency test data. The need to undertake an estimation of the measurement uncertainty using the ISO component-by-component approach is not necessary if the other forms of data are available and used to estimate the uncertainty. In many cases the overall uncertainty may be determined by an inter-laboratory (collaborative) study by a number of laboratories and a number of matrices by the IUPAC/ISO/AOAC INTERNATIONAL (3) or by the ISO 5725 Protocols (4).



3. The measurement uncertainty and its level of confidence must, on request, be made available to the user (customer) of the results.



### **Does Measurement Uncertainty Apply to both Sampling and Analysis?**

Measurement uncertainty applies to the whole measurement process. For analysts only “analytical” measurement uncertainty has been considered but it is now increasingly being recognised that the whole system must be considered, and so “sampling” measurement uncertainty is gaining an increasing importance.



### **What is the Relationship between Measurement Uncertainty, the Analytical Result and the Method Used to Obtain the Result?**

It is the estimation of the measurement uncertainty associated with an analytical result that is important. Measurement uncertainty is not associated with a method.



### **Measurement Uncertainty and ISO/IEC 17025:2005**

The estimation of measurement uncertainty is an integral part of the accreditation process. The 17025 Standard states that measurement uncertainty must be estimated and then made available to the customer if requested by the customer



### **Use of Measurement Uncertainty and Definition of a Dispute Situation**

If the value after deduction is still greater than the specification, then it may be stated, ***beyond reasonable doubt***, that the sample is not compliant with the specification.

#### **Procedural Manual: Measurement Uncertainty**

An allowance is to be made for the measurement uncertainty when deciding whether or not an analytical result falls within the specification. This requirement may not apply in situations when a direct health hazard is concerned, such as for food pathogens.



### **Values of Measurement Uncertainty Estimations**

There is concern that some laboratories underestimate the size of their uncertainties and report unrealistically small uncertainties to their customers.

For chemical analyses, using the results from collaborative trials, it would not be unreasonable to anticipate that the (expanded) uncertainties reported by laboratories would be of the following orders:



**Concentration      Expanded Uncertainty Range      of Acceptable Concentrations**

100g/100g	4%	96 to 104g/100g
10g/100g	5%	9.5 to 10.5g/100g
1g/100g	8%	0.92 to 1.08g/100g
1g/kg	11%	0.89 to 1.11g/kg
100mg/kg	16%	84 to 116mg/kg
10mg/kg	22%	7.8 to 12.2mg/kg
1mg/kg	32%	0.68 to 1.32mg/kg
< 100µg/kg	44%	56 to 144µg/kg



**Procedures for Estimating Measurement Uncertainty**

There are many procedures available for estimating the measurement uncertainty of a result. Some of the more common of these are outlined by my colleagues.

But all available information should be used to avoid duplication of work.



## **Next Week's Papers**

**Guidance on measurement uncertainty**

**Guidance on uncertainty from sampling**



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Emphasis is on what we do with MU, not how we measure it.

Very simple guidance

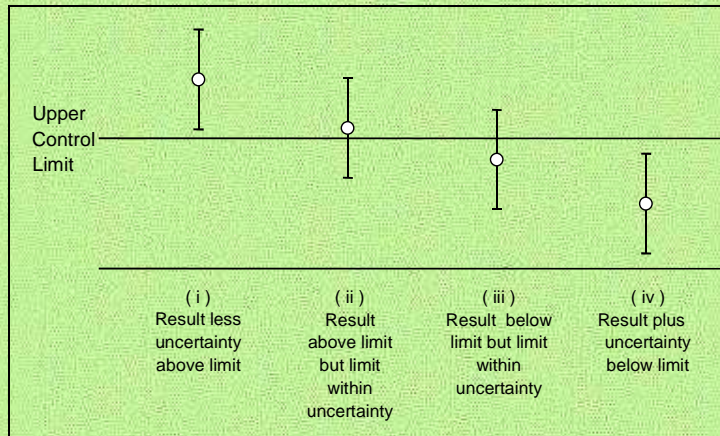


## **EXPLANATORY NOTES TO THE CODEX GUIDELINES ON MEASUREMENT UNCERTAINTY**

1. What is Measurement Uncertainty?
2. Does the Measurement Uncertainty have to be Estimated in Codex?
3. Does Measurement Uncertainty Apply to both Sampling and Analysis?
4. What is the Relationship between Measurement Uncertainty, the Analytical Result and the Method Used to Obtain the Result?
5. Procedures for Estimating Measurement Uncertainty



