Eurachem

A focus for analytical chemistry in Europe

Reporting results and assessment of compliance

Eurachem workshop

Quality in Analytical Measurements

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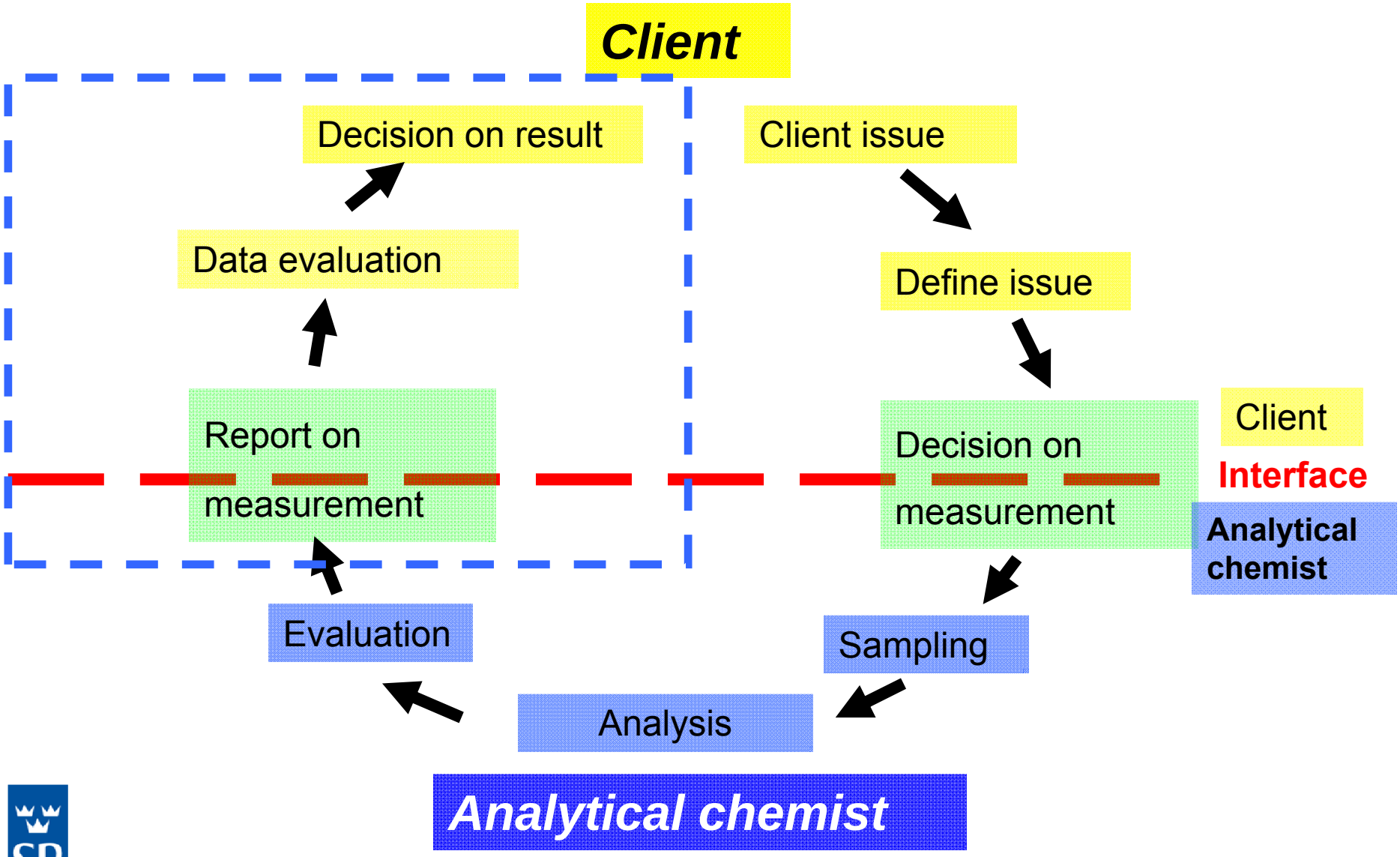
The measurement cycle



Content

Reporting results

- What have been measured
  - The measurand including the sample, the test item
- The sampling target – laboratory sample or ?
- ISO recommendations for reporting
- Reporting and number of significant figures
- Info about quality/accreditation and method/procedure

For compliance assessment we need

- External or internal specification/legal limit etc
- Measurement result
- Decision rule

Summary

Correct reporting of results

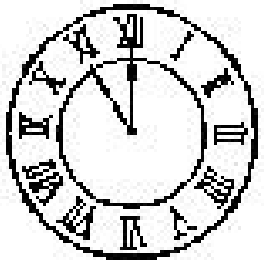
accurately, clearly, unambiguously and objectively,

and in accordance with

any specific instructions in the test …method.

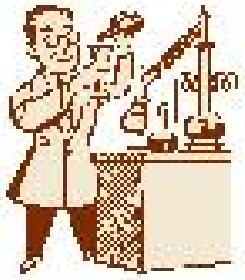
(ISO/IEC 17025)

Corrected reported we may compare results and assess compliance



Time

Place



Laboratory/operator/procedure

Specification of measurand (VIM3*)

Measurand - **quantity** intended to be measured

NOTE 1 The specification of a measurand requires knowledge of the

- kind of quantity
- description of the state of the phenomenon, body, or substance carrying the quantity including any relevant component,
- the chemical entities involved.

