Reporting results and assessment of compliance

Eurachem workshop
Quality in Analytical Measurements
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The measurement cycle

Client

Decision on result

Data evaluation

Client issue

Define issue

Decision on result

Report on measurement

Evaluation

Sampling

Analysis

Analytical chemist

Client

Interface

Analytical chemist

2014-05-19 Reporting results and compliance
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
**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.

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)

Sampling target

Sampling

Physical sample preparation

Sampling Target

Collection of a single sample, or several increments combined into composite sample

Primary Sample

Communion and/or splitting

Sub-sample

Further communion and/or splitting

Laboratory sample

Physical preparation, e.g. drying, sieving, milling, splitting, homogenisation

Test sample

Selection of test portion for chemical treatment preceding chemical analysis

Test portion

Chemical treatment leading to analytical determination

Test solution

Determination of analyte concentration

Analysis

Process step

Form of material

Description of process step
Some ISO recommendations for reporting measurement results

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

<table>
<thead>
<tr>
<th>Issue</th>
<th>Recommended</th>
<th>Not recommended</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clear indication of unit</td>
<td>$23 \pm 2 , ^\circ \text{C}$ or $(23 \pm 2) , ^\circ \text{C}$</td>
<td>$23 \pm 2 , ^\circ \text{C}$</td>
</tr>
<tr>
<td>Separate information and unit</td>
<td>the water content is 20 ml/kg and not “&quot;</td>
<td>20 ml H2O/kg or 20 ml of water/kg</td>
</tr>
<tr>
<td>Do no mix units</td>
<td>$(230 \pm 11,5) , \text{V}$</td>
<td>$230 , \text{V} \pm 5 , %$</td>
</tr>
</tbody>
</table>

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 your 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 important to state that.
Example of wording is here “as received” 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;
Content

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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

EURACHEM / CITAC Guide

Use of uncertainty information in compliance assessment

First Edition 2007
Four results with uncertainty and an upper limit

(i) Result plus expanded uncertainty above limit
(ii) Result above limit: limit within expanded uncertainty interval
(iii) Result below limit; limit within expanded uncertainty interval
(iv) Result minus expanded uncertainty below limit

Let 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

Let's 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 $0.221 \text{ mg/g } \pm 0.013$ (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

<table>
<thead>
<tr>
<th>Product/item to be tested (Sampled and analysed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Result</td>
</tr>
</tbody>
</table>

Acceptance zone with decision limits

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 % (\(\alpha =0,001\) 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, \( g \):

\[
g = 3.1 \cdot u_c = 3.1 \cdot 0.065 = 0.200 \text{ mg/g}
\]

\( g \approx 0.1 \% \)

\( \approx 99.9 \% \)

**Blood alcohol**

Measurement result: 0.221 mg/g

\( 0.220 = 0.200 + 0.020 \)

**Upper Limit**  **Decision Limit**

Ethanol concentration mg/g
What do we need for compliance assessment?

1. A measurand clearly specified including the \textbf{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 % ($\alpha=0.05$) 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 ± 2 u

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![Diagram of normal distribution with confidence intervals](image-url)
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.
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).”

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>Regulatory &amp; Decision limit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>mg kg⁻¹</td>
</tr>
<tr>
<td>Antimony, Sb</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>60</td>
</tr>
<tr>
<td>Arsenic, As</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>25</td>
</tr>
<tr>
<td>Barium, Ba</td>
<td>273</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>1000</td>
</tr>
<tr>
<td>Cadmium, Cd</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>75</td>
</tr>
<tr>
<td>Chromium, Cr</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>60</td>
</tr>
<tr>
<td>Lead, Pb</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>90</td>
</tr>
<tr>
<td>Mercury, Hg</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>60</td>
</tr>
<tr>
<td>Selenium, Se</td>
<td>&lt;25</td>
<td>&lt;25</td>
<td>&lt;25</td>
<td>500</td>
</tr>
</tbody>
</table>

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

**Client**

- Decision on result
- Client Issue
- Define issue
- Use of uncertainty information in compliance assessment
  Eurachem 2007

**Client Issue**

- Decision on measurement

**Interface**

- Measuring scientist

**Measuring scientist**

- Report on measurement
- Evaluation
- Analysis
- Sampling
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

Client

Decision on result

Client Issue

Define issue

Use of uncertainty information in compliance assessment
Eurachem 2007

Report on measurement

Decision on measurement

Client Interface

Measuring scientist

Evaluation

Sampling

Analysis

Measuring scientist

SP Technical Research Institute of Sweden

Reporting results and compliance

2014-05-19
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?