codex alimentarius commission

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS

WORLD HEALTH ORGANIZATION

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Agenda Item 5 **CX/MAS 04/5**

JOINT FAO/WHO FOOD STANDARDS PROGRAMME

CODEX COMMITTEE ON METHODS OF ANALYSIS AND SAMPLING
Twenty-fifth Session
Budapest, Hungary, 8 – 12 March 2004

PROPOSED DRAFT GUIDELINES FOR EVALUATING ACCEPTABLE METHODS OF ANALYSIS
GOVERNMENT COMMENTS AT STEP 3

BRAZIL

This document presents minimum requirements for evaluating acceptable methods of analysis, and in order to improve it, we would like to suggest the following comments:

- To define validation according ISO 17025 and to establish when to validate.
- To define checking according ISO 17025 and to establish when to verify.
- To define the procedures and the documentation.
- To change the title in Requirement for Criteria for performance.
- To include Criteria for acceptance the methods .
- To include in Accuracy the definition of trueness, according the following:

Trueness: it is the closeness of agreement between averaged value, obtained of the set of test results, and the accepted reference value (ISO 3534-1)

- Number of essays to be accomplished to determine the trueness

Number of repetition	Reference
Minimum 9 (3 repetition for 3 different concentrations)	Brittain, H. Pharmaceutical Tech. Junho, 1998
≥ 5 for each concentration	Hill, R. C. Analyst v. 124, p. 953-958, 1999
3 times for each concentration and 1 control	European Commission SANCO/825/00 ver.6
10 times (blank of reagents and CRM)	EURACHEM
≥ 7 times sample-blank	DOC-CGCRE-008/2002 INMETRO

- In Accuracy after note include the formula: $RE = \frac{X_{lab} - X\nu}{X_\nu} \times 100$

Where:

X_{lab} = experimental value, or obtained averaged values

X_v = accepted value as true

Include after the second formula Z the formula:

$$Z = \frac{X_{lab} - X_v}{S}$$

❖ To include after second formula of Z the formula

$$Z = \frac{X_{lab} - X_v}{S}$$

Where:
X_{lab} = obtained value by laboratory
X_v = accepted value as true (certified value of CRM)
S = unity of standard deviation (uncertainty of CRM)

DOC-CGCRE-008/2002 INMETRO

❖ To include the formula

$$Z = \frac{(X_{exp} - X_{certi})}{\sqrt{(\sigma^2_{exp} + \sigma^2_{certi})}}$$

Bode, P.; Dijk, C. P. van. Operational management of results in INAA utilizing a versatile system of control charts. Journal of Radioanalysis and Nuclear Chemistry. V. 215, n. 1, p. 87-94, 1997

❖ To include in Applicability

A protocol describing, the equipment, reagents, procedure (permissible variation in specified instructions; to heat a 100 ± 5°C for 30 ± 5 min), procedure of calibration and quality, and some precaution of especial security needed.
The intended application and critical uncertainty (the analysis of food to proposal of trial. The standard uncertainty u(c) of result must be smaller than 0.1 x c)
Thompson, M. ; Ellison, S. R.; Wood, R. Pure and Applied Chemistry. V. 74, p. 835-855, 2002

❖ To include after table of determination limit

Determination or quantification limit is the lowest point of calibration curve and it must not be determined for extrapolation
UKAS United Kingdom Accreditation Service (www.ukas.com)

❖ To include in linearity

Linearity: minimum 5 points with 3 replicate, considering the upper and lower limits of the range work. To consider quantification limit, the point of range work lower. To register the coefficient of linear regression (minimum 0.99), slope and visualize the line. To consider the matrix effect when observe the matrix interference, principle in atomic absorption technique for graphite oven.

❖ To include after table working and linear range

It can be evaluate doing short changes in the analytical procedure and comparing the effect in the obtained results.
Suggestions of changes:
-different analyst
-different equipments
-different brands of reagents
-temperature of derivatization reaction

-time of process step
-pH

❖ To include in selectivity after the table confirmation of identity and selectivity/specify

If the matrix of sample without analysis or a group satisfactory of reference samples are available, can be applied F test of homogeneity variances and t test the comparison of averages, or realize the analysis of deviation in relation reference values.
DOC-CGCRE-008/2002 INMETRO

❖ To include in selectivity

One quantitative measure is selectivity index b_{an}/b_{int} , where b_{an} is the sensitivity of method (slope of the calibration function) and b_{int} the slope of response independently produced by a potential interference, provides a quantitative measure of interference. b_{int} can be determined approximately by execution of the procedure on a matrix blank and same blank spiked with the potential interference at one appropriate concentration.
IUPAC 2002

❖ To include in precision characteristics

Precision under run-to-run conditions, describing variations in run bias δ_{run} as exception 0, standard deviation σ_{run} . Usually both of these sources of error are operating on individual analytical results, which therefore have a combined precision $\sigma_{tot} = (\sigma^2_r/n + \sigma^2_{run})½$, where n is the number of repeat results averaged within a run for the reported result. The two precision estimates can be obtained most simply by analyzing the selected test material in duplicate in number of successive runs. The separate variance components can then be calculated by the application of one-way analysis of variance. Each duplicate analysis must be an independent execution of the procedure applied to a separate test portion. Alternatively the combined precision σ_{tot} can be estimated directly by analysis of the test material once in successive runs, and estimating the standard deviation from the usual equation.
IUPAC 2002

❖ To include the title Recovery

And after table Recoveries to introduce the table Recovery (%) for different concentrations of analyto

Concentration of analyte	ration	unity	Recovery
100	1	100%	98 – 102
≥ 10	10^{-1}	10%	98 – 102
≥ 1	10^{-2}	1%	97 – 103
≥ 0.1	10^{-3}	0.1%	95 – 105
0.01	10^{-4}	100ppm	90 – 107
0.001	10^{-5}	10ppm	80 – 110
0.0001	10^{-6}	1ppm	80 – 110
0.00001	10^{-7}	100ppb	80 – 110
0.000001	10^{-8}	10ppb	60 – 115
0.0000001	10^{-9}	1ppb	40 - 120

AOAC Peer verified methods program, manual on policies and procedure, Arlington, VA, Nov. 1993. Apud Huber, 1. Validation of analytical methods: review and strategy. LC/GC International Feb 1998, 95-105.