Quality assurance of chemical analysis: classification, modeling and quantification of human errors

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IUPAC/CITAC Guide (2012) Investigating OOS results based on metrological concepts

Noncompliance: any OOS test result can indicate an analyte concentration violating the specification/legal limit, or be caused by measurement problems, i.e., be metrologically-related.

A metrological approach used for investigating OOS test results allows detection of those of them which can be considered as metrologically-related.

Errare humanum est (to err is human)

The newest applications of chromatography and mass spectrometry using detailed libraries of mass spectra of pesticides, their metabolites and derivatives, cannot exclude HE in the analysis.

Moreover, HE are the greatest source of failures in pesticide identification and confirmation, even if performed by the most diligent and intelligent analysts.

Lehotay SJ et al. (2008) Trends in Anal Chem 27:1070-1090
Lehotay SJ et al. (2011) J Agric Food Chem 59:7544-7556

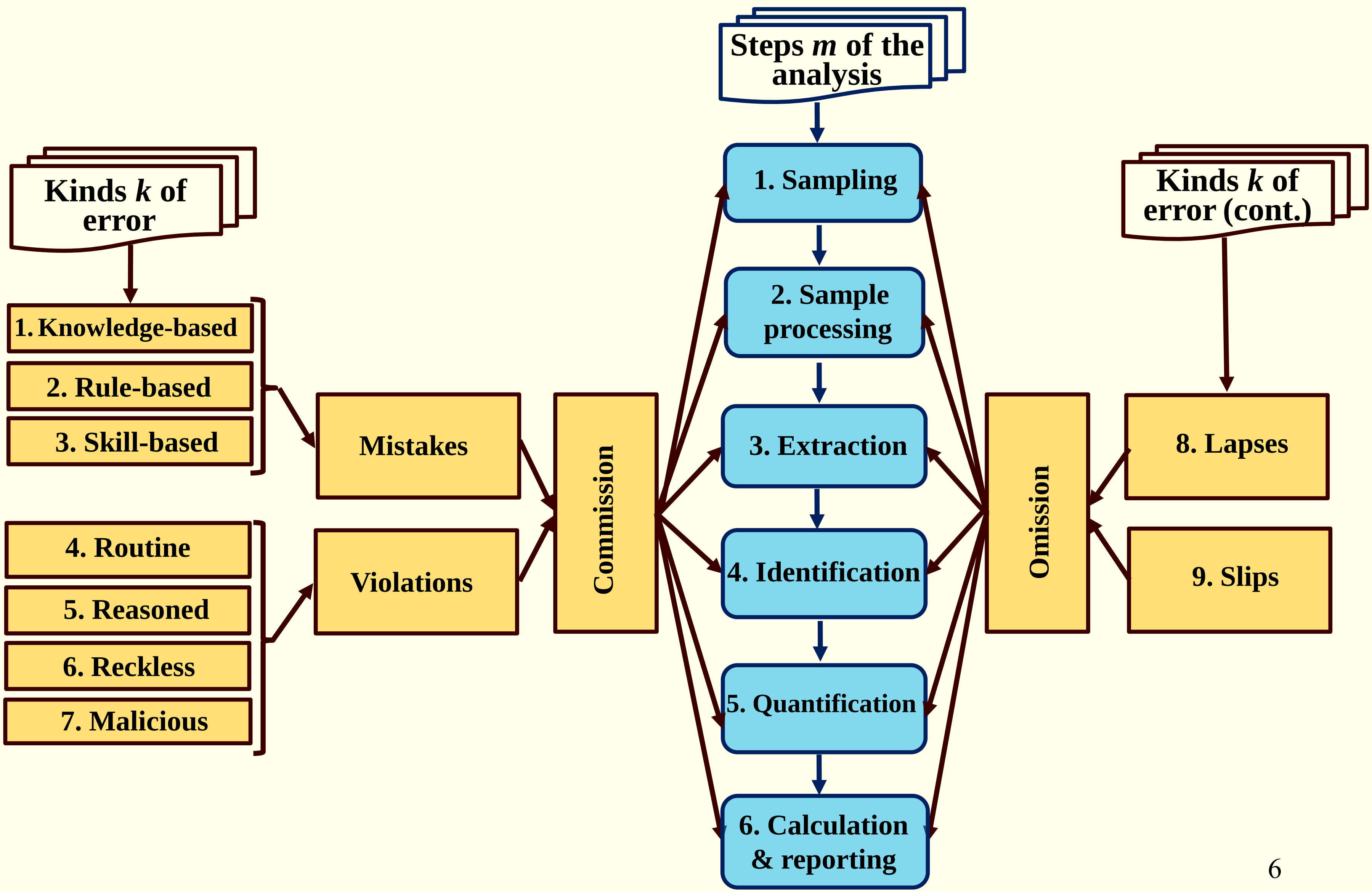
Classification of errors and their location

There are errors of commission and errors of omission. Errors of commission are inappropriate actions (mistakes and violations) resulted in something other than was intended.

