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Determination and use of polynomial calibration functions

Détermination et utilisation des fonctions d'étalonnage polynômial

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Foreword

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This document was prepared by Technical Committee ISO/TC 69, *Application of statistical methods*, Subcommittee SC 6, *Measurement methods and results.*

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

0.1 Calibration is central to measurement science and involves fitting to measured data a function that describes the relationship of a response (dependent) variable y to a stimulus (independent) variable x. It also involves the use of that calibration function. This document considers calibration functions in the form of polynomial models that depend on a set of parameters (coefficients). The purpose of a calibration procedure is the following.

a) To estimate the parameters of the calibration function given suitable calibration data provided by a measuring system and evaluate the covariance matrix associated with these parameter estimates. Any uncertainties provided with the data are taken into consideration.

b) To use an accepted calibration function for inverse evaluation, that is, to determine the stimulus value corresponding to a further measured response value, and also to obtain the stimulus value standard uncertainty given the response value standard uncertainty. A calibration function is sometimes used for direct evaluation, that is, to determine the response value corresponding to a further stimulus value, and also to obtain the response value standard uncertainty given the stimulus value standard uncertainty.

This document describes how these calculations can be undertaken using recognized algorithms. It provides examples from a number of disciplines: absorbed dose determination (NPL), flow meter characterization (INRIM), natural gas analysis (VSL), resistance thermometry (DFM) and isotope-based quantitation (NRC).

0.2 The nature of the calibration data uncertainty information influences the manner in which the calibration function parameters are estimated and how their associated covariance matrix is provided. This uncertainty information may include quantified measurement covariance effects relating to dependencies among the quantities involved.

0.3 Since in any particular instance the degree of the polynomial calibration function is not generally known, this document recommends the determination of polynomial functions of all degrees up to a stipulated maximum (limited by the quantity of data available), followed by the selection of one of these degrees according to suitable criteria. One criterion relates to the requirement that the calibration function is monotonic (strictly increasing or decreasing) over its domain. A second criterion relates to striking a balance between the polynomial calibration function providing a satisfactory explanation of the data and the number of parameters required to describe that polynomial. A further criterion relates to visual acceptance of the polynomial function.

0.4 The determination and use of a polynomial calibration function thus consist of the following steps:

1 obtaining calibration data and available uncertainty information including covariance information when available;

2 determining polynomial functions of all degrees up to a prescribed maximum in a manner that respects the uncertainty information;

3 selecting an appropriate function from this set of polynomial functions according to the criteria in Subclause 0.3;

4 providing estimates of the parameters of the chosen polynomial function and obtaining the covariance matrix associated with those estimates;

5 using the calibration function for inverse evaluation and associated uncertainty evaluation;

6 using the calibration function for direct evaluation and associated uncertainty evaluation.

0.5 This document treats steps 2 to 6 listed in Subclause 0.4 employing the principles of ISO/IEC Guide 98-3:2008 (GUM). Therefore, as part of step 1, before using this document, the user should provide available standard uncertainties and covariances associated with the measured *x*- and *y*-values. Account should be taken of the provisions of the GUM in obtaining these uncertainties on the basis of a measurement model that is specific to the area of concern.

Determination and use of polynomial calibration functions

1 Scope

1.1 This document is concerned with polynomial calibration functions that describe the relationship between a stimulus variable and a response variable. These functions contain parameters estimated from calibration data consisting of a set of pairs of stimulus value and response value. Various cases are considered relating to the nature of any uncertainties associated with the data.

1.2 Estimates of the polynomial function parameters are determined using least-squares methods, taking account of the specified uncertainty information. It is assumed that the calibration data are fit for purpose and thus the treatment of outliers is not considered. It is also assumed that the calibration data errors are regarded as drawn from normal distributions. An emphasis of this document is on choosing the least-squares method appropriate for the nature of the data uncertainties in any particular case. Since these methods are well documented in the technical literature and software that implements them is freely available, they are not described in this document.

1.3 Commonly occurring types of covariance matrix associated with the calibration data are considered covering (a) response data uncertainties, (b) response data uncertainties and covariances, (c) stimulus and response data uncertainties, and (d) stimulus data uncertainties and covariances, and response data uncertainties and covariances. The case where the data uncertainties are unknown is also treated.

1.4 Methods for selecting the degree of the polynomial calibration function according to prescribed criteria are given. The covariance matrix associated with the estimates of the parameters in the selected polynomial function is available as a by-product of the least-squares methods used.

1.5 For the chosen polynomial function this document describes the use of the parameter estimates and their associated covariance matrix for inverse and direct evaluation. It also describes how the provisions of ISO/IEC Guide 98-3:2008 (GUM) can be used to provide the associated standard uncertainties.

1.6 Consideration is given to accounting for certain constraints (such as the polynomial passing through the origin) that may need to be imposed and also to the use of transformations of the variables that may render the behaviour of the calibration function more polynomial-like. Interchanging the roles of the variables is also considered.

1.7 Examples from several areas of measurement science illustrate the use of this document.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/IEC Guide 98-3:2008, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

ISO/IEC Guide 99:2007 (corr. 2010), *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/IEC Guide 98-3:2008 and ISO/IEC Guide 99:2012 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at https://www.iso.org/obp

3.1
measurement uncertainty
non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used

[SOURCE: ISO/IEC Guide 99:2007 (corr. 2010), 2.26, modified - Notes 1 to 4 have been deleted.]

3.2
standard measurement uncertainty
standard uncertainty
measurement uncertainty (3.1) expressed as a standard deviation

[SOURCE: ISO/IEC Guide 99:2007 (corr. 2010), 2.30.]

3.3
measurement covariance matrix
covariance matrix
symmetric positive-definite matrix of dimension $N \times N$ associated with an estimate of a vector quantity of dimension $N \times 1$, containing on its diagonal the squared standard uncertainties associated with the components of the estimate of the quantity, and, in its off-diagonal positions, the covariances associated with pairs of components of the estimate of the quantity

Note 1 to entry: A measurement covariance matrix $\boldsymbol{V}_x$ of dimension $N \times N$ associated with the estimate $\boldsymbol{x}$ of a vector quantity $\boldsymbol{X}$ has the representation

$$\boldsymbol{V}_x = \begin{bmatrix} u\left(x_1, x_1\right) & \cdots & u\left(x_1, x_N\right) \\ \vdots & \ddots & \vdots \\ u\left(x_N, x_1\right) & \cdots & u\left(x_N, x_N\right) \end{bmatrix},$$

where $u\left(x_i, x_i\right) = u^2\left(x_i\right)$ is the variance (squared standard uncertainty) associated with x_i and $u\left(x_i, x_j\right)$ is the covariance associated with x_i and x_j. $u\left(x_i, x_j\right) = 0$ if elements X_i and X_j of $\boldsymbol{X}$ are uncorrelated.

Note 2 to entry: A covariance matrix is also known as a variance-covariance matrix.

