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)

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.


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.

**Decision on Result**

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 ($LR(+)$:)

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

$LR(+) \text{ quantifies how more likely a positive result is truth than false.}$

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

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

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.

$$LR(+) = LR (+;RRT) \cdot LR (+;MS)$$

$LR(+)\text{: Likelihood ratio from GC-MS identification;}$

$LR(++;RRT): \text{Likelihood ratio from RRT;}$

$LR(++;MS): \text{Likelihood ratio from MS.}$
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].

<table>
<thead>
<tr>
<th>Value of likelihood ratio</th>
<th>Verbal equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;1–10</td>
<td>Weak support for proposition</td>
</tr>
<tr>
<td>10–100</td>
<td>Moderate support</td>
</tr>
<tr>
<td>100–1000</td>
<td>Moderately strong support</td>
</tr>
<tr>
<td>1000–10,000</td>
<td>Strong support</td>
</tr>
<tr>
<td>10,000–1,000,000</td>
<td>Very strong</td>
</tr>
<tr>
<td>&gt;1,000,000</td>
<td>Extremely strong</td>
</tr>
</tbody>
</table>


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%.
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; ν=20; c.l.=95 %) is compared with a maximum limit of 10 μg L⁻¹ and wine is considered “not compliant” since:

\[ |11.12-10| \leq t_{1\cdot}(0.91/2.08) \]
\[ 1.12 \leq 0.758 \]

(where \( t_{1\cdot} \) 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]

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.

\[ TP(RT): \text{set at 99.9\%}; \]
\[ TP(AR): \text{set at 98\%}; \]
\[ FP(RT): \text{estimated as 10\% based on analyst experience}; \]
\[ FP(AR): 0.2\% \] (estimated from simulations of signal's noise for 0.24 mg kg⁻¹ of CM).

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

("Very strong evidence") [3]
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.