Eurachem
A Focus for Analytical Chemistry in Europe

Assessment of performance and uncertainty in qualitative chemical analysis: The Eurachem/CITAC Guide

Ricardo Bettencourt da Silva[1,2], Stephen Ellison[1,3]

(1) Eurachem/CITAC Qualitative Analysis Working Group

(2) CQE, IMS, FC, Universidade de Lisboa

(3) LGC Limited

Workshop:
Quality Assurance Challenges of Measurements from Field to Laboratory with a Focus on ISO/IEC 17025:2017 Requirements

1

Eurachem
A Focus for Analytical Chemistry in Europe

Outline

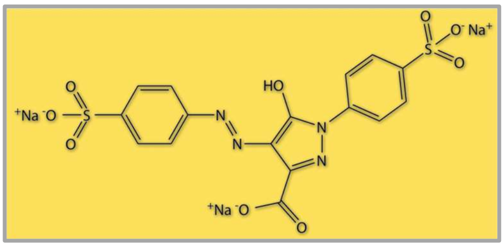
- Types of chemical analysis
- Eurachem/CITAC Guide aim
- Content
  - Types of qualitative analysis
  - Performance assessment for qualitative analysis
  - Expressions of confidence in qualitative analysis
  - Reporting the qualitative analytical result
  - Conclusions and recommendation
  - Examples
- Final message

2

2

Types of chemical analysis

- Quantitative (Measurements)
- Qualitative (Examinations)



Tartrazine (E 102)

Concentration

1. JCGM, International vocabulary of metrology – Basic and general concepts and associated terms (VIM) (JCGM 200), 3rd edition, BIPM. 2012.

Types of chemical analysis

Qualitative analysis is defined as:

“*Classification according to specified criteria*”

Analytical methods (procedures) used in qualitative analysis must be:

- Applicable to an adequate scope
- Have fit for purpose quality/ uncertainty

Eurachem
A Focus for Analytical Chemistry in Europe

Eurachem/CITAC Guide aim

- Highlight the need to check if qualitative analyses are fit for the intended use

- Describe tools, including their limitations, for assessing qualitative analysis performance

5

Eurachem
A Focus for Analytical Chemistry in Europe

Content

6

Eurachem
A Focus for Analytical Chemistry in Europe

Types of Qualitative Analysis

Qualitative analysis can be based on:

- Qualitative data

  Ex. Detection of aliphatic aldehydes in a solution by colour change after the addition of Schiff's reagent.

- Quantitative data

  Ex. Identification of a pesticide residue in fruit using measured fragment masses and relative fragment abundances in GC-MS.

The transformation of the comparison of a measured value with a threshold in a qualitative output ('conforming' or 'nonconforming') is described in Annex B.

7

Eurachem
A Focus for Analytical Chemistry in Europe

Performance assessment for qualitative analysis

The performance of qualitative analysis is conveniently described using a contingency table:

		Case		
		Positive (*pc*)	Negative (*nc*)	Results totals
Result	Positive (*p*)	*tp*	*fp*	*p*
	Negative (*n*)	*fn*	*tn*	*n*
	Case totals	*pc*	*nc*	

True positive rate = $TP = tp/pc$

False positive rate = $FP = fp/nc$

8

Eurachem
A Focus for Analytical Chemistry in Europe

Performance assessment for qualitative analysis

The performance of qualitative analysis is conveniently described using a contingency table:

		Case		
		Positive (*pc*)	Negative (*nc*)	Results totals
Result	Positive (*p*)	*tp* = 228	*fp* = 1	*p* = 229
	Negative (*n*)	*fn* = 5	*tn* = 300	*n* = 305
	Case totals	*pc* = 233	*nc* = 301	

True positive rate = *TP* = *tp*/*pc* = *228/233 = 97.8 %*

False positive rate = *FP* = *fp*/*nc* = *1/301 = 0.33 %*

9

9

Eurachem
A Focus for Analytical Chemistry in Europe

Performance assessment for qualitative analysis

Performance can be assessed:

- experimentally
- database search
- quantitative data modelling

10

Eurachem
A Focus for Analytical Chemistry in Europe

Expressions of confidence in qualitative analysis

- Likelihood ratio

$$LR(+) = \frac{TP}{FP}$$

Advantage: Only requires performance data
Easy to consider the use of independent pieces of evidence
Disadvantage: Does not characterise the analysed sample
Difficult to interpret

11

Eurachem
A Focus for Analytical Chemistry in Europe

Expressions of confidence in qualitative analysis

- Posterior probability of positive case, *PP*

If the prevalence of positive cases is known, $P(+)$, if can be estimated the probability of a sample that produced a positive result being a positive case:

$$PP = \frac{\frac{P(+)}{1-P(+)}LR(+)}{\frac{P(+)}{1-P(+)}LR(+)+1}$$

12

Eurachem
A Focus for Analytical Chemistry in Europe

Reporting the qualitative analytical result

Example 3 (*the italic text mentions the qualitative analysis uncertainty*)**:**

Cocaine is present in sample 123

(identification with a likelihood ratio of 4.9×10^4 *and considered 'very strong' evidence of analyte presence)*

Example 4 (*the italic text mentions the qualitative analysis uncertainty*)**:**

Gasoline residues were identified in the fire debris with sample code 456

(identification with a posterior probability of 99.998 %*, estimated from signal model simulation and assuming analyte presence or absence are equally probable)*

Eurachem
A Focus for Analytical Chemistry in Europe

Conclusions and recommendation

- The most critical false response rates should be checked
- Parameters that affect analysis performance should be controlled
- The reporting of analysis uncertainties should avoid misinterpretation
- Test results can be reported as 'inconclusive'/insufficiently certain

Eurachem
A Focus for Analytical Chemistry in Europe

Examples

E1: Identification of compounds by low-resolution mass spectrometry using database searching or the presence of characteristic ions

E2: Identification of purified compounds by infrared spectrometry

E3: Identification of drugs of abuse in urine by the enzyme multiplied immunoassay technique (EMIT) and an alternative technique

E4: Identification of human SRY gene in biological material by qPCR

E5: Identification of pesticide residues in foodstuffs by GC-MS/MS based on retention time and ion abundance ratio

E6: Identification of SARS-CoV-2 RNA by nucleic acid amplification testing

15

Eurachem
A Focus for Analytical Chemistry in Europe

FINAL MESSAGE

The QAWG wishes the new guide is useful for the community

Eurachem and CITAC members are invited to join the working group

16