Measurement object/test item

Example of a measurand specification

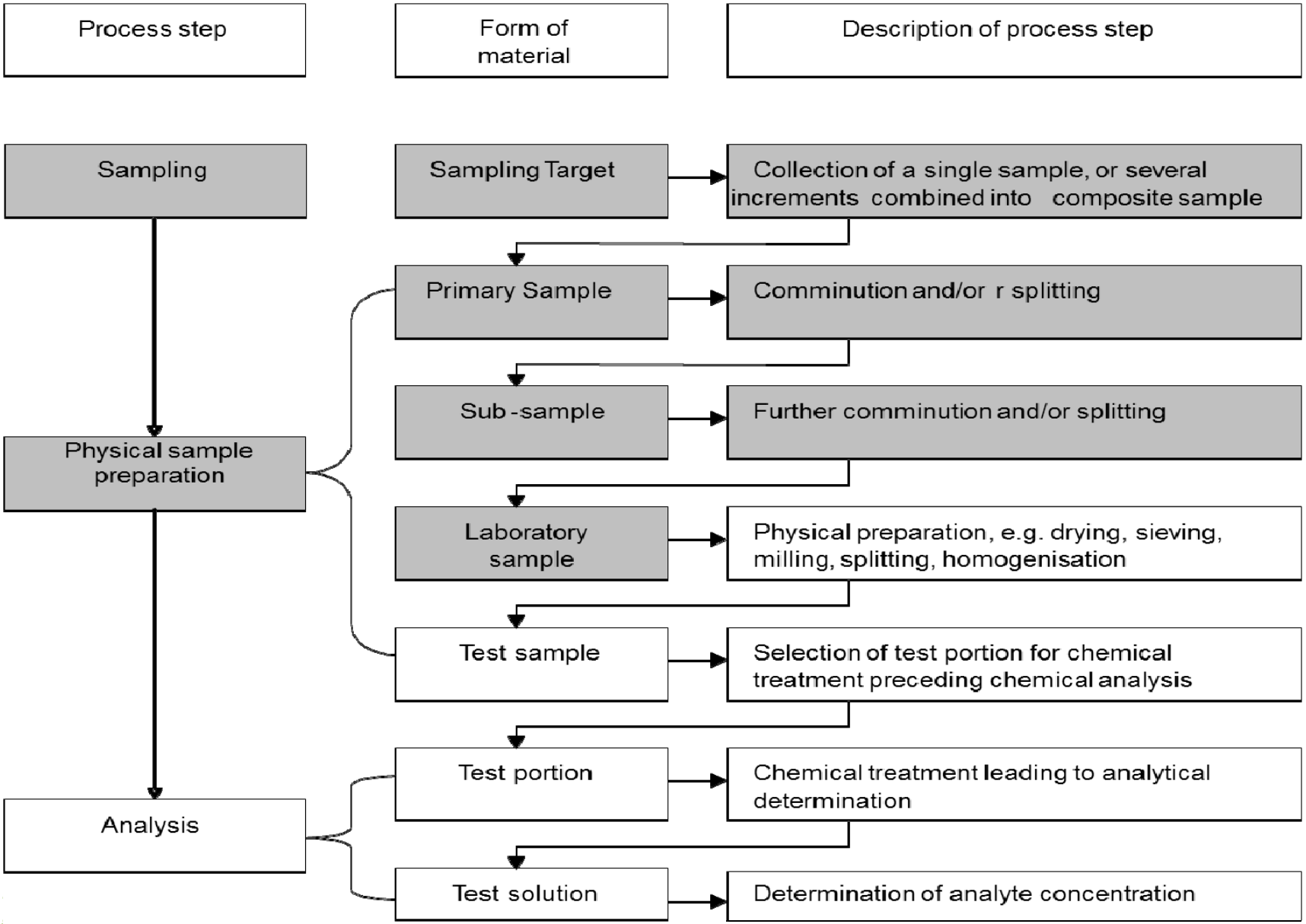
mass fraction of total Cd in mg/kg in a

certain soil batch

reported on dry mass basis (105 °C, 2h)

*ISO Guide 99 (2007) International Vocabulary of Metrology – Basic and General Concepts and Associated Terms VIM 3rd edition, ISO, Geneva

Sampling target



Some ISO recommendations for reporting measurement results

For writing ISO standards the following is recommended regarding reporting results*

Issue	Recommended	Not recommended
Clear indication of unit	23 °C ± 2 °C or (23 ± 2) °C	23 ± 2 °C
Separate information and unit	the water content is 20 ml/kg and not “	20 ml H2O/kg or 20 ml of water/kg
Do no mix units	(230 ± 11,5) V	230 V ± 5 %

*ISO/IEC Directives, Part 2, Edition 6.0, Rules for the structure and drafing of Inernational Standards, ISO/IEC, Geneva, (2011).

How to report high uncertainties

For analysis with high uncertainty

e.g. result 1 % lower 0,5 % and higher 2 %

I report *ca 1 %*

Discussion with your colleagues – How to avoid gross errors in reporting

Which questions shall i ask myself?

Think about you own experience!

What errors could we avoid?

I will later give you some examples of errors

How to report

If we now trust

definition of the measurand

the result and

its uncertainty

Reporting results and significant figures

It suffice to quote $u_c(y)$ and U to at most two significant digits, although in some cases it may be necessary to retain additional digits to avoid round-off errors in subsequent calculations ”
(GUM 7.2.6)

The number of decimals for the result and the uncertainty is the same.
Example from Eurachem Uncertainty guide

Total nitrogen: (3.52 ± 0.14) g/100 g *

*The reported uncertainty is an expanded uncertainty calculated using a coverage factor of 2 which gives a level of confidence of approximately 95 %.

Base for reporting?

Basis for reporting

For some hygroscopic sample types the basis for reporting is crucial

Some examples – Result is reported on:

- dry mass basis (105 °C 2h)
- dry mass basis (80 °C 2h) according to ISO xxx
- sample equilibrated according to ISO xxx
- ignited basis (800 °C 1h)

And if no treatment is performed it might be importatnt to state **that**

Example of wording is here ”as reveived” or ”as is”

Info about quality/accreditation and method/procedure

For accredited methods the accreditation body logo is mandatory for all test results issued by the laboratory

According to ISO/IEC 17025 – regarding reporting results

*reference to the sampling plan and **procedures** used by the laboratory or other bodies where these are relevant to the validity or application of the results;*

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- Decision rule

Summary

Compliance

According to ISO/IEC 17025 a test report shall, where necessary for the interpretation of the test results, include:

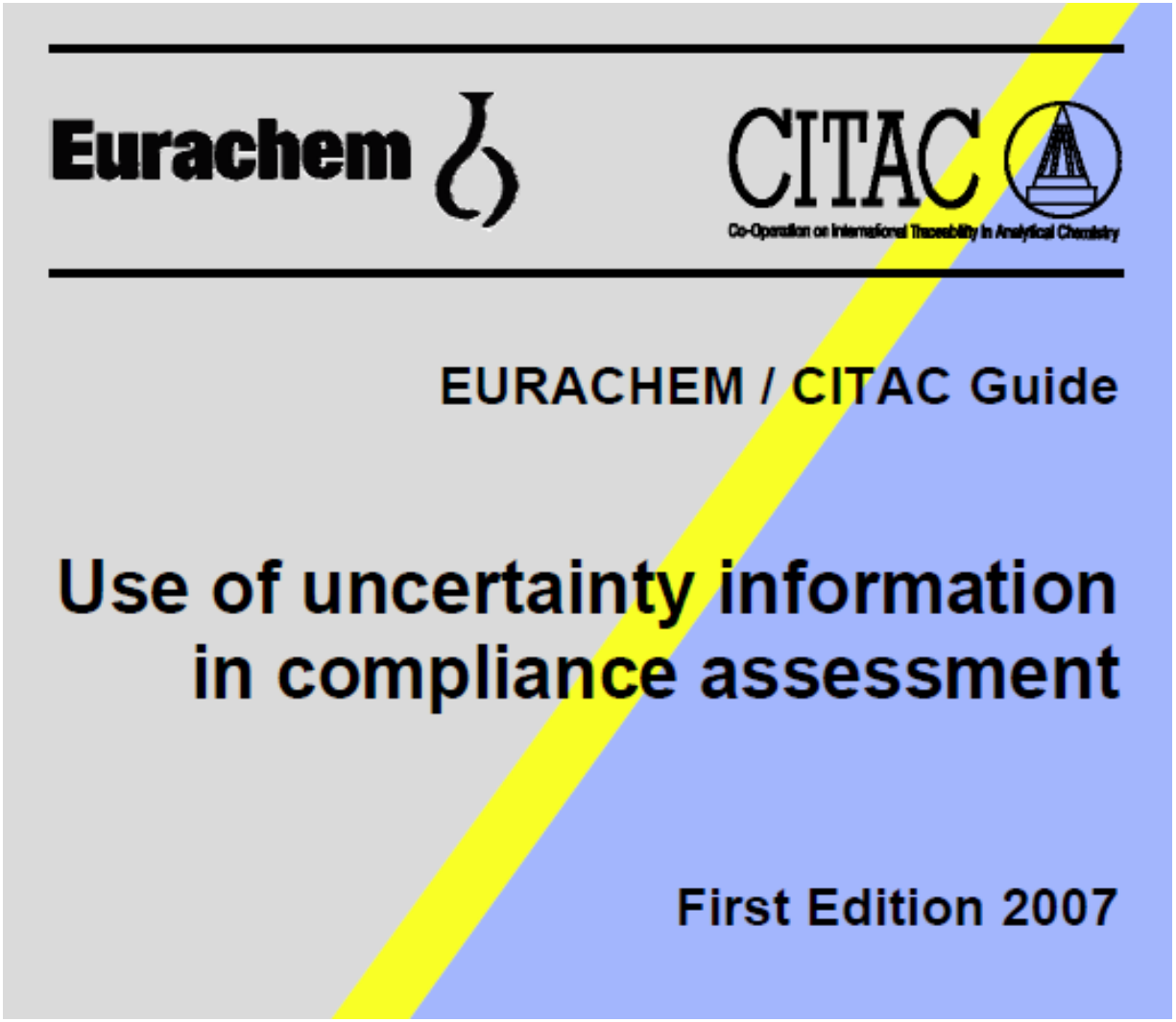
…..