6. Considerations when Estimating Measurement Uncertainty within the Context of Codex
7. Values of Measurement Uncertainty Estimations
8. Significance of the Section in the Procedural Manual of the “use of analytical results: sampling plans, relationship between the analytical results, the measurement uncertainty, recovery factors and provisions in Codex Standards” (from Codex Procedural Manual, 18th Edition)
9. Use of Measurement Uncertainty and Definition of a Dispute Situation
10. Useful References



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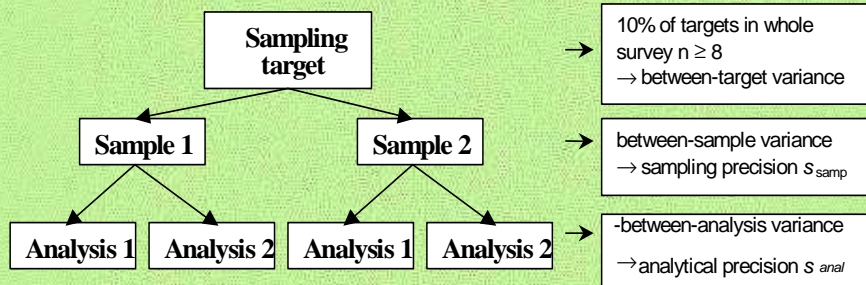