[SOURCE: ISO/IEC Guide 98-3:2008/Suppl. 1:2008, 3.11 (definition of uncertainty matrix), modified - definition slightly modified, Note 2 deleted, Note 3 becomes Note 2 to entry, slightly modified.]

3.4
correlation matrix
symmetric positive-definite matrix of dimension $N \times N$ associated with an estimate of a vector quantity of dimension $N \times 1$, containing the correlations associated with pairs of components of the estimate

Note 1 to entry: A correlation matrix $\boldsymbol{R}_x$ of dimension $N \times N$ associated with the estimate $\boldsymbol{x}$ of a vector quantity $\boldsymbol{X}$ has the representation

$$\boldsymbol{R}_x = \begin{bmatrix} r\left(x_1, x_1\right) & \cdots & r\left(x_1, x_N\right) \\ \vdots & \ddots & \vdots \\ r\left(x_N, x_1\right) & \cdots & r\left(x_N, x_N\right) \end{bmatrix},$$

where $r\left(x_i, x_i\right) = 1$ and $r\left(x_i, x_j\right)$ is the correlation associated with x_i and x_j. When elements X_i and X_j of $\boldsymbol{X}$ are uncorrelated, $r\left(x_i, x_j\right) = 0$.

Note 2 to entry: Correlations are also known as correlation coefficients.

Note 3 to entry: $\boldsymbol{R}_x$ is related to $\boldsymbol{V}_x$ (see definition 3.3) by

$$\boldsymbol{V}_x = \boldsymbol{D}_x \boldsymbol{R}_x \boldsymbol{D}_x,$$

where $\boldsymbol{D}_x$ is a diagonal matrix of dimension $N \times N$ with diagonal elements $u\left(x_1\right), \ldots, u\left(x_N\right)$. Element $\left(i, j\right)$ of $\boldsymbol{V}_x$ is given by

$$u\left(x_i, x_j\right) = r\left(x_i, x_j\right) u\left(x_i\right) u\left(x_j\right).$$

[SOURCE: ISO/IEC Guide 98-3:2008/Suppl. 2:2011, 3.21, modified - definition slightly modified, Notes 4 and 5 deleted.]

3.5
measurement model
mathematical relation among all quantities known to be involved in a measurement

[SOURCE: ISO/IEC Guide 99:2007 (corr. 2010), 2.48, modified - Notes 1 and 2 deleted.]

3.6
calibration
operation that, under specified conditions, in a first step, establishes a relation between the quantity values with measurement uncertainties provided by measurement standards and corresponding indications with associated measurement uncertainties and, in a second step, uses this information to establish a relation for obtaining a measurement result from an indication

Note 1 to entry: A calibration may be expressed by a statement, calibration function, calibration diagram, calibration curve, or calibration table. In some cases, it may consist of an additive or multiplicative correction of the indication with associated *measurement uncertainty* (3.1).

Note 2 to entry: Calibration should not be confused with adjustment of a measuring system, often mistakenly called 'self-calibration', nor with verification of calibration.

Note 3 to entry: Often the first step alone in the above definition is perceived as being calibration.

[SOURCE: ISO/IEC Guide 99:2007 (corr. 2010), 2.39.]

3.7
stimulus interval
interval in the stimulus variable over which a calibration function is defined

3.8
stimulus
quantity that effects a *response* (3.9) in a measuring system

3.9
response
quantity resulting from stimulating a measuring system

3.10
inverse evaluation
use of a calibration function to provide the stimulus value corresponding to a response value

3.11
direct evaluation
use of a calibration function to provide the response value corresponding to a stimulus value

4 Conventions and notation

For the purposes of this document the following conventions and notations are adopted.

4.1 The quantity whose values are provided by measurement standards is termed the independent variable x (also called 'stimulus') and the quantity described by measuring system indication values is termed the dependent variable y (also called 'response').

4.2 x_i and y_i denote the measured values of the Cartesian co-ordinates of the ith point $\left(x_i, y_i\right)$, $i = 1,\ldots,m,$ in a calibration data set of m points. Vector and matrix notation is frequently used. The values of x_i and y_i are often expressed as vectors, with 'T' denoting 'transpose':

$$\boldsymbol{x} = \left[x_1, \ldots, x_m\right]^{\mathsf{T}}, \quad \boldsymbol{y} = \left[y_1, \ldots, y_m\right]^{\mathsf{T}}.$$

A matrix or vector of zeros is denoted by $\mathbf{0}$.

4.3 True values (that would be achieved with perfect measurement) of the co-ordinates of the ith point are denoted by ξ_i and η_i. Measured values of points expressed in Cartesian co-ordinates and corresponding true values are related by:

$$x_i = \xi_i + d_i, \quad y_i = \eta_i + e_i,$$

where d_i and e_i denote the errors in x_i and y_i, respectively. Errors are unknowable, but can often be estimated.

4.4 The standard uncertainties associated with x_i and y_i are denoted by $u\left(x_i\right)$ and $u\left(y_i\right)$, respectively. The covariance associated with x_i and x_j is denoted by $u\left(x_i, x_j\right)$. Similarly, the covariance associated with y_i and y_j is denoted by $u\left(y_i, y_j\right)$.

NOTE This document does not consider cross-variances $u\left(x_i, y_j\right)$ since no practical calibration application has been identified in which cross-variances are prescribed.

4.5 The uncertainty information for the specification of a polynomial calibration problem is represented by matrices $\boldsymbol{V_x}$ and $\boldsymbol{V_y}$ each of dimension $m \times m$ holding the variances (squared standard uncertainties) $u^2\left(x_i\right) \equiv u\left(x_i, x_i\right)$ and $u^2\left(y_i\right) \equiv u\left(y_i, y_i\right)$, and the covariances $u\left(x_i, x_j\right)$ and $u\left(y_i, y_j\right)$. Formula (1) denotes the covariance matrix associated with $\boldsymbol{x}$ and Formula (2) denotes the covariance matrix associated with $\boldsymbol{y}$:

$$\boldsymbol{V}_x = \begin{bmatrix} u\left(x_1, x_1\right) & \cdots & u\left(x_1, x_m\right) \\ \vdots & \ddots & \vdots \\ u\left(x_m, x_1\right) & \cdots & u\left(x_m, x_m\right) \end{bmatrix}, \tag{1}$$

$$\boldsymbol{V}_y = \begin{bmatrix} u\left(y_1, y_1\right) & \cdots & u\left(y_1, y_m\right) \\ \vdots & \ddots & \vdots \\ u\left(y_m, y_1\right) & \cdots & u\left(y_m, y_m\right) \end{bmatrix}. \tag{2}$$

For a particular calibration problem, either of $\boldsymbol{V_x}$ and $\boldsymbol{V_y}$ may be equal to $\mathbf{0}$.

NOTE This document is concerned with problems in which the $u\left(x_i\right)$ or the $u\left(y_i\right)$ are generally different (heteroscedastic case).

