SLOVENSKI STANDARD
SIST ISO 8466-2:1996

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Kakovost vode - Umerjanje in vrednotenje analitskih metod in določitev delovnih karakteristik - 2. del: Umerjalna strategija za nelinearne umerjalne funkcije drugega reda

Water quality -- Calibration and evaluation of analytical methods and estimation of performance characteristics -- Part 2: Calibration strategy for non-linear second order calibration functions

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Qualité de l'eau -- Étalonnage et évaluation des méthodes d'analyse et estimation des caractères de performance -- Partie 2: Stratégie d'étalonnage pour fonctions d'étalonnage non linéaires du second degré

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ICS:

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Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics —

Part 2:
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Reference number
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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 8466-2 was prepared by Technical Committee ISO/TC 147, *Water quality*, Sub-Committee SC 7, *Precision and accuracy*.

ISO 8466 consists of the following parts, under the general title *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics*:

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- — *Part 1: Statistical evaluation of the linear calibration function*
- — *Part 2: Calibration strategy for non-linear second order calibration functions*
- — *Part 3: Method of standard addition*
- — *Part 4: Estimation of limit of detection and limit of determination of an analytical basis method*

Annex A forms an integral part of this part of ISO 8466. Annex B is for information only.

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Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics —

Part 2:
Calibration strategy for non-linear second order calibration functions

1 Scope

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It is not always possible to accurately describe the relationship between a set of calibration points with a rectilinear curve, even by decreasing the working range. Instead of the linear regression analysis, a least squares fit to a second order polynomial is applied (see test for linearity in 4.1.3 of ISO 8466-1:1990). Using this, it is possible to calculate not only the calibration function but also the confidence interval associated with it.

This part of ISO 8466 is intended primarily for use in method development and may not necessarily be applicable to all routine analyses.

2 Symbols

x_i	Concentration of the ith standard sample.
i	Subscript of the concentration levels, where $i = 1, 2, ..., N$.
N	Number of concentration levels (for this part of ISO 8466, $N = 10$).
x_1	Concentration of the standard sample at the lower level of the working range (1st standard sample).
x_{10}	Concentration of the standard sample at the upper level of the working range (10th standard sample).
$y_{i,j}$	j th information value for the concentration x_i.
j	Subscript of the replicates of level i, where $j = 1, 2, ..., n_i$.
n_i	Number of replicates per level x_i.
$\bar{y}_i$	Mean of the information values $y_{i,j}$ of standard samples, having the concentration x_i.
s_i^2	Variance of the information values for the analyses of standard samples, having the concentration x_i.
PW	Test value for the F-test.
$F(f_1, f_2, P)$	Tabled value of the F-distribution with f_1 and f_2 degrees of freedom and a confidence level of P (%).
a, b, c	Coefficients of the calibration function.
$\bar{x}$	Mean of the standard concentrations x_i, resulting from the calibration experiment.

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$\bar{y}$	Mean of the information values y_i, resulting from the calibration experiment.
$\hat{y}_i$	Information value of the standard concentration x_i calculated from the calibration function.
s_y	Residual standard deviation.
f	Degree of freedom for the residual standard deviation ($f = N - 3$).
e	Sensitivity = first derivative of the calibration function.
E	Sensitivity in the centre of the working range.
S_{xo}	Standard deviation of the procedure.
V_{xo}	Coefficient of variation of the procedure.
$\hat{y}$	Information value of an analytical sample.
$\hat{x}$	Concentration of the analytical sample, calculated from the information value $\hat{y}$.
$\hat{N}$	Number of replicates on the same analytical sample.
VB($\hat{x}$)	Confidence interval for the concentration $\hat{x}$.
$t(f_1,P)$	Tabled value of the t-distribution with $f_1 = N - 3$ degrees of freedom and a confidence interval of P (%) (t-factor of Student's distribution).
x^*	Concentration at which the calibration function has minimum or maximum value.

3 Performance

3.1 Choice of working range

The calibrating experiment requires the establishment of a preliminary working range depending on

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a) the practice-related objective of the calibration.

The working range may cover the application range required for the analysis of water, waste water, and sludge. The most frequently expected sample concentration should lie near the centre of the working range;

b) The values obtained near the lower limit of the working range being distinguishable from the blanks of the procedure.

The lower limit of the working range should therefore be equal to or greater than the limit of determination of the procedure. Dilution or concentration steps should be feasible and free from the risk of bias.

3.2 Test for the homogeneity of the variances

The variance of the information values shall be homogeneous and independent of the concentration.

After the establishment of the preliminary working range, information values of at least $N = 5$ (recommended $N = 10$) standard samples are determined. The concentrations, x_i, of these standard samples shall be distributed equidistantly over the working range. In order to examine the homogeneity of the variances, n_i standards of each of the lowest and highest concentrations of the working range are measured as replicates. n_i information values ($y_{i,j}$) result from these series of measurements.

Both data sets of the concentrations x_1 and x_{10} are used to calculate the variances s_1^2 and s_{10}^2 as given in equation (1):

$$s_i^2 = \frac{\sum_{j=1}^{n_i} (y_{i,j} - y_i)^2}{n_i - 1} \qquad \ldots (1)$$

where $f_i = n_i - 1$

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with the mean

$$\bar{y}_i = \frac{\sum\limits_{j=1}^{n_i} y_{i,j}}{n_i} \qquad \ldots (2)$$

for $i = 1$ or $i = 10$.

The variances are submitted to a simple test of variance (one-sided F-test), in order to examine for significant differences at the lower and upper limits of the working range.

The test value PW required for the F-test is determined as follows:

$$\mathrm{PW} = \frac{s_{10}^2}{s_1^2} \quad \text{for } s_{10}^2 > s_1^2 \qquad \ldots (3)$$

$$\mathrm{PW} = \frac{s_1^2}{s_{10}^2} \quad \text{for } s_1^2 > s_{10}^2 \qquad \ldots (4)$$

PW is compared with the tabled values of the F-distribution (see annex A).

Decision:

a) If $\mathrm{PW} \leqslant F(f_1,\ f_2,\ 99\ \%)$: the difference between the variances is not significant.

b) If $\mathrm{PW} > F(f_1,\ f_2,\ 99\ \%)$: the difference between the variances is significant.

The preliminary working range in case b) should be decreased until the difference between the variances is found to be random only.

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3.3 Measurement

After the establishment of the final working range, prepare $N = 10$ standard solutions whose concentrations x_i are equidistantly distributed over the working range. Measure the respective information values y_i.

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4 Estimation of the polynomial coefficients

Using the values of the standard concentrations as independent variables and the measured information values as dependent variables, calculate the calibration coefficients of the polynomial using equation (5)

$$y = a + bx + cx^2 \qquad \ldots (5)$$

The following intermediate values are required for the calculation of the coefficients a, b and c:

$$Q_{xx} = \sum x_i^2 - \frac{\left(\sum x_i\right)^2}{N} \qquad \ldots (6)$$

$$Q_{xy} = \sum (x_i y_i) - \left(\sum x_i \times \frac{\sum y_i}{N}\right) \qquad \ldots (7)$$

$$Q_{x^3} = \sum x_i^3 - \left(\sum x_i \times \frac{\sum x_i^2}{N}\right) \qquad \ldots (8)$$

$$Q_{x^4} = \sum x_i^4 - \frac{\left(\sum x_i^2\right)^2}{N} \qquad \ldots (9)$$