On the flip side, errors of omission are inactions (lapses and slips) contributed to a deviation from the intended path or outcome.

A kind k of HE and a step m of the analysis/test, in which the error may happen (location of the error), form the event scenario i.

54 scenarios of human error in the analysis

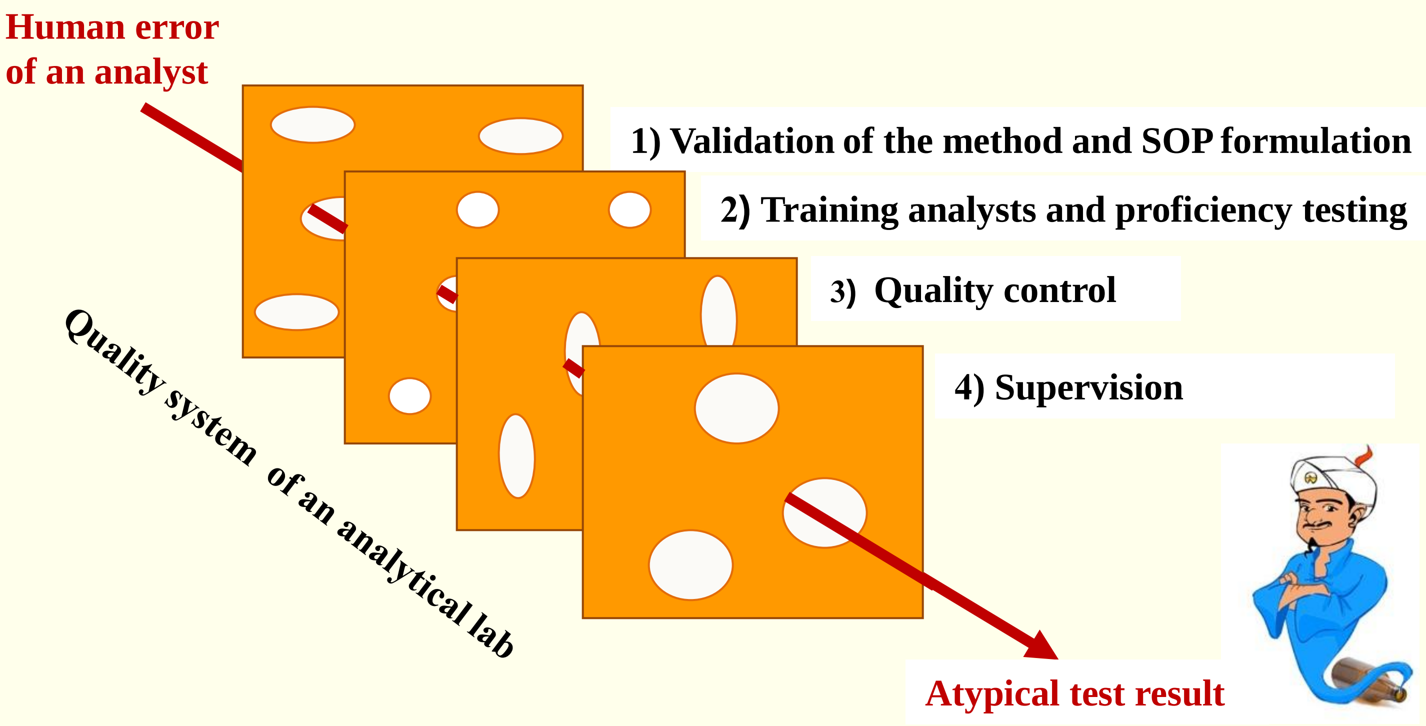


Knowledge-based mistakes, k = 1

Scenario i =1 in sampling, *m* =1. E.g., the mistake is when an inspector picks grapes from an outer part of a bush, which is usually sprayed by pesticides much more than the bush internal part.

Scenario i = 2 in sample processing, *m* = 2. Grinding fresh grapes is a mistake, since leads to inhomogeneous mixture of the grape rinds and pulp, which have different concentrations of pesticide residues. Therefore, the correct processing requires freezing the sample before grinding.