4.6 If the covariances $u\left(x_i, x_j\right)$ $(i \neq j)$ are all zero, $\boldsymbol{V_x}$ is a diagonal matrix:

$$\boldsymbol{V}_x = \begin{bmatrix} u^2\left(x_1\right) & & \\ & \ddots & \\ & & u^2\left(x_m\right) \end{bmatrix} = \operatorname{diag}\left[u^2\left(x_1\right), \ldots, u^2\left(x_m\right)\right] \tag{3}$$

and similarly for the $u\left(y_i, y_j\right)$.

4.7 The elements below the main diagonal of a symmetric matrix are generally not displayed. Thus, for instance, the representation of the matrix

$$\begin{bmatrix} 1,2 & -0,7 & 0,8 \\ -0,7 & 2,5 & 0,5 \\ 0,8 & 0,5 & 1,7 \end{bmatrix} \quad \text{is} \quad \begin{bmatrix} 1,2 & -0,7 & 0,8 \\ & 2,5 & 0,5 \\ \text{sym.} & & 1,7 \end{bmatrix}.$$

4.8 A polynomial calibration function relating y and x is denoted by $p_n\left(x\right)$, where n is the degree of the polynomial. It is denoted by $p_n\left(x, \boldsymbol{a}\right)$ when it is necessary to indicate that it depends on $n+1$ parameters $\boldsymbol{a} = \left[a_0, \ldots, a_n\right]^{\mathsf{T}}$.

4.9 An estimate of a quantity q is denoted by $\hat{q}$. Model values corresponding to the data point $\left(x_i, y_i\right)$, namely, satisfying $\hat{y}_i = p_n\left(\hat{x}_i, \hat{\boldsymbol{a}}\right)$ are denoted by $\hat{x}_i$ and $\hat{y}_i$.

4.10 The function that is minimized to estimate the polynomial function parameters $\boldsymbol{a}$ is termed the objective function.

4.11 While data values in examples are provided to a given number of decimal digits, results of calculations are sometimes provided to a greater number, for comparison purposes, for example.

5 Other Standards using polynomial calibration functions

Other Standards concerned with polynomial calibration are as follows.

a) ISO 6143:2006[23] is concerned with comparison methods for determining and checking the composition of calibration gas mixtures. It contains clauses on the determination (and use) of 'analysis functions' given calibration data. The analysis functions considered are polynomials of degrees 1, 2 and 3 representing the stimulus as a function of response. Uncertainties are permitted

in the stimulus data values and the response data values. Covariances are permitted in the stimulus data, but not in the response data.

b) ISO 7066-2:1988[24] covers basic methods for determining and using polynomial calibration functions in the context of the measurement of fluid flow: assessment of uncertainty in the calibration and use of flow measurement devices. It handles, in the language of this document, standard uncertainties associated with the data y-values, and inverse evaluation.

c) ISO 11095:1996[20] specifically addresses reference materials, outlining general principles needed to calibrate a measuring system and to maintain that system in a state of statistical control. It provides a basic method for estimating a straight-line calibration function when stimulus values are known exactly.

d) ISO 11843-2:2000[21] concerned with capability of detection, uses straight-line calibration functions when the standard uncertainties in the response values are constant or depend linearly on stimulus. ISO 11843-5:2008[22] extends the provisions of ISO 11843:2000 to the non-linear case.

e) ISO/TS 28037:2010[25] covers the same uncertainty structures as in the current document, and is concerned with straight-line calibration. The current document can be regarded as an extension of ISO/TS 28037 to polynomial functions of general degree.

6 Calibration data and associated uncertainties

6.1 Calibration consists of two stages (definition 3.6). The first stage establishes a relation between (stimulus) values provided by measurement standards and corresponding instrument response values. The second stage uses this relation to obtain stimulus values from further instrument response values (inverse evaluation). The relation also allows a response value to be obtained given a further stimulus value (direct evaluation). In this document the relation takes the form of a polynomial calibration function, which is described by a set of parameters, estimates of which are deduced from the calibration data and the associated uncertainties.

NOTE This document is not concerned with determining a mathematical form from which a stimulus value can be determined explicitly given a response value. Such a form is known in some fields of application as an analysis function.

6.2 The calibration of a measuring system should take into account prescribed calibration data uncertainties and any prescribed covariances.

6.3 An acceptable calibration function will satisfy a statistical test for compatibility with the calibration data and the accompanying uncertainties. In many circumstances it will also have to be monotonic (strictly increasing or decreasing).

6.4 Standard uncertainties and covariances accompany the parameter estimates, and the information concerning the calibration function is used to provide a stimulus value (or response value) and the associated standard uncertainty corresponding to a given response value (or stimulus value, respectively).

6.5 Any particular set of calibration data $\left(x_i, y_i\right)$, $i = 1, \ldots, m$, will have an uncertainty structure specific to that data. At one extreme, nothing is known about the uncertainties and covariances and, to proceed, assumptions are necessary. At the other extreme, all standard uncertainties $u\left(x_i\right)$ and $u\left(y_i\right)$

and all covariances $u\left(x_i, x_j\right)$ and $u\left(y_i, y_j\right)$ are prescribed. In practice, the provided information often lies between these extremes.

NOTE In this document any uncertainty or covariance that is not prescribed is taken as zero.

6.6 The following five cases can be distinguished, the first four in approximately increasing order of complexity of uncertainty structure. The fifth is different in character in the sense that the uncertainty information is unknown.

a) *Response data uncertainties*. Standard uncertainties $u(y_i)$, $i = 1,...,m$, prescribed.

b) *Response data uncertainties and covariances*. As 6.6 a) with covariances $u(y_i, y_j)$, $i = 1,...,m$, $j = 1,...,m$ $(i \neq j)$, also prescribed.

c) *Stimulus and response data uncertainties*. As 6.6 a) with standard uncertainties $u(x_i)$, $i = 1,...,m$, also prescribed.

d) *Stimulus and response data uncertainties and covariances*. As 6.6 c) with covariances $u(x_i, x_j)$ and $u(y_i, y_j)$, $i = 1,...,m$, $j = 1,...,m$ $(i \neq j)$, also prescribed.

e) *Unknown data uncertainties*.

In cases 6.6 a) to 6.6 d), the prescribed uncertainties and covariances are summarized as covariance matrices $\boldsymbol{V}_{\boldsymbol{x}}$ and $\boldsymbol{V}_{\boldsymbol{y}}$ as appropriate according to Subclause 4.5.