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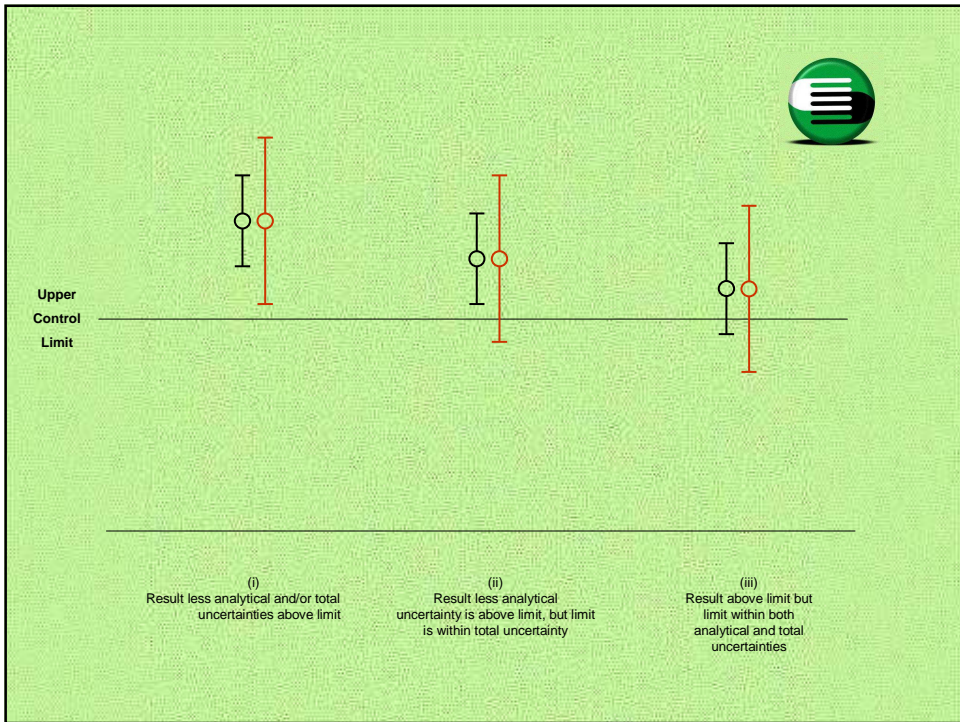
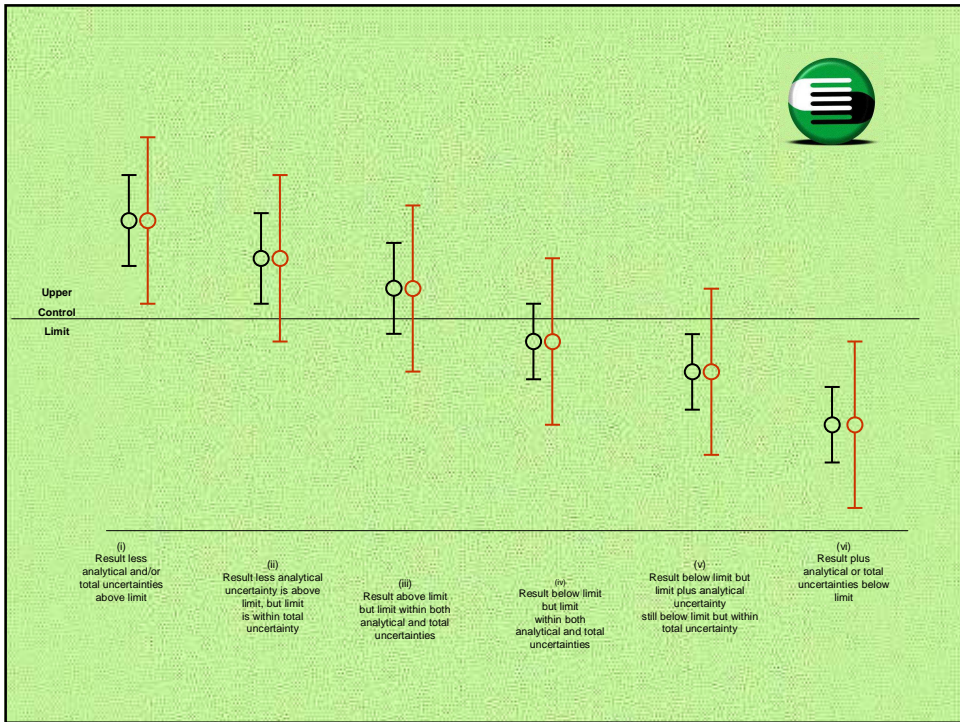
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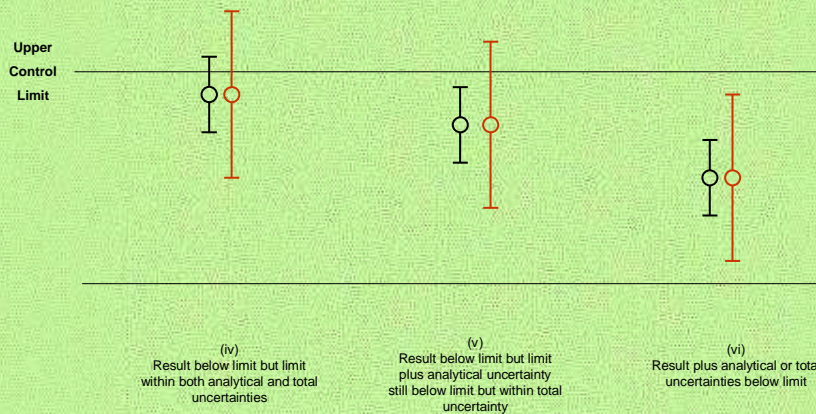


6. Procedures for Estimating Measurement Uncertainty
7. Duplicate method – general principles



8. Considerations when Estimating Measurement Uncertainty within the Context of Codex
9. Values of Measurement Uncertainty Estimations
10. Significance of the Section in the Procedural Manual of the “use of analytical results: sampling plans, relationship between the analytical results, the measurement uncertainty, recovery factors and provisions in Codex Standards” (from Codex Procedural Manual, 18th Edition)
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## Conclusions

Measurement uncertainty has to be estimated.

Important that we do not do extra work – method verification will help here.

Need colleagues to understand significance of MU.

MU vital when assessing compliance.

Where do we go with sampling uncertainty?