The Swiss cheese model of error blocking



Kuselman I, Pennecchi F, Fajgelj A, Karpov Yu (2013) *Human errors and reliability of test results in analytical chemistry*. ACQUAL 18/1:3-9

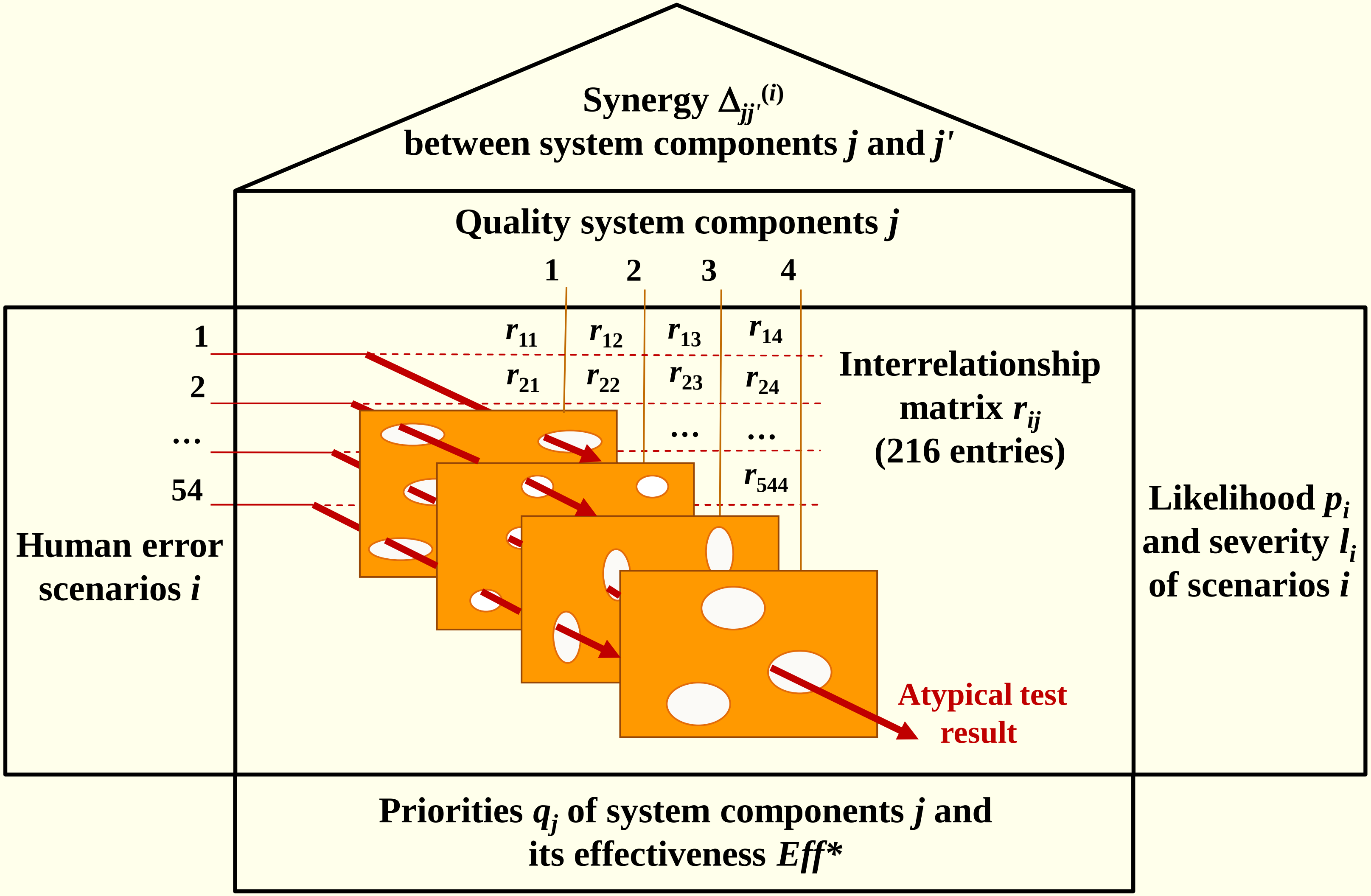
House of security (HOS) approach

HOS was developed for prevention of terrorist and criminal attacks against an organization: Dror S, Bashkansky E, Ravid R (2012) *House of security: a structured system design & analysis approach*. Int J of Safety and Security Eng 2/4:317-329.

For adaptation of the approach to quantification of HE, the following substitutions were made:

1) HE instead of a terrorist attack,
2) a chemical lab instead of an organization undergoing the attacks, and
3) a lab QS instead of security system of an organization.