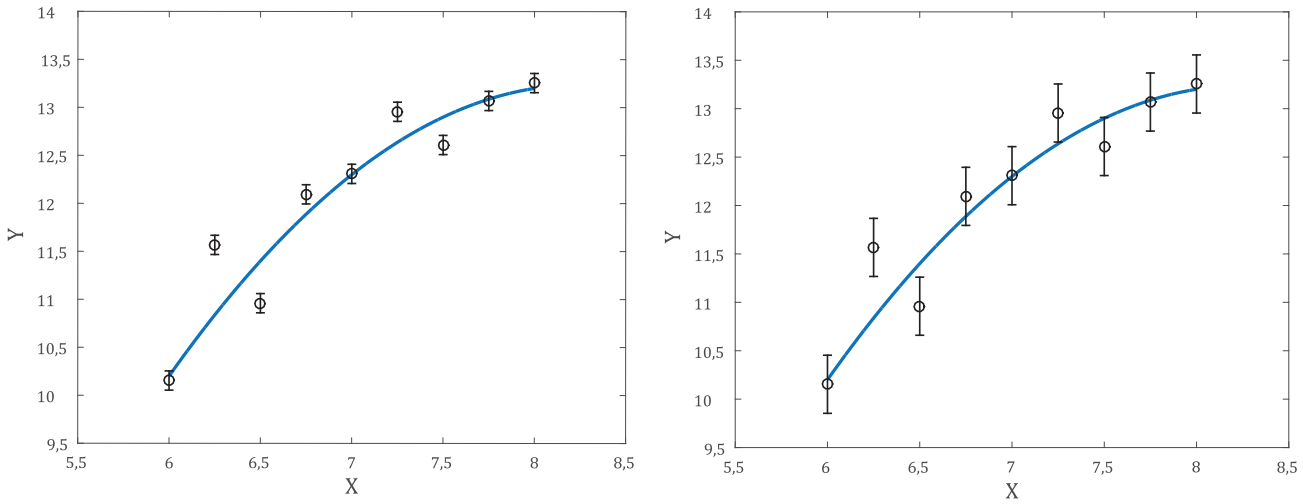
NOTE Cases 6.6 a) to 6.6 c) can be treated as special cases of 6.6 d), but computationally less efficiently.

6.7 The key distinction between calibration data with prescribed uncertainties and calibration data with unknown uncertainties made in this document is the following.

a) For calibration data with prescribed uncertainties and covariances [cases 6.6 a) to 6.6 d)] a metric, such as the chi-squared statistic (Subclause 7.7.1), that uses the uncertainties and covariances may be employed to decide whether a candidate calibration function, in this document a polynomial of a particular degree, is statistically valid. This approach assumes the plausibility of the specified uncertainty information.

b) For calibration data with unknown uncertainties [case 6.6 e)] a chi-squared statistic can still be calculated for candidate polynomial models. The assumptions are made that the data errors in the response variable are homogeneous and the data errors in the stimulus variable are negligible. The value of the chi-squared statistic can be used to estimate the response variable standard uncertainty and the provisions of 6.7 a) then applied.

6.8 A polynomial is selected from a set of candidate polynomials of various degrees according to a suitable criterion such as AIC (Subclause 7.7.3). For some data sets with prescribed uncertainties there might be no suitable polynomial (or any other smooth) representation consistent with this information. For the data in Figure 1 a), the only uncertainties are associated with the *y*-values, the vertical bars represent ± 1 standard uncertainty, and the covariances are zero. The smallness of the standard uncertainties prevent a monotonic function that is consistent with the data from being obtained. For the data in Figure 1 b), identical to those in Figure 1 a) except that the standard uncertainties are some three times as large, a monotonic polynomial of low degree is suitable. An acceptable calibration function should be both monotonic (Subclause 7.6) and statistically adequate[30].



a) Statistical inadequacy **b) Statistical adequacy**

Key

X stimulus (a.u.)

Y response (a.u.)

NOTE Error bars denote ±1 standard uncertainty. 'a.u.' denotes arbitrary units.

Figure 1 —Statistical inadequacy and adequacy

NOTE Figure 1 a) appears to relate to mis-specification of the standard uncertainties associated with the calibration data; their possible rectification is beyond the scope of this document.

6.9 Estimates of the calibration function parameters depend on the calibration data and, apart from case 6.6 e), the prescribed data uncertainties and covariances. The law of propagation of uncertainty (LPU) in the ISO/IEC Guide 98-3:2008 (GUM) can be applied to propagate calibration data uncertainties and covariances through the computation of the calibration function parameters to obtain parameter uncertainties and covariances. When there is no uncertainty associated with the stimulus values (Subclauses 9.2, 9.3 and 9.6), the propagation is exact, since the parameters of a polynomial calibration function depend linearly on the data response values and LPU applies with no approximation error in such cases (see Subclause 7.2.1). For other cases (Subclauses 9.4 and 9.5), the propagation is approximate, based on a linearization about the parameter estimates. The approximation incurred by the linearization will often be fit for purpose for practical calibration problems.

NOTE If linearization is unfit for purpose, such as when the stimulus value uncertainties are large, the propagation of distributions may be used to obtain parameter estimates, uncertainties and covariances. This approach (ISO/IEC Guide 98-3:2008/Suppl. 2:2011), which uses a Monte Carlo method, is beyond the scope of this document.

6.10 Uncertainty information concerning the calibration function parameters takes the form of a covariance matrix for (estimates of) those parameters. That information can equally be represented as the standard uncertainties associated with those parameters together with their correlation matrix (definition 3.4), which may be a more useful form. Either form can be used in the evaluation of the standard uncertainty associated with inverse or direct evaluation.

6.11 When the calibration function is used for inverse evaluation (Subclause 12.2), the application of LPU is approximate, even for polynomials of degree one, because when used inversely the polynomial is

non-linear in its parameters. Again, the approximation incurred by the linearization will often be fit for purpose.

NOTE When it is acceptable to express a polynomial calibration function as x in terms of y, the polynomial calibration function determined is used directly and there is no linearization error in that stage of the calculation.

7 Polynomials as calibration functions

7.1 General

7.1.1 Given calibration data, this clause considers the determination of a relationship $y = p_n\left(x\right)$ describing the dependent variable y as a polynomial function of degree n of the independent variable x.

7.1.2 If the degree n is not known in advance, as is commonly the case, an appropriate polynomial degree is to be determined. Subclause 7.7 describes determination of the degree such that the resulting function satisfies suitable criteria.

7.1.3 The information used to determine the polynomial calibration function is the calibration data and any calibration data uncertainties and covariances. In this document, the calibration data are denoted by $\left(x_i, y_i\right),\ i = 1,\ldots,m,$ that is, m pairs of measured values of x and y. The highest degree $n_{\max}$ of polynomial to be considered is also to be specified, where $n_{\max}$ is less than the number of distinct values of x_i.

NOTE Annex D of ISO/TS 28037:2010 indicates how the uncertainties and covariances associated with the measured response and stimulus variables can be provided in some cases, giving an interpretation of that information.

