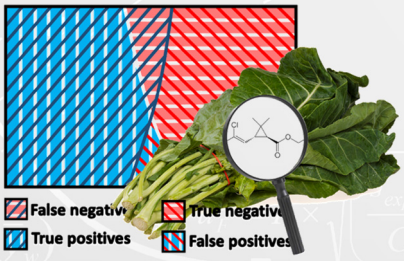
Traceability and uncertainty in qualitative analysis

Nicosia, 29 May 2017



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Overview

1. Problem
2. Terminology
3. Traceability and uncertainty in qualitative analysis
4. Qualitative analysis types
5. Examples
6. Conclusions

1. Problem

- Many analytical evaluations are qualitative
  (*e.g.* most forensic analysis and the classification of a product as "compliant" or "not-compliant" with a specification);

- Most measurements in chemistry are performed after a qualitative evaluation.
  (*e.g.* quantification of permethrin in cabbage)

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2. Terminology

- The VIM3 [1] designates qualitative analysis as an "examination of a nominal property";

- An IUPAC project produced a Vocabulary for Nominal Properties (VIN) [2]. This document is under discussion.

VIM & VIN

1. JCGM, *International Vocabulary of Metrology - Basic and General Concepts and Associated Terms*, 3rd edition, JCGM 200, 2012.
2. G. Nordin, R. Dybkaer, U. Forsum, X. Fuentes-Arderiu, F. Pontet, *Vocabulary for nominal properties and nominal examinations - basic and general concepts and associated terms (IFCC-IUPAC Recommendation 201x)*, Project number 2004-023-1-700, IUPAC, 2012.

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3. Traceability and uncertainty of qualitative analysis

• As for measurements, qualitative analysis results are only fit for the intended use if supported on adequate references and if results have known and adequate uncertainty.

3.1. Traceability of qualitative analysis result

Examples:
Identification of permethrin in cabbage by GC-MS:
Case 1: Identification is supported on mass spectrum, MS, equivalence between the spectrum of a library (e.g. NIST Library) and the spectrum of a peak of the sample.

» Identification is traceable to permethrin identity described in mass spectrum X of NIST Library Y;

Case 2: Identification is supported on the agreement between Relative Retention Times, RRT, and mass spectra, MS, of analyte peak from a calibrator and a peak of the sample.

» Identification is traceable to compound identity of the reference material A.

3.1. Traceability of qualitative analysis result

Examples:
Identification of permethrin in cabbage by GC-MS:
Case 1: Identification is supported on the mass spectrum of a library (…)
Case 2: Identification is supported on the agreement between RRT, and MS of analyte peak and sample peak (…)

The reference used in Case 2 is more adequate.

3.2. Uncertainty of qualitative analysis result

The reliability of a result from a qualitative analysis can be quantified using a pair of parameters:

If result is a "positive":
- TP » True positive results rate;
- FP » False positive results rate;

If result is a "negative":
- TN » True negative results rate;
- FN » False negative results rate.

3.2. Uncertainty of qualitative analysis result

(…)
For positive results, TP and FP can be combined in the likelihood ratio of positive results (*LR*(+)):

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

LR(+) quantifies how more likely a positive result is truth than false.

For negative results, TN and FN can be combined in (*LR*(-)):

$$LR(-) = \frac{TN}{FN}$$

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3.2. Uncertainty of qualitative analysis result

(…)
If qualitative analysis results are based on independent evidences, respective LR can be combined. (…)

Example:
GC-MS identifications are based on the agreement of RRT and MS of analyte peak and peak of the sample.

$$LR(+) = LR\ (+;\text{RRT}) \cdot LR\ (+;\text{MS})$$

LR(+): Likelihood ratio from GC-MS identification;
LR(+;RRT): Likelihood ratio from RRT;
LR(+;MS): Likelihood ratio from MS.

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3.2. Uncertainty of qualitative analysis result

(…)

In some cases, target values of LR are used to decide if qualitative results can support decisions with high impact:

Table: Interpretation of likelihood ratio proposed for forensic sciences by the UK's Association of Forensic Science Providers [3].

Value of likelihood ratio	Verbal equivalent
>1–10	Weak support for proposition
10–100	Moderate support
100–1000	Moderately strong support
1000–10,000	Strong support
10,000–1,000,000	Very strong
>1,000,000	Extremely strong

3. Association of Forensic Science Providers, Science and Justice 49 (2009) 161–164.

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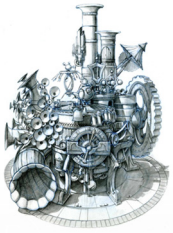
3.2. Uncertainty of qualitative analysis result

(…)

Difficulties of estimating a LR:

The TP can be defined by the confidence level of the identification criterion (e.g. confidence level of RRT acceptance interval);



The FP must be estimated from:

- Analyst experience (type B);
- Models or simulations of negative results.

In most cases, it is not possible to estimate, experimentally, FP smaller than 10 %.

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4. Qualitative analysis types

- Qualitative analysis referenced to a measurement result (type Q1);
  (*e.g.* compliance with a maximum limit)

- Qualitative analysis involving the determination of a quantitative property (type Q2);
  (*e.g.* identification based on the match of two IR spectra)

- Qualitative analysis involving direct nominal property determination (type Q3).
  (*e.g.* sensory analysis)

All these types of qualitative analysis can involve different strategies of estimating LR.

5. Example: Q1

- If a procymidone content in wine of (11.12±0.91) μg L^{-1} (k=2.08; v=20; c.l.=95 %) is compared with a maximum limit of 10 μg L^{-1} and wine is considered "not complaint" since:

$$|11.12\text{-}10| \leq t_1 \cdot (0.91/2.08)$$
$$1.12 \leq 0.758$$

(where t_1 is the one-tailed t-value of the Student's t distribution)

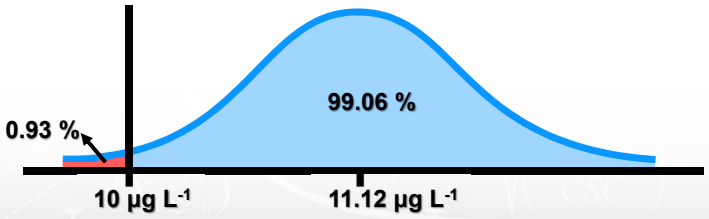
In this case:
(…)

5. Example: Q1

- Procymidone content in wine of (11.12±0.91) μg L^{-1} is compared with a maximum limit of 10 μg L^{-1} (…)

In this case:
TN = 99.06 % = TDIST((11.12-19)/(0.91/2.08),20,TRUE)
FN = 100 % - TN = 0.93 %

LR(-)= 99.6/0.93=106 ("Moderately strong support") [3]



3. Association of Forensic Science Providers, Science and Justice 49 (2009) 161-164.

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5. Example: Q2

- Identification of chlorpyriphos-methyl, CM, in foodstuffs by GC-MS [4]:
  Based on retention time, RT, and on the ratio of the abundance, AR, of ions of the mass spectrum.

  TP(RT): set at 99.9 %;
  TP(AR): set at 98 %;

  FP(RT): estimated as 10 % based on analyst experience;
  FP(AR): 0.2 % (estimated from simulations of signal's noise for 0.24 mg kg^{-1} of CM).

$$LR(+) = \frac{99.9\ \%}{10\ \%} \cdot \frac{98\ \%}{0.2\ \%} = 4.8 \times 10^5$$

("Very strong evidence") [3]

3. Association of Forensic Science Providers, Science and Justice 49 (2009) 161-164.
4. R. B. Silva, Talanta 150 (2016) 553-567.

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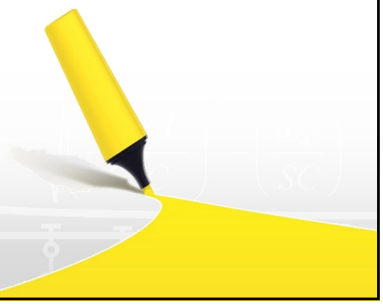
6. Conclusions

- Qualitative analysis reliability can even be more important than measurement reliability;
- Qualitative analysis results are only fit for the intended use if used reference and result uncertainty are adequate for the goal of the evaluation;
- Statistical tools adequate for reporting qualitative analysis results with uncertainty are well-known;
- Some good examples of reporting qualitative analysis results with uncertainty are available in the bibliography.



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