•where relevant, a statement of compliance/non-compliance with requirements and/or specifications

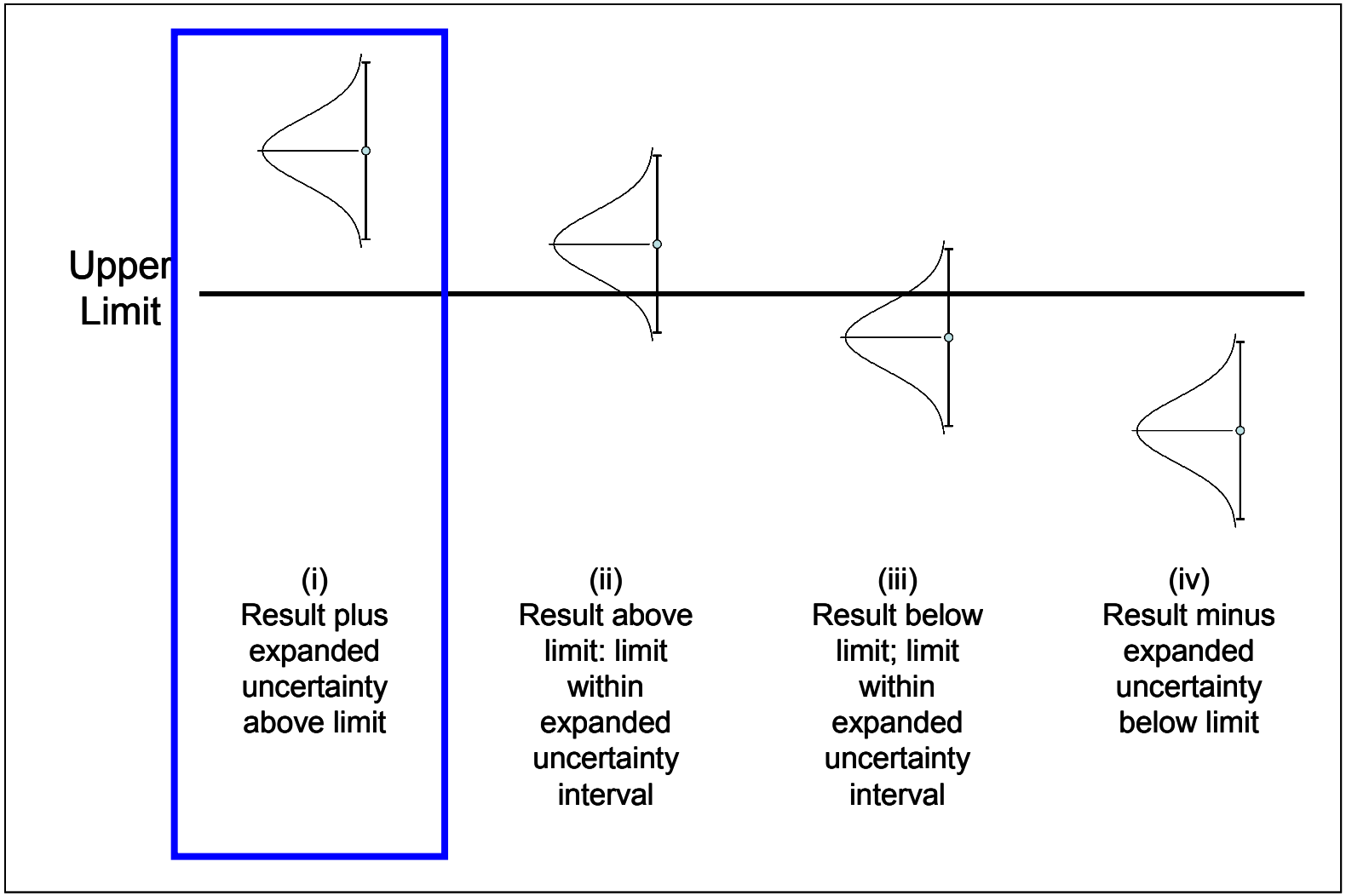
•where applicable, a statement on the estimated uncertainty of measurement; information on uncertainty is needed …when the uncertainty affects compliance to a specification limit;

•….

Eurachem guide on compliance by Uncertainty and Traceability WG



Four results with uncertainty and an upper limit



Lets us first look at terminology

Terminology

- *decision rule:* a documented rule that describes how measurement uncertainty will be allocated with regard to accepting or rejecting a product according to its specification and the result of a measurement.
- *acceptance zone:* the set of values of a characteristic, for a specified measurement process and decision rule, that results in product acceptance when a measurement result is within this zone.
- *rejection zone:* the set of values of a characteristic, for a specified measurement process and decision rule, that will give non-compliance when a measurement result is within this zone.
- *guard band, g:* the magnitude of the offset from the specification limit to the acceptance or rejection zone boundary
- decision limit – the point between the rejection and acceptance zone