7.2 Working with polynomials

7.2.1 For a degree higher than one a polynomial is non-linear in terms of its variable x, but it is linear in its parameters (coefficients). A polynomial of degree n (order $n + 1$) has $n + 1$ coefficients. It can be expressed in *monomial form*, with coefficients $h_0,\ldots,h_n,$ as:

$$p_n\left(x\right) = h_0 + h_1 x + h_2 x^2 + \cdots + h_n x^n = \sum_{r=0}^{n} h_r x^r . \tag{4}$$

7.2.2 The functions $1, x, x^2,\ldots,x^n$ are known as the *monomial* basis functions for polynomials of degree n. A polynomial of degree 1 is a straight line, degree 2 a quadratic function, degree 3 a cubic function, etc. An immediate appeal of polynomials is that their evaluation requires only some n additions and n multiplications (Subclause 7.4).

7.2.3 Polynomials are often suitable for representing a smooth curve or data generated from a smooth curve over a given interval. They are extremely flexible: mathematically a polynomial of an appropriate degree can approximate any smooth (continuous) curve to a given numerical precision. Polynomials of modest degree are less appropriate for representing curves with abrupt changes in value or gradient, or describing a saturation effect.

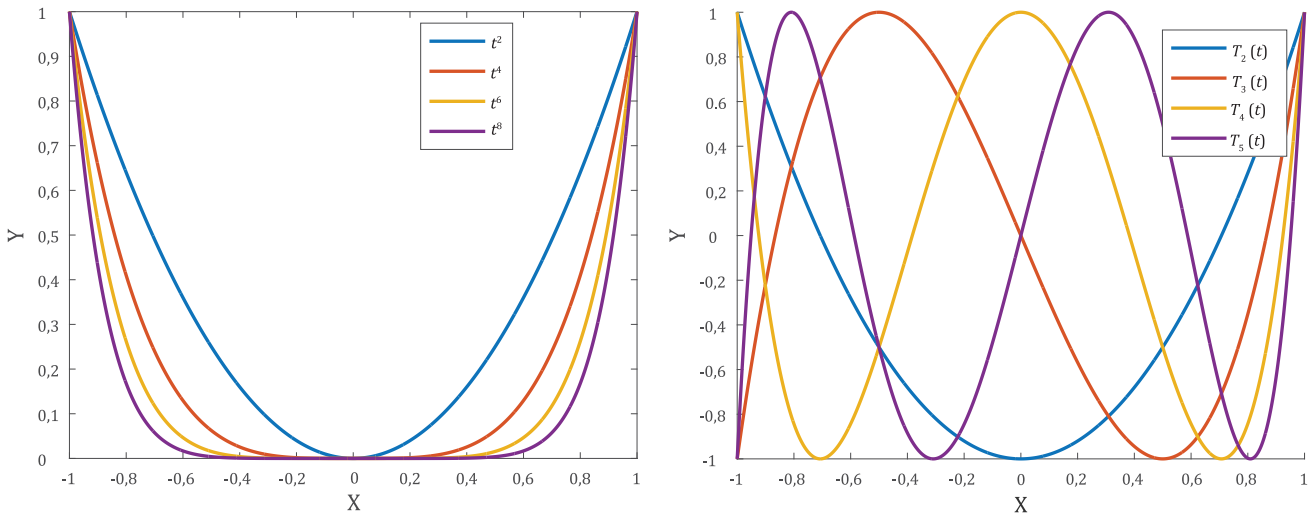
7.2.4 Whilst the description of polynomial functions in the monomial form [Formula (4)] makes clear their nature, the use of this form can lead to difficulties with numerical computation and interpretation of the contribution of individual terms. A first difficulty is that for $|x| \gg 1$, the terms x^r become very large in magnitude as r increases. Similarly, for $|x| \ll 1$, the terms x^r become very small in magnitude as r increases. This imbalance is alleviated by working with polynomials in a normalized variable t lying in the interval [−1, 1] that depends linearly on x, thus ensuring that the (transformed) polynomial is also of degree n in t. If x lies in the interval $\left[x_{\min}, x_{\max}\right]$,

$$t = \frac{2x - x_{\min} - x_{\max}}{x_{\max} - x_{\min}}, \tag{5}$$

with all its powers lying in the interval [−1, 1]. The polynomial can then be expressed as

$$P_n(t) = q_0 + q_1 t + q_2 t^2 + \cdots + q_n t^n = \sum_{r=0}^{n} q_r t^r \tag{6}$$

for some coefficients $q_0, \ldots, q_n$. A second difficulty arises from the fact that, especially for large *r*, the monomial basis function t^{r+2} looks similar to t^r in the interval [−1, 1]. Figure 2 a) depicts the monomials t^2 (uppermost curve), t^4, t^6 and t^8 (lowermost curve). The similarity of these basis functions leads to *ill-conditioning* in determining the monomial parameters, which will mean a loss of numerical precision. This ill-conditioning worsens rapidly as the degree increases, with the consequence that the loss of numerical precision can become catastrophic for higher polynomial degrees. A third difficulty relates to the interpretation of the coefficients in the monomial form in the original variable, namely, Formula (4). However, in Formula (6), the monomial form in the transformed variable t, the term involving t^r contributes an amount lying between $-|q_r|$ and $|q_r|$, with at least one of these values attained at the endpoints of the interval [−1, 1].



a) Monomial functions t^2, t^4, t^6 and t^8 on the interval [−1,1]

b) Chebyshev polynomials $T_2(t)$, $T_3(t)$, $T_4(t)$, and $T_5(t)$

Key

X independent variable t

Y dependent variable

Figure 2 — Monomial functions and Chebyshev polynomials

7.2.5 There are other forms for the basis functions that have even better properties than Formula (6). The Chebyshev polynomials $T_r(t)$, used in this document, are one such set of basis functions. They are defined by recurrence on the interval [−1,1] (see reference [6], page 1):

$$T_0(t) = 1, \quad T_1(t) = t, \quad T_r(t) = 2tT_{r-1}(t) - T_{r-2}(t), \quad r \geq 2. \tag{7}$$

Chebyshev polynomials can also be defined using the trigonometrical relationship

$$T_r(\cos\theta) = \cos r\theta, \quad \cos r\theta = t. \tag{8}$$

Figure 2 b) depicts $T_2(t)$ (least oscillatory), $T_3(t)$, $T_4(t)$ and $T_5(t)$ (most oscillatory). The intertwining of the $T_r(t)$ can be shown generally to lead to much better numerical conditioning than the use of the t^r. The Chebyshev representation of a polynomial of degree n is

$$p_n(x) \equiv P_n(t) = a_0T_0(t) + \cdots + a_nT_n(t) = \sum_{r=0}^{n} a_rT_r(t). \tag{9}$$

NOTE Another class of basis functions due to Forsythe[16] is described in reference [7] where an algorithm is given for converting from the Forsythe form to the Chebyshev representation. The Forsythe form is based on generating a set of basis functions that are orthogonal with respect to the data x-values. Although the Forsythe form has excellent numerical properties, the Forsythe basis functions depend on the data x-values, rendering their use in conjunction with polynomials from other sources inconvenient. Moreover, the Forsythe form has not been generalized to data possessing x-value uncertainties or any covariances.

