

## Uncertainty and compliance assessment

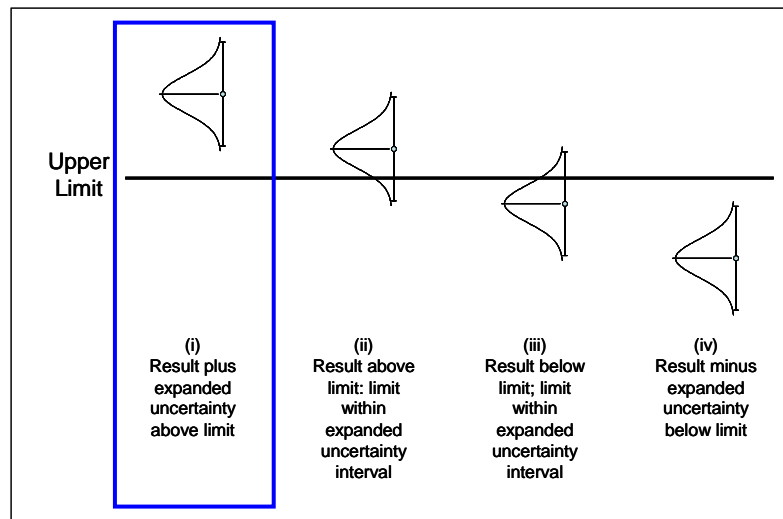
Eurachem workshop 06 June 2011



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### Four results with uncertainty and an upper limit



Lets us take an example of blood alcohol & Swedish legislation

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## A result with uncertainty clearly over the limit

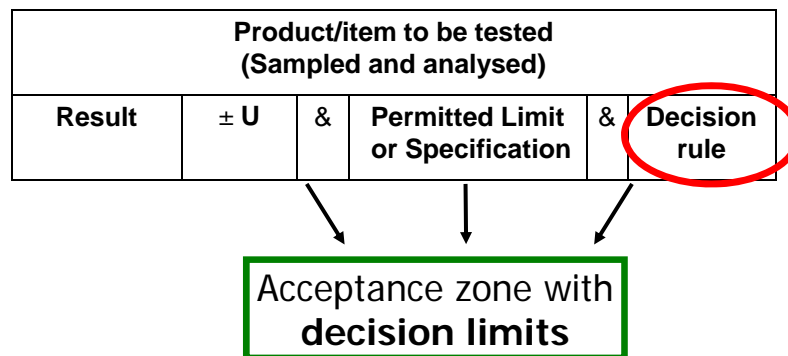
Blood alcohol  
Sample taken from a driver in Sweden and  
analysed at a laboratory

Analytical Report  
Concentration of ethanol in blood sample is  
**0,221 mg/g  $\pm$  0,013 (k=2)**

**Limit is 0,200 mg/g  
(20 mg/100g)  
Will this driver be punished?**



## Using a decision rule we calculate an acceptance zone



Comment: Different focus for an upper limit/specification

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

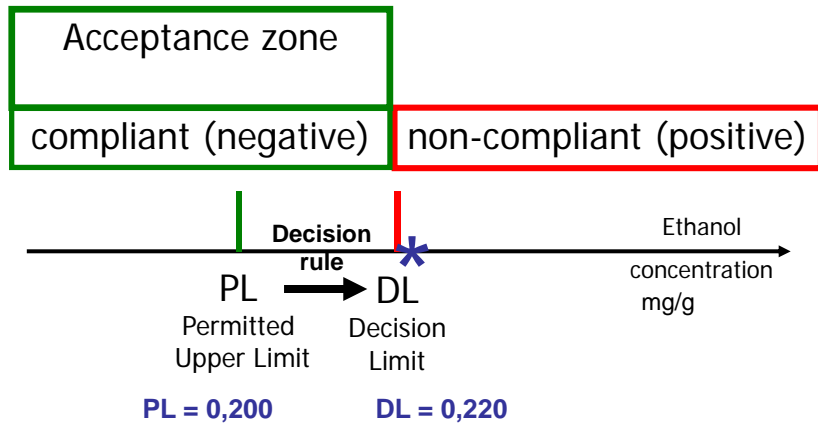
Regarding a product specification we must be sure (>95 %) that the value of the measurand is BELOW an upper specification.