Lets look at a legal case

Blood alcohol - a result clearly over an upper limit

Sample taken from a driver in Sweden and analysed at a laboratory

Analytical Report

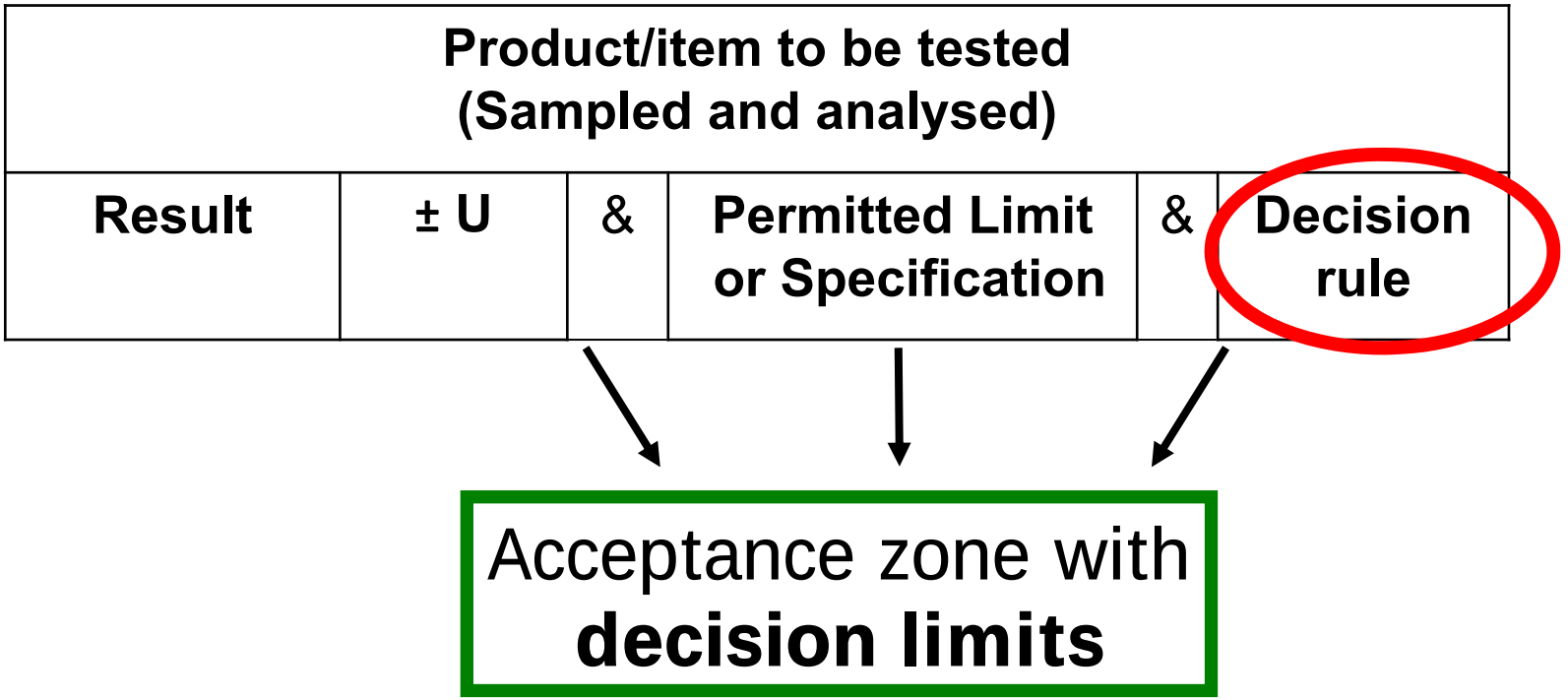
- Mass fraction of ethanol in blood sample is **0,221 mg/g ± 0,013 (k=2)**

Limit in Sweden is 0,200 mg/g

(20 mg/100g)

Will this driver be punished?

Using a decision rule we calculate an acceptance zone



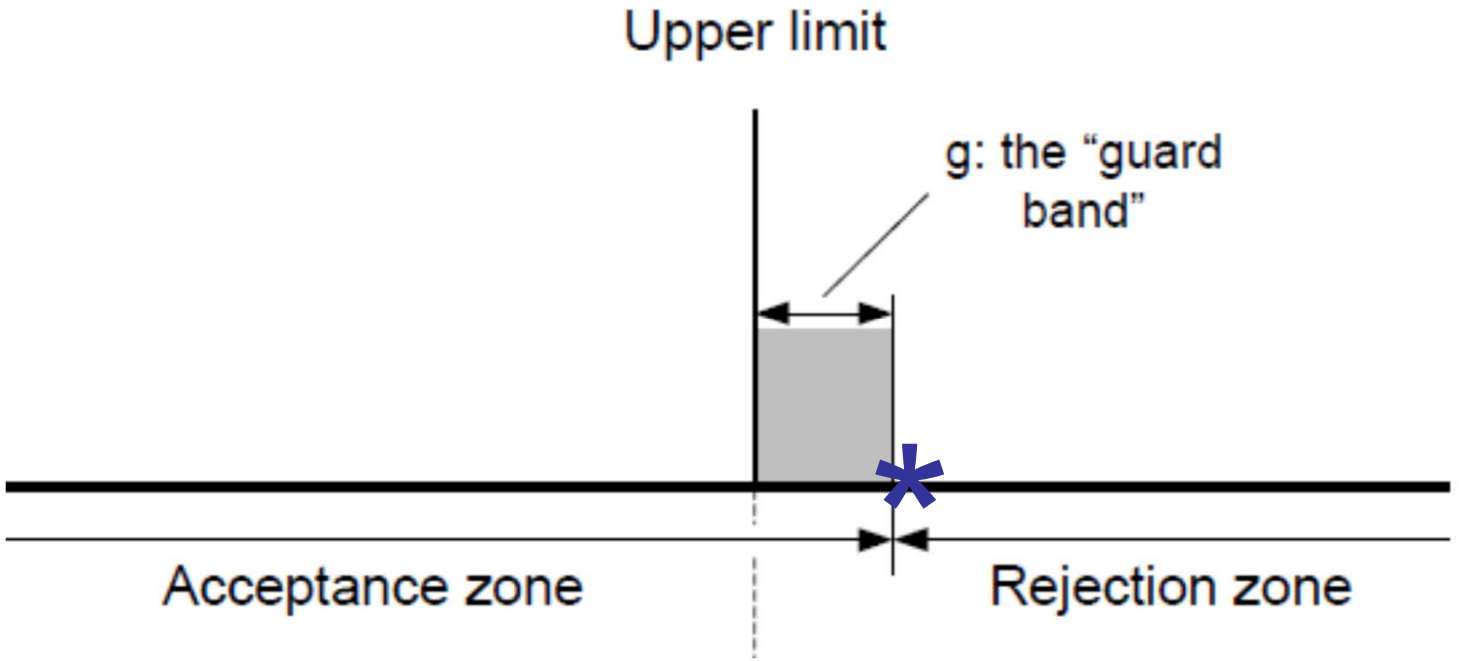
In legal cases we must be very sure (> 99 %) that the “true” value of the measurand is OVER the permitted limit.

Regarding a product specification we must be sure (>95 %) that the value of the measurand is BELOW an upper specification.

Acceptance zone for a legal case with an upper limit

Upper limit is 0.200 mg/g
From decision rule is calculated a guard band.
The guard band is 0.02 mg/g

* **Blood alcohol**
  Measurement result 0,221 mg/g



We repeat this example – Blood sample from a driver to be tested for alcohol content

- Measurement of blood alcohol where we want to be sure to only punish those drivers that truly has exceeded the limit
- Measurement procedure: *Ethanol in blood by Head-Space GC*
- *Quality routine: Two independent results – different analysts using different instrument - Max difference (range) 0,003 mg/kg*