7.3 Choice of defining interval for the calibration function

7.3.1 Consider the use of a determined calibration function $p_n(x)$ for inverse evaluation (Subclause 12.2), that is, to provide the value x_0 of the stimulus variable x corresponding to a value y_0 for the response variable y, particularly in the case where x_0 would lie near an extremity of the interval $[x_{\min}, x_{\max}]$ over which $p_n(x)$ is defined. Assume $p_n(x)$ is strictly increasing over $[x_{\min}, x_{\max}]$; a similar argument applies in the decreasing case. The y-values at the interval endpoints are $y_{\min} = p_n(x_{\min})$ and $y_{\max} = p_n(x_{\max})$. For any value y_0 in the interval $[y_{\min}, y_{\max}]$, x_0 is given uniquely by solving the equation $p_n(x_0) = y_0$. However, since y_0 is subject to uncertainty, it may lie outside the interval $[y_{\min}, y_{\max}]$, with the consequence that x_0 would lie outside the defining interval $[x_{\min}, x_{\max}]$.

NOTE There is no problem in the above respect for direct evaluation.

7.3.2 There are two ways of treating such a situation. The first is to allow only values of y_0 within the interval $[y_{\min}, y_{\max}]$, which would limit the applicability of the calibration function. The second way is to extend the interval over which the calibration function is defined. One possibility is to extend the interval $[\min_i x_i, \max_i x_i]$ as little as possible, say to $[\min_i x_i - \Delta x, \max_i x_i + \Delta x]$, where $\Delta x = 0{,}1(\max_i x_i - \min_i x_i)$. Some experimentation may be required to determine an appropriate interval in any particular case. There may be application-specific reasons to select an appropriate interval. The most extreme case arises when the gradient of the calibration curve is small in magnitude, since a small change in response induces a large change in stimulus [illustrated in the optical density-absorbed dose calibration function shown in Figure 5 b) for response values of approximately 0,45]. For the examples given in this document, suitable intervals $[x_{\min}, x_{\max}]$ were chosen.

7.3.3 The interval $[\min_i x_i, \max_i x_i]$ should be extended as little as possible to reduce extrapolation beyond the span of the data, which is generally considered unsafe.

NOTE For the optical density-absorbed dose example (Subclauses 7.5.3 and 9.2), the use of $\Delta x = 0{,}1(\max_i x_i - \min_i x_i)$ is inadequate for inverse interpolation for some y_0 close to $y_{\max}$ as defined in Subclause 7.3.1 with $u(y_0) = 0{,}003$, but the replacement of 0,1 by 0,15 proves satisfactory.

7.4 Using the Chebyshev representation of a polynomial

7.4.1 By using Chebyshev polynomials in a normalized variable [Formula (5)] it is possible to use polynomial functions of moderate to high degree in a numerically stable way[2]. Further benefits and properties are described in Subclauses 7.4.2 to 7.4.4 and illustrated throughout this document.

7.4.2 The Chebyshev representation [Formula (9)] of a polynomial $p_n\left(x, \boldsymbol{a}\right)$ of degree n ($n > 0$) constitutes the parameters (coefficients) $\boldsymbol{a} = \left(a_0, \ldots, a_n\right)^{\mathsf{T}}$ and constants $x_{\min}$ and $x_{\max}$ specifying the defining interval. It is recommended that the evaluation of p_n at any value x within $[x_{\min}, x_{\max}]$ is carried out using Clenshaw's algorithm[5] as in Table 1. For comparison, Horner's evaluation scheme[19] for the monomial form $p_n = h_0 + h_1 x + \ldots + h_n x^n$ (Subclause 7.2.1) is also given in Table 1. The Chebyshev form can be evaluated in some $2n$ additions (or subtractions) and n multiplications compared with n additions and n multiplications for the monomial form.

Table 1 — Evaluation of a polynomial from its Chebyshev form and its monomial form

Step	Chebyshev form	Monomial form
1	$t = \left(2x - x_{\min} - x_{\max}\right) / \left(x_{\max} - x_{\min}\right)$	
2	$b_{n+1} = b_{n+2} = 0$	$g_{n+1} = 0$
3 $\left(\text{for } r = n,\ n-1, \ldots, 0\right)$	$b_r = 2tb_{r+1} - b_{r+2} + a_r$	$g_r = xg_{r+1} + h_r$
4	$p_n = (b_0 - b_2 + a_0) / 2$	$p_n = g_0$

7.4.3 For many polynomial calibration functions the polynomial degree is modest, often one, two, three or four. For such cases, the use of a *monomial* [Formula (6)] in a normalized (rather than the raw) variable generally presents few numerical difficulties. It is nevertheless recommended that, particularly when the magnitude of either endpoint of the *x*-interval over which the calibration function is to apply is very large or very small compared with unity, the Chebyshev representation is used in constructing the polynomial calibration function.

7.4.4 There are cases, such as the International Temperature Scale ITS-90[13], where the reference functions involved take relatively high degrees such as 12 or 15. For such functions, working with a normalized variable as in Formula (5) offers considerable numerical advantages and the Chebyshev form confers even more, not only numerically, but also in terms of giving a manageable and sometimes a more compact representation. Some of these advantages are introduced by way of an example.

EXAMPLE Thermoelectric voltage (based on reference [9]).

The monomial representation of thermoelectric voltage

$$E = \sum_{r=0}^{8} c_r T^r$$

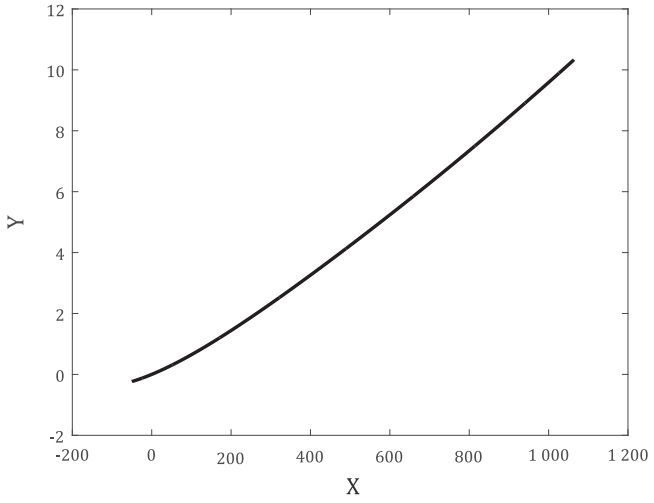
in the reference function for Type S Thermocouples, for Celsius temperature T in the interval [−50 °C, 1 064,18 °C], is given in a NIST database[1]. There is a factor of some 10^{21} between the non-zero coefficients of largest and smallest magnitude, which are held to 12 significant decimal digits (12S); presumably it was considered that care is needed in working with this particular representation. The c_r are given to 5S (five significant decimal digits) in Table 2 (column 'Raw, c_r').