HOS for multi-residue analysis of pesticides



Likelihood of an error scenario

Kuselman I et al. (2013) *House of security approach to measurement in analytical chemistry: quantification of human error using expert judgments*. ACQUAL 18:459-467

An expert may estimate likelihood p_i of a scenario i by the following scale: likelihood of an unfeasible scenario – as $p_i = 0$, weak likelihood - as $p_i = 1$, medium – as $p_i = 3$, and strong (maximal) likelihood – as $p_i = 9$.

For characterization of HE in an analytical method as a whole, the likelihood score P^* is:

$$P^* = (100\%/9)\sum_{i=1}^{54} p_i/54.$$

Severity of a scenario

Severity of scenario i is estimated as expected loss l_i of reliability of the test results, when the error is not blocked: no severity - as $l_i = 0$, light severity - as $l_i = 1$, medium - as $l_i = 3$, and high (maximal) severity – as $l_i = 9$.

For characterization of HE severity overall, the following value is proposed :

$$L^* = (100\%/9)\sum_{i=1}^{54} l_i \,/54.$$

Interrelationship matrix

To characterize the QS, one should estimate the possible reduction r_{ij} of likelihood of HE scenario i as a result of the error blocking by QS layer j.

Such an estimation is again the task of the expert in the chemical analytical method: no interaction – r_{ij} = 0, low – r_{ij} = 1, medium - r_{ij} = 3, and high (maximal) interaction – r_{ij} = 9. The matrix of r_{ij} is the main content of the house.

Synergy between quality system components

Blocking scenario i by a QS component j can be more effective in presence of another component $j' \neq j$ because of synergy $\Delta_{jj'}^{(i)}$ between them. In such a case the synergy is $\Delta_{jj'}^{(i)} = +1$. When the synergy is absent, $\Delta_{jj'}^{(i)} = 0$.

The synergy factor summarizing the effect for all QS is:

$$s_{ij} = 1 + \sum_{j' \neq j}^{4} \Delta_{jj'}^{(i)}/3 \,, \; 0 \leq \; s_{ij} \leq 2.$$

Quality system priorities

Priority of the QS component j (a score of its importance) in decreasing losses from HE is:

$$q_j = \sum_{i=1}^{54} p_i l_i r_{ij} s_{ij}.$$

The score of the priority q_j^* is:

$$q_j^* = 100\%\, q_j / \sum_{j=1}^{4} q_j.$$

Effectiveness score of the QS, as a whole, against HE is:

$$Eff^* = (100\%/9) \sum_{j=1}^{4} q_j / \sum_{j=1}^{4} \sum_{i=1}^{54} p_i l_i s_{ij}$$

Score of QS influence at step m of the analysis

The score is:

$$\tilde{q}_m = \sum_{i'}^{m+48} \sum_{j=1}^{4} p_{i'} l_{i'} r_{i'j} \, s_{i'j} \text{ , and}$$

$$\tilde{q}^*_m = 100\% \, q_m / \sum_{m=1}^{6} q_m \text{ ,}$$

where scenario numbers $i' = m + 6(k - 1)$ are related to the same error location, i.e., the same step m. For example, for sampling ($m = 1$) there are $i' = 1, 7, \ldots, 49$.

Applications: the score values (%)

Analytical method	**Scenarios mapping, *I***	***P****	***L****	**Max q_j***	**Min q_m***	***Eff****
pH testing of groundwater	36 (34)	26	67	37 (train.)	7 (report.)	59
Pesticide resi-dues in fruits	54	19	84	27 (super.)	7 (samp.)	71
ICP-MS of geo-samples	36	22	56	27 (QC)	14 (calibr.)	55

Robustness of the scores

Any expert feels a natural doubt during a choice of close values from the proposed scale: 0 or 1? 1 or 3? 3 or 9?

What will happen with the score values at a judgment change from $p_i = 0$ to $p_i = 1$ and vice versa ($p_i = 1 \leftrightarrow 0$), $p_i = 1 \leftrightarrow 3$, and from $p_i = 3 \leftrightarrow 9$?

One change of an expert judgment on likelihood $p_i = 0 \leftrightarrow 1$ leads to the change of the score from 11.11% for one scenario to 0.21% for 54 scenarios: $P^* = (100\%/9) \sum_{i=1}^{I} p_i / I$.

Models of an expert behavior

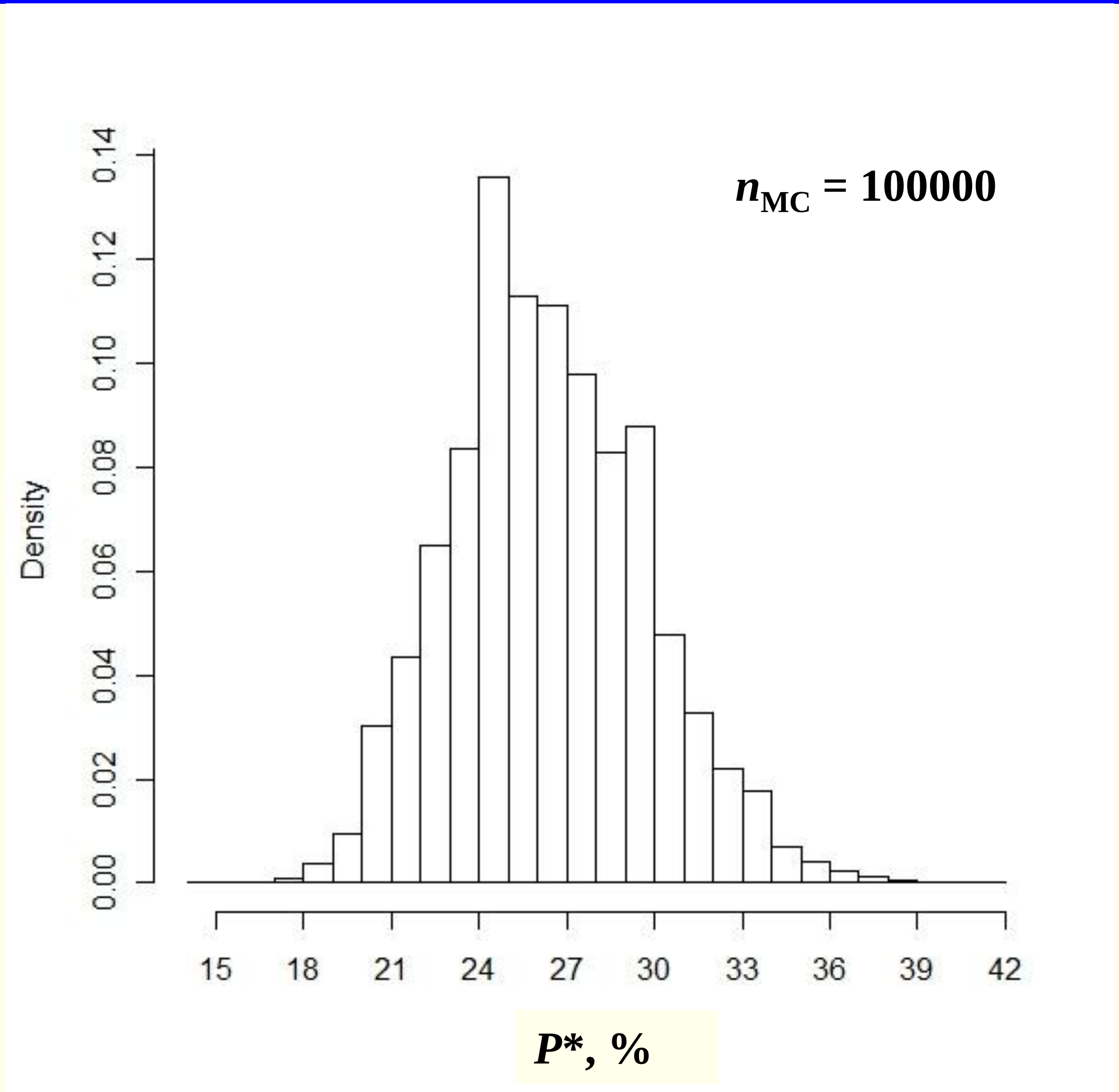
An expert judgment is a discrete quantity, whose value is chosen from the scale (0, 1, 3, 9). The expert doubts can be characterized by pmf:

1) confident expert judgments, when pmf of a chosen scale value is 0.90, whereas close values have in total pmf = 0.10;

2) reasonably doubting expert judgments, when pmf of a chosen value is 0.70, whereas pmf of close values is 0.30;

3) irresolute expert judgments, when pmf of a chosen value is 0.50, and the close values on the scale have in total the same pmf = 0.50.

MC simulation of P score for reasonably doubting expert judgments in ICP-MS*



Conclusions

1. Classification of HE which may occur in testing is necessary for understanding the error scenarios which should be treated by a lab QS.

2. Modeling of interaction of HE with QS components by different scenarios is important for prevention and reduction of the errors.

3. Quantification of HE using judgments of experts in the testing is helpful for evaluation of effectiveness of the QS in prevention of the errors and its improvement.

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CITAC
Cooperation on International Traceability in Analytical Chemistry

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13 January 2015, Dan Panorama Hotel, Tel Aviv
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14-15 January 2015, David Intercontinental Hotel, Tel Aviv
www.isranalytica.org.il