## Acceptance zone for a legal case

*if the measurement result lies  
in the acceptance zone  
the sample is declared compliant*

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



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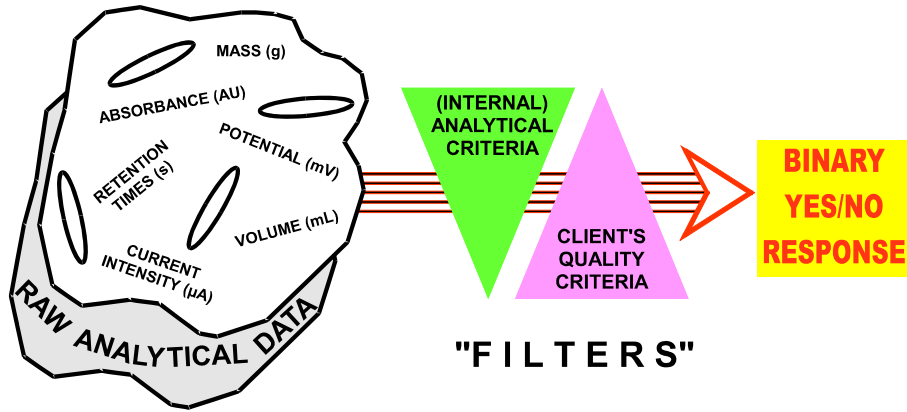
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## Assessing compliance\*



\*Courtesy QUANAL project by Valcarcel et al

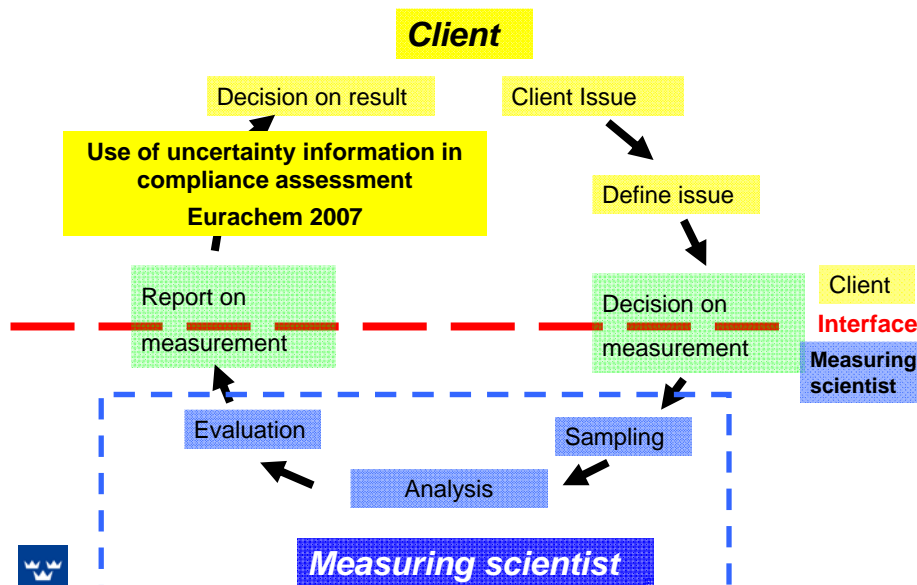
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## Measurement cycle



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## 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



## 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**

VIM2 quantity subject to measurement'.

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)



## Example of a decision rule

Appendix B Example 1

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 % ( $\alpha=0.05$ ) that the batch has a mass fraction **below** the upper limit.*

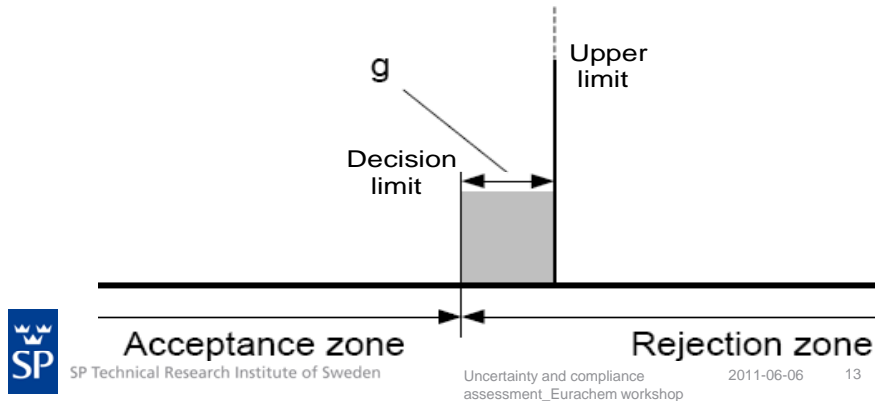


## Conformity assessment – Cd result 1.82 mg/kg

The guard band is calculated as  $1.65u = 0.165$  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  $u$