Table 2 — Polynomial coefficients for a Type S thermocouple

Degree r	Raw, c_r	Scaled, $\tilde{c}_r$	Normalized	Chebyshev
0	0	0	4,303 6	4,639 1
1	5,403 1 × 10^{-3}	5,749 9	5,527 8	5,371 1
2	1,259 3 × 10^{-5}	14,261 8	0,478 4	0,370 6
3	−2,324 8 × 10^{-8}	−28,017 4	−0,054 3	−0,072 9
4	3,220 3 × 10^{-11}	41,300 5	0,220 6	0,037 1
5	−3,314 7 × 10^{-14}	−45,239 0	−0,163 7	−0,013 0
6	2,557 4 × 10^{-17}	37,144 7	0,021 6	0,002 2
7	−1,250 7 × 10^{-20}	−19,331 0	−0,024 9	−0,000 4
8	2,714 4 × 10^{-24}	4,464 8	0,025 2	0,000 2

A scaled variable $\tilde{T} = T / B$ has been used in ITS-90 work in recent years, where in this instance $B = 1\,064{,}18$ °C is the upper interval endpoint. Then, letting $\tilde{c}_r = B^r c_r$, $E = \sum_{r=0}^{n} \tilde{c}_r \tilde{T}^r$. The scaling implies that the contribution from the r th term in the sum is bounded in magnitude by $\left|\tilde{c}_r\right|$. Values of E in mV are typically required to 3D (three decimal places). Accordingly, the coefficients $\tilde{c}_r$ are given in Table 2 (column 'Scaled, $\tilde{c}_r$') to 4D (including a guard digit) and are much more manageable. Alternatively, the variable can be normalized to the interval $\left[-1, 1\right]$ (not done in ITS-90) using Formula (5) with $x \equiv T$, $x_{\min} = -50\,°\text{C}$ and $x_{\max} = B$. The corresponding coefficients are given in column 'Normalized' and the Chebyshev coefficients in column 'Chebyshev', both to 4D, obtained using references [7] and [31].

Figure 3 depicts the reference function. It curves very gently, but the non-linearity present cannot be ignored. The coefficients in the monomial representation in terms of the raw or scaled variable in Table 2 give no indication of the gently curved form. However, the normalized and Chebyshev forms (again see Table 2), because the first two coefficients are dominant, indicate that the calibration function has an appreciable linear (straight-line) component. The Chebyshev coefficients for degree 8 and arguably for degree 7 could be replaced by zero, yielding a lower-degree polynomial, since to 3D they make little or no contribution. Such reasoning could not be applied directly to the other polynomial representations.



Key

X temperature, T (°C)

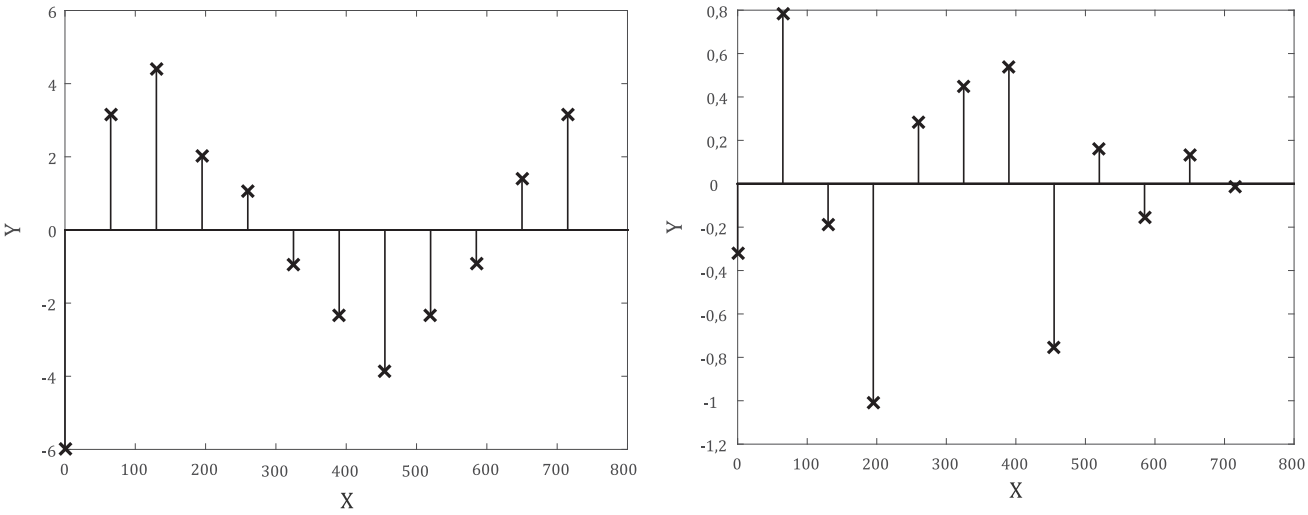
Y thermoelectric voltage, E (mV)

Figure 3 — Relationship between temperature and thermoelectric voltage

7.5 Assessing suitability of a polynomial function: visual inspection

7.5.1 As in many problems involving data analysis, visual inspection of candidate results is valuable. It is especially useful for calibration problems where available data is limited. In such cases, statistical tests alone used to assess candidate solutions often do not have great statistical power.

7.5.2 An immediate visual test is of the residuals of a candidate polynomial model $p_n\left(x\right)$, that is, the deviations (in the y-direction) of the model from the data. When there is no covariance associated with the y_i, and the x_i have no uncertainty, a graph of the residuals $e_i = y_i - p_n\left(x_i\right)$ against the x_i can be informative. A graph displaying the extent to which the weighted residuals $\left[y_i - p_n\left(x_i\right)\right] / u\left(y_i\right)$ (plotted against the x_i) exhibit random behaviour can be helpful. Figure 4 shows for the optical density calibration example in Subclause 9.2 the weighted residuals for a polynomial function of degree 2 [Figure 4 a)] and for degree 4 [Figure 4 b)]. The residuals for degree 2 exhibit a clear trend with respect to x, whereas those for degree 4 behave more randomly.