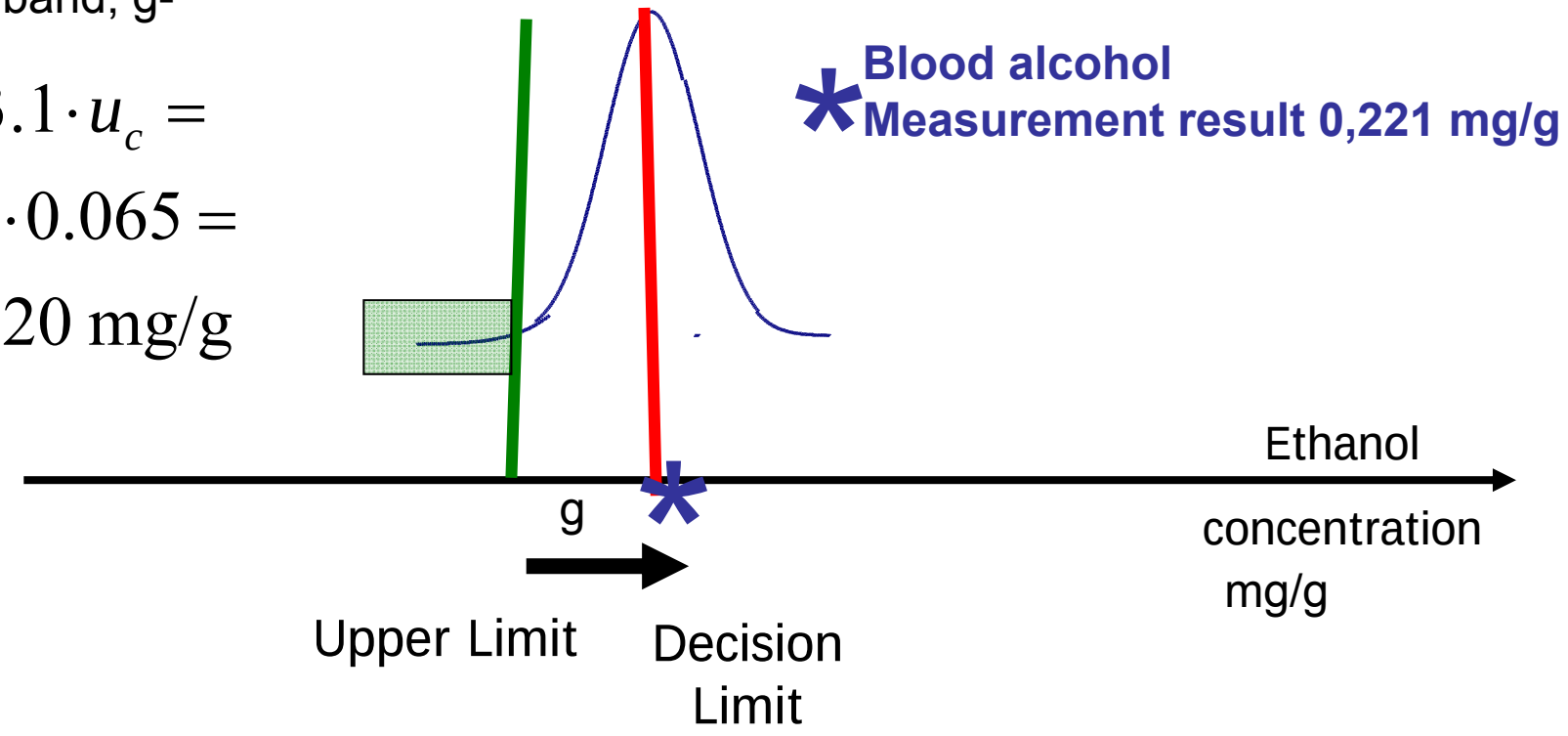
1. Measurand – Massfraction total EtOH in a laboratory blood sample
2. Analytical result - C (EtOH)= 0,221 mg/g
3. Uncertainty – U = 0,013 mg/g, k=2 (95 %),
   combined standard uncertainty, u_c is 0.0065 mg/g.
4. "Specification" – Upper permitted limit 0,200 mg/g
5. Decision rule - *The decision limit is the concentration above which it can be decided with a statistical certainty **of about** 99.9 %*
   (alfa =0,001) that the permitted limit has been truly exceeded

For calculation of guard band - one sided 99.9 % t = 3.1

Probability that the true value of the measurand is over the limit is high (about 99.9 %)

Calculation of guard band, g-

$$g = 3.1 \cdot u_c =$$
$$= 3.1 \cdot 0.065 =$$
$$= 0{,}020 \text{ mg/g}$$



What do we need for compliance assessment?

1. A measurand clearly specified including the **measurement object/test item**
2. An analytical result
3. The uncertainty – For an expanded uncertainty the k factor and the corresponding confidence level should be stated e.g. k = 2 for 95 % confidence
4. A specification giving upper and/or lower limits
5. A decision rule

Example of a decision rule

Decision rule

The batch will be considered to be non-compliant if the probability of the value of the concentration being greater than the upper limit exceeds 95%

1.A specification of the measurand including the object/test item

Batch

2.An analytical result - Single value, mean value, each single value?

Mean value

3.An uncertainty - Normally an expanded uncertainty at 95% confidence level

4.A specification giving upper and/or lower permitted limits

Upper limit

5.A decision rule how to take measurement uncertainty into account

Non-compliant if probability for out of specification is higher than 95%

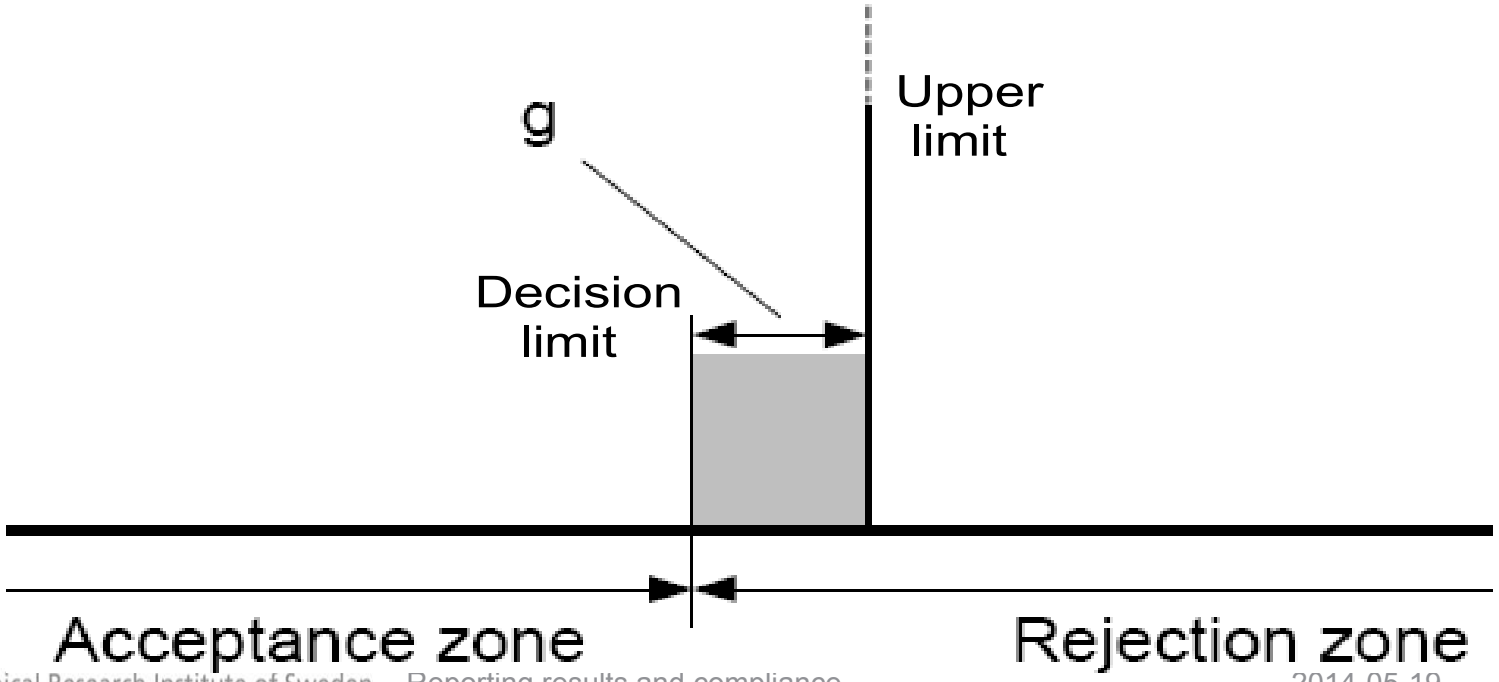
Example - Sludge from water purification plants

Sludge from water purification plants can be used for soil improvement. One of the toxic metals that can be a problem is cadmium. The upper limit on the total cadmium in sludge is set to 2 mg/kg.