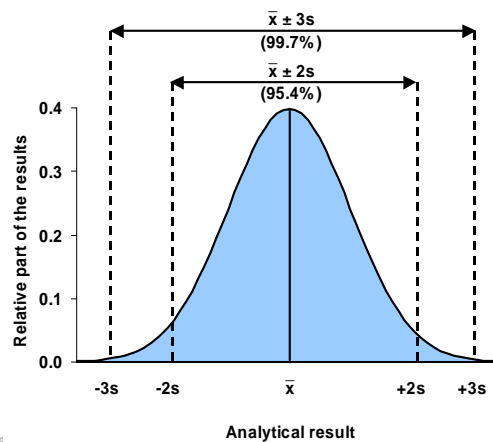
**99,9 %** result + 3,09  $u$

where  $u$  is the standard uncertainty

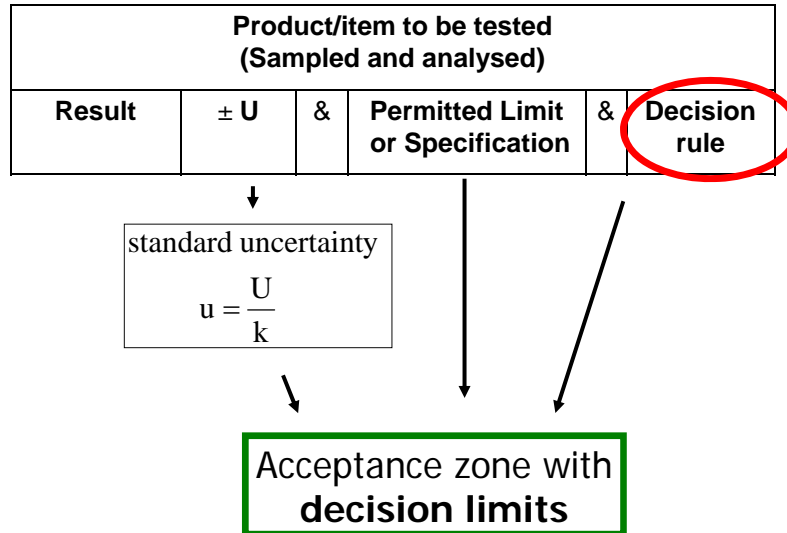
### Measurement result

Confidence interval

95 % result  $\pm 2 u$

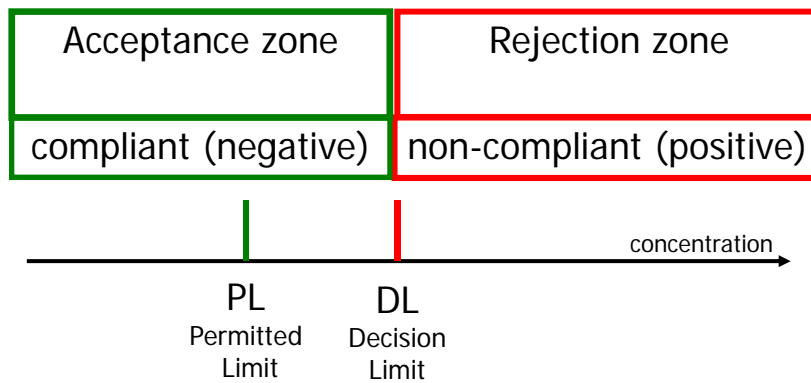


## From these input we calculate an acceptance zone



## Acceptance zone and rejection zone

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





## Example – Blood sample from a driver to be tested for alcohol content

Example with 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 range 0,003 mg/kg*

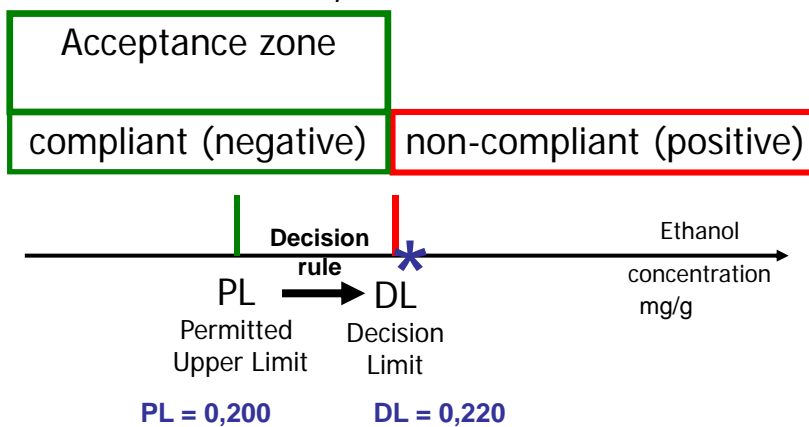
1. Measurand – Concentration (massfraction) of total EtOH in a blood sample delivered to the laboratory
2. Analytical result -  $C(\text{EtOH}) = 0,221 \text{ mg/g}$
3. Uncertainty –  $U = 0,013 \text{ mg/g}$ ,  $k=2$  (95 %)
4. “Specification” – Upper permitted limit  $0,200 \text{ mg/g}$
5. Decision rule - *The decision limit is the concentration above which it can be decided with a statistical certainty of about 99.9 % ( $\alpha = 0,001$ ) that the permitted limit has been truly exceeded*



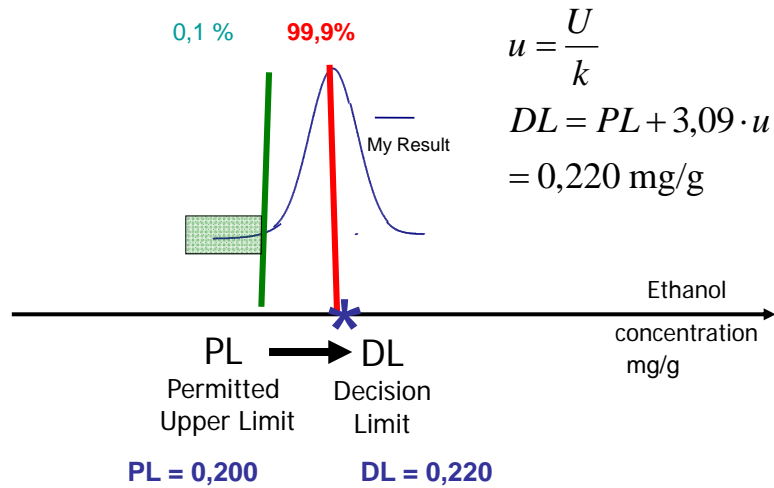
## Conformity assessment - Result $C_{\text{EtOH}} 0,221 \text{ mg/g}$

*the measurement result lies outside the acceptance zone  
the results is declared non compliant*

\* Blood alcohol  
Measurement result  
 $0,221 \text{ mg/g}$



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



## Example where we can find decision rules

### Commission Decision

of 12/08/2002

implementing Council Directive 96/23/EC  
 concerning the **performance** of analytical methods  
 and the **interpretation of results**

(notified under document number C(2002) 3044)

For food sector



## A decision rule giving you a decision limit

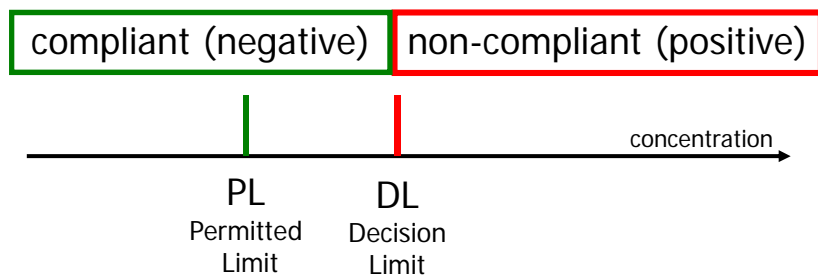
- Decision rule
- If a permitted (higher) limit has been established for a substance,  
the decision limit is the concentration above which it can be decided with a statistical certainty of  $(1-\alpha)$  that the permitted limit has been truly exceeded.
  - Permitted limit = maximum residue limit, maximum level or other maximum tolerance
  - Decision limit, DL (also  $CC\alpha$ ) = limit at (and above) which it can be concluded with an error probability  $(1-\alpha)$  that the sample is non-compliant (positive result)



## Example of assessing compliance/no compliance

Decision rule

The result of an analysis shall be considered non-compliant if the **decision limit** of the confirmatory method for the analyte is exceeded.



**What is a positive result?  
With upper limit - non-compliant is a positive result?**

Test result	Women	
	Non-pregnant	Pregnant
Negative	True negative	False negative
Positive	False positive	True positive

↑  
 **$\alpha$  error**

**$\alpha$  error** = probability that women is non-pregnant, even though a positive measurement result is obtained (FP)



## 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*: the magnitude of the offset from the specification limit to the acceptance or rejection zone boundary

**Alpha error ( $\alpha$ )** = probability that tested sample is compliant, even though a non-compliant measurement is obtained (FP)



## Summary

### 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



## Summary

### From these input we can decide on compliance!

Product/item to be tested (Sampled and analysed)				
Result	$\pm U$	&	Permitted Limit or Specification	& Decision rule

THANK  
YOU FOR  
LISTENING

Acceptance zone with  
decision limits

Compliance or No Compliance