a) Degree 2 **b) Degree** 4

Key

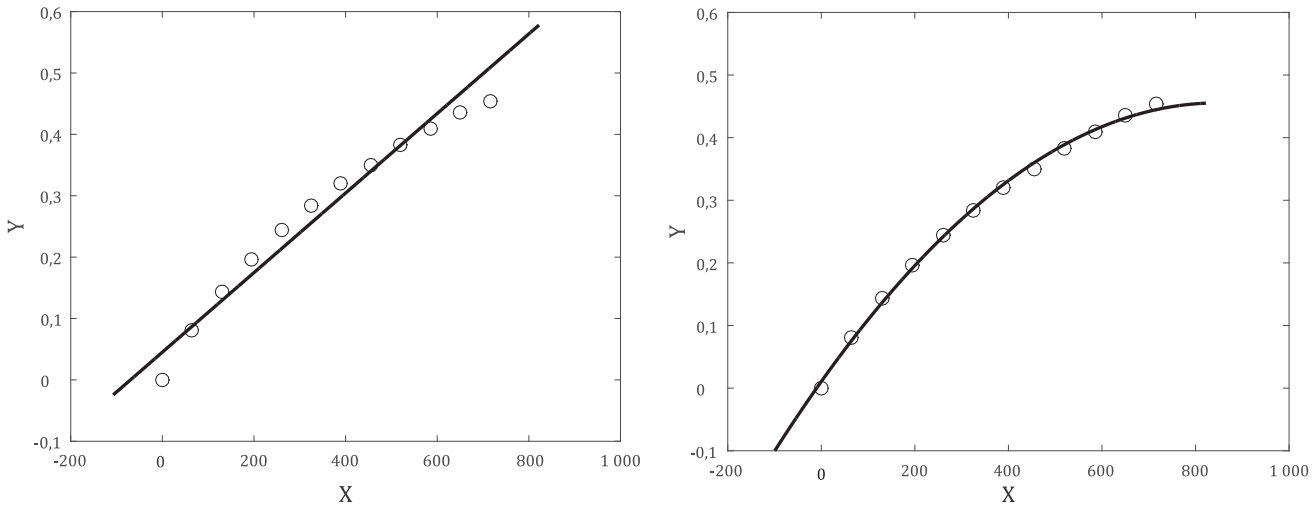
X stimulus variable *x*

Y weighted *y*-residual

NOTE Different vertical scales are used for the two cases.

Figure 4 — Optical density-absorbed dose weighted y-residuals for a polynomial calibration function

7.5.3 When the data have very small uncertainties, to graphical accuracy it may be difficult to see the deviations of some candidate models from the data, because the magnitudes of these deviations may be much less than those of the data response values. Figure 5 a) shows a case in which a polynomial of degree 1 exhibits clear departures from the data, whereas [Figure 5 b)] for a polynomial of degree 2 (and greater) the deviations are not so apparent. However, that the polynomial of degree 2 is not an explanatory model for the data is apparent by examining the weighted *y*-residuals displayed in Figure 4 a). The sequence of banks of signs of the residuals (negative, positive, negative, positive) and the relative magnitudes of those residuals indicate a clear underlying trend. In such cases it is recommended to use a correction polynomial for purposes of visualization, that is, to subtract a polynomial of lower degree from the candidate polynomial and also to subtract the values of that polynomial corresponding to the data *x*-values from the data *y*-values. A graph of the polynomial and data so adjusted would be expected more readily to depict the deviations.



a) Degree 1 **b) Degree** 2

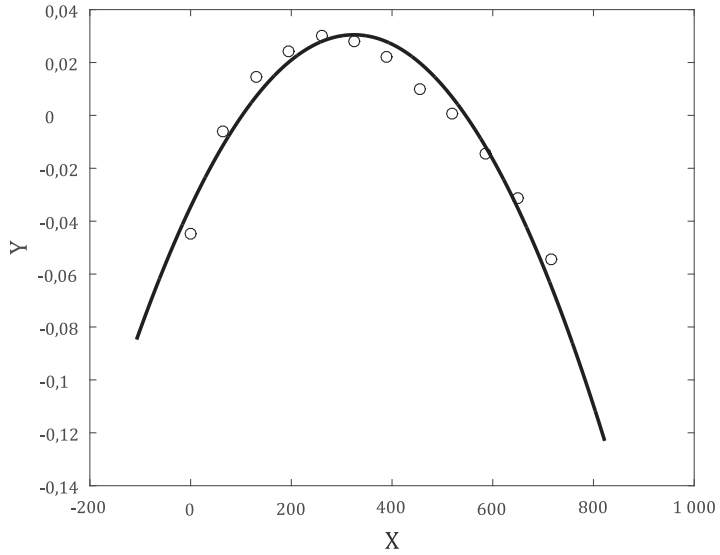
Key

X stimulus variable *x*

Y response variable *y*

Figure 5 — Optical density-absorbed dose calibration data and polynomial model

7.5.4 Figure 6 is identical to Figure 5 b) except that a polynomial of degree 1 (in fact the degree 1 polynomial fit) has been subtracted as above, and can be seen to be consistent with Figure 4 a).



Key

X stimulus variable *x*

Y response variable *y*

Figure 6 — Optical density-absorbed dose calibration data and polynomial model of degree 2 **[Figure 5 b)] both corrected by a polynomial of degree** 1

7.5.5 When there are covariances associated with the y_i, a graph of the transformed weighted residuals $\boldsymbol{L}_{\boldsymbol{y}}^{-1}\boldsymbol{e}$ against $\boldsymbol{x}$ can be informative. Similarly, when there are covariances associated with the x_i, a graph of the transformed weighted residuals $\boldsymbol{L}_{\boldsymbol{x}}^{-1}\boldsymbol{d}$ against $\boldsymbol{y}$ can be helpful. Here $\boldsymbol{L}_{\boldsymbol{y}}$ and $\boldsymbol{L}_{\boldsymbol{x}}$ are lower triangular matrices given by the Cholesky factorizations[18], $\boldsymbol{V}_{\boldsymbol{y}} = \boldsymbol{L}_{\boldsymbol{y}}\boldsymbol{L}_{\boldsymbol{y}}^{\mathsf{T}}$ and $\boldsymbol{V}_{\boldsymbol{x}} = \boldsymbol{L}_{\boldsymbol{x}}\boldsymbol{L}_{\boldsymbol{x}}^{\mathsf{T}}$.

NOTE Standardizing by the standard uncertainties $u\left(e_i\right)$ associated with the e_i can also be useful.

7.6 Assessing suitability of a polynomial function: monotonicity

7.6.1 A calibration function is often used to provide a stimulus value given a response value or *vice versa*. Alternatively, a function that is to be used for this purpose might be composed of the sum of a 'reference' function and a calibration function, such as in the use of the International Temperature Scale ITS-90[13] (also see the example in Subclause 7.4.4). In the latter case, any test for monotonicity would apply to the composite function.

7.6.2 To be useful as a calibration function, a function generally has to be *strictly monotonic*, that is, the function must be strictly increasing or decreasing throughout the interval over which it is defined and to be used. This condition is necessary to ensure that a unique stimulus value will be given for any feasible response value. A simple way to check monotonicity, which is not fool-proof, is to evaluate the calibration function at a fine interval in x (1 000 uniformly spaced points, say, over the stimulus interval) to see whether these values form an increasing or decreasing set. When the calibration function is a polynomial, Annex A gives a more rigorous way to check monotonicity.

NOTE In extreme cases, a non-monotonic calibration function might be appropriate. In such a case, a rule would need to be established to select the appropriate value of the stimulus variable given a value of the response variable and relevant accompanying information.

7.7 Assessing suitability of a polynomial function: degree

7.7.1 The degree n of the polynomial calibration function is often unknown *a priori*. It can be chosen by fitting polynomial functions of increasing degree, forming a goodness-of-fit