1. Measurand – Mass fraction of cadmium, Cd, in a consignment delivered to a customer
2. Analytical result - mass fraction (Cd) = 1.82 mg/kg
3. Uncertainty – U = 0.20 mg/kg, k = 2 (95 %). Standard uncertainty, u = 0.10 mg/kg. The uncertainty includes both sampling and analytical uncertainty
4. Specification – Upper permitted limit 2.0 mg/kg
5. Decision rule - *The decision limit is the mass fraction where it can be decided with a confidence level of approximately 95 % (α=0.05) that the batch has a mass fraction* ***below*** *the upper limit.*

Conformity assessment – Cd result 1.82 mg/kg

- The guard band is calculated as 1.65*u* = 0.165 mg/kg with *k* value 1.65 for one tailed *t* value at 95 % confidence.
  The decision limit will be 2 – 0.165 = 1.84 mg/kg. All values below this value are in the acceptance zone. All values equal to or above are in the rejection zone.
  The sludge sample meets the compliance requirements.



One sided and two sided confidence intervals

Upper permitted limit

Then decision limit at:

95 % result + 1,6 u

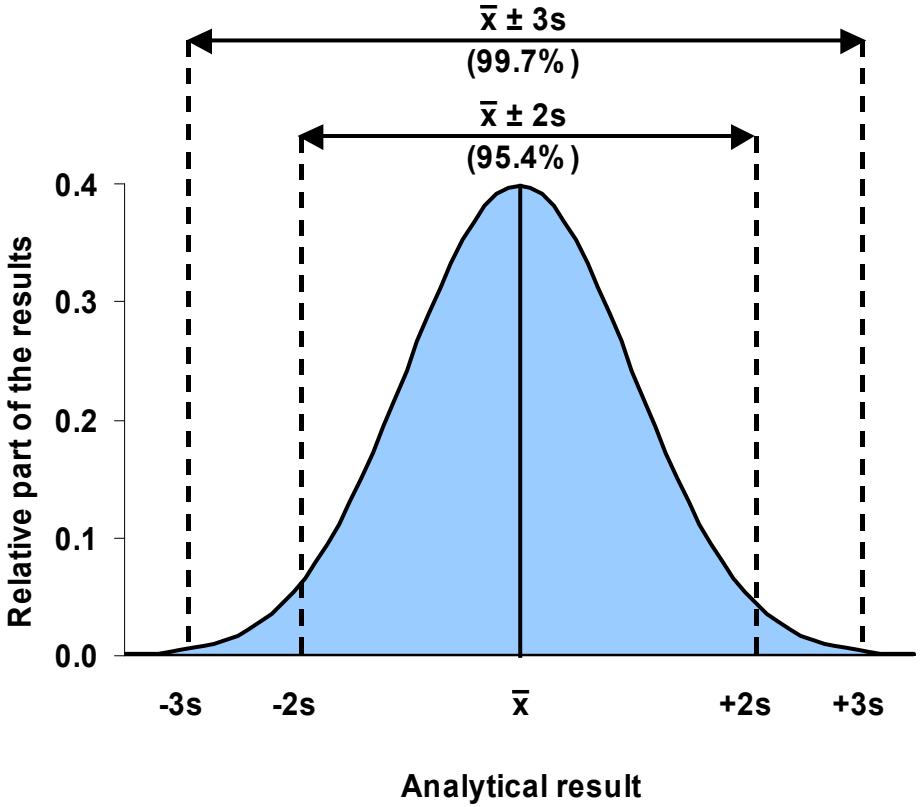
99,9 % result + 3,09 u

where u is the standard uncertainty

Measurement result

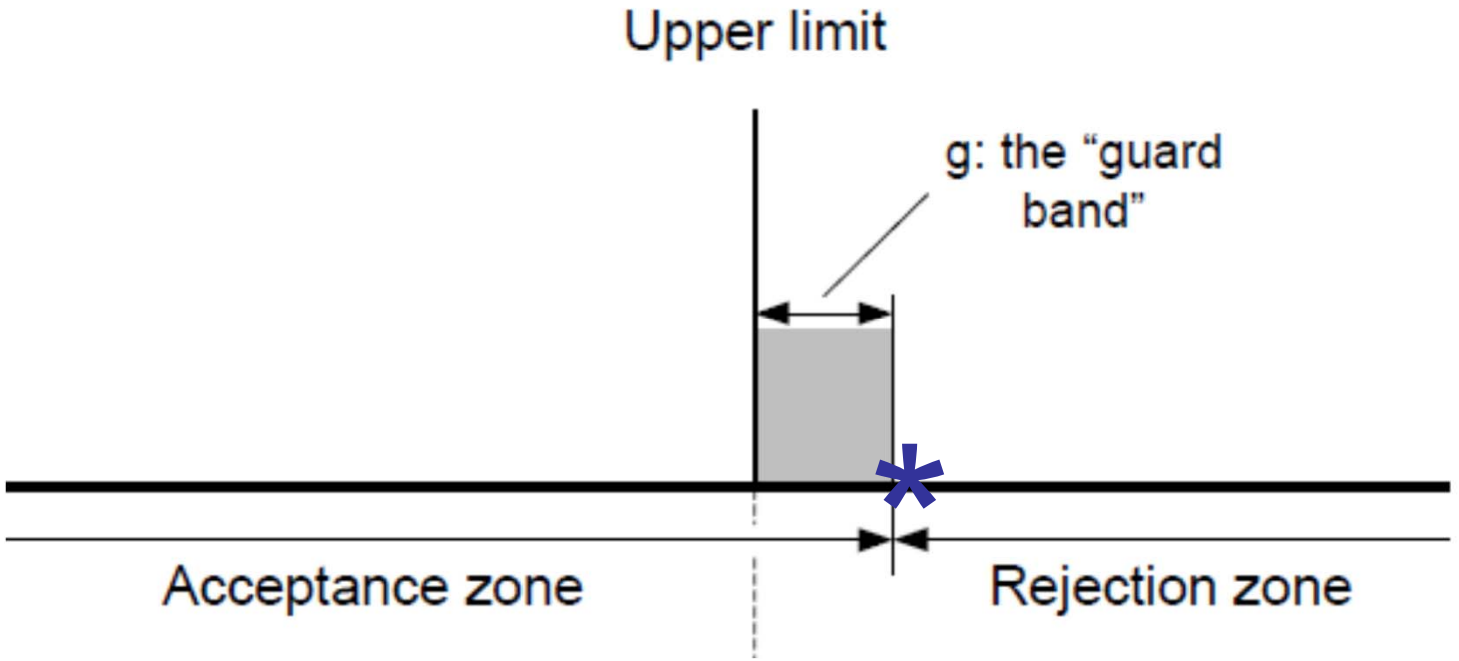
Confidence interval

95 % result ± 2 u



Acceptance & rejection zones for a legal case

Case: An upper permitted limit (legal case).
Decision rule – for non compliance , rejection we should be very sure that the true value of the measurand is greater than the limit



Example of Toy testing according to EN 71-3 Safety regulations – Part 3: Migration of certain elements

This standard refers to Eurachem Guide for calculation of the guard band. In this case the guard band is used as an analytical correction on the results

The analytical correction of the test result is 30 to 60 % before comparing the test result with a limit value

SP Technical Research Institute of Sweden

Assignment – test of a perambulator

Parts sampled according to EN1888 and test of parts according to European standard EN 71-3. Toys - Safety regulations - Part 3: Migration of certain elements.

- A = White paint coating
- B = White plastic
- C = Blue plastic

After leaching the elements were determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

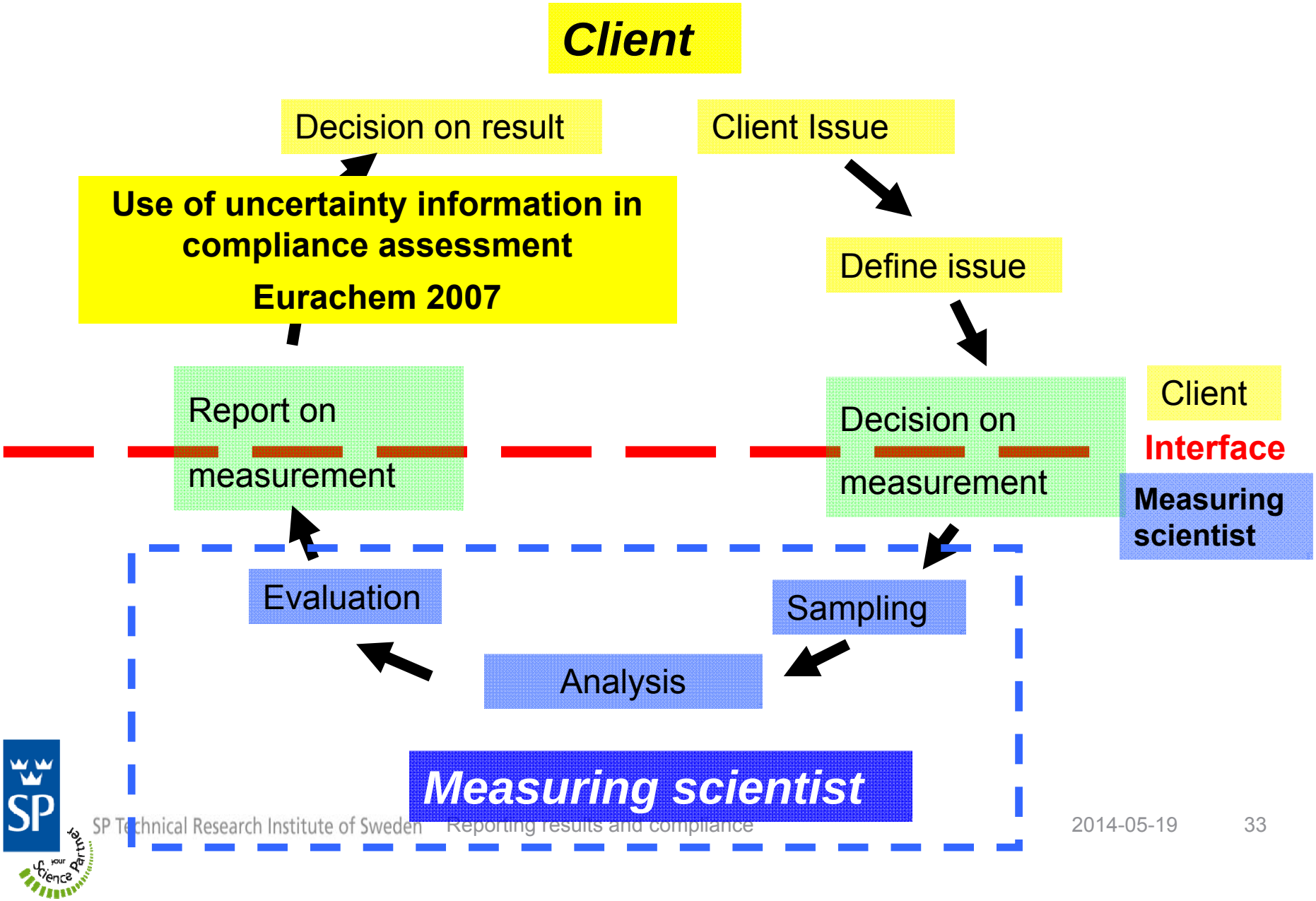
Results

EN 71-3: “The results are expressed as mg soluble element/kg material after **analytical correction** according to EN 71-3 section 4.2 (Interpretation of results).”

	A	B	C	Regulatory &Decision limit
	mg kg^{-1}			
Antimony, Sb	<5	<5	<5	60
Arsenic, As	<5	<5	<5	25
Barium, Ba	273	<5	<5	1000
Cadmium, Cd	<5	<5	<5	75
Chromium, Cr	<5	<5	<5	60
Lead, Pb	<10	<10	<10	90
Mercury, Hg	<5	<5	<5	60
Selenium, Se	<25	<25	<25	500

Compliance?
All the tested parts fulfil the requirements according to EN 71-3

Measurement cycle



Which parameter is relevant for compliance

Compliance with a legal limit or an external specification

u_c combined standard measurement uncertainty,

Compliance in production – is my process stable

s_{Rw} where s_{Rw} is the intermediate precision,
the within laboratory reproducibility standard deviation

Comparison in research – is there any difference between sample A and treated sample B

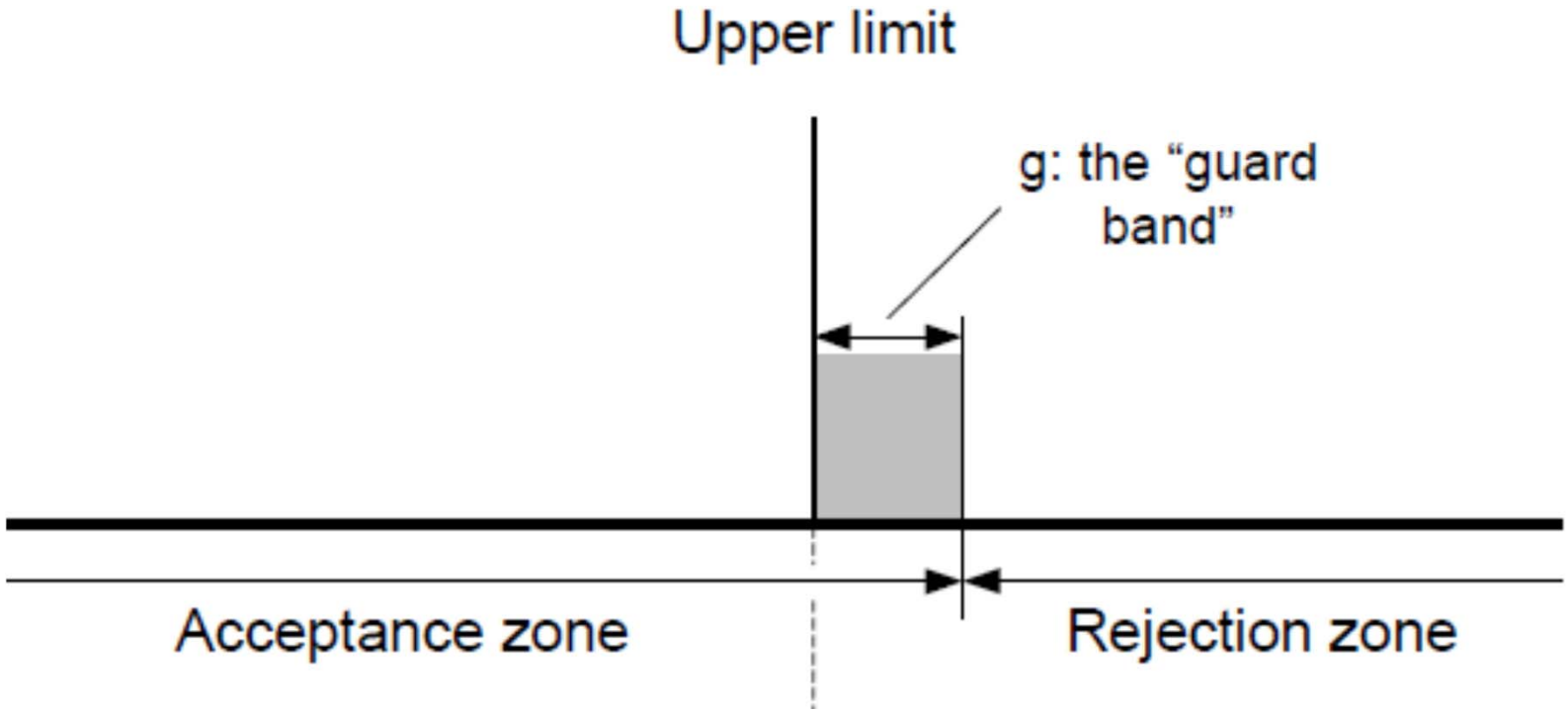
s_r where s_r is the repeatability standard deviation

Summary
What do we need for compliance assessment?

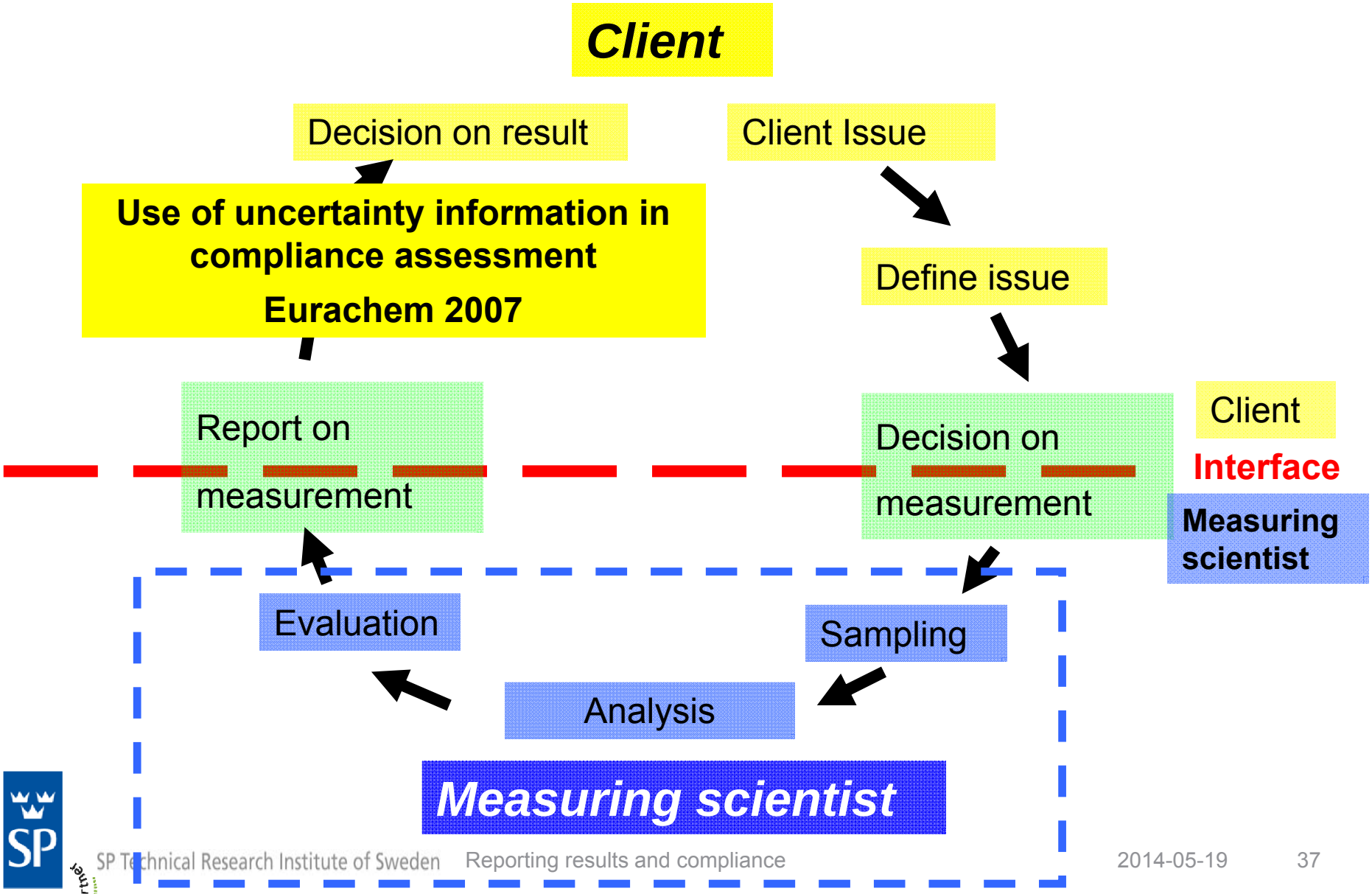
1. A measurand clearly specified including the **measurement object/test item**
2. An analytical result reported with all information, e.g.

   mass fraction of total Cd is 1.82 mg/kg ± 0.20 mg/kg in a **soil batch** xxx, 2014-05-20 reported on dry mass basis (105 °C, 2h)
3. The relevant standard “uncertainty”
4. A specification giving upper and/or lower limits
5. A decision rule
6. From this we calculate acceptance and rejection zones

Acceptance and rejection zones



Measurement cycle



Examples

- Is the result possible?
- Did I use the correct unit?
- Did I analyse the correct sample?
- Did I followed the SPO?
- Did I use the correct dilution factor?
- Have I included the information about the used procedure?
- Did I correct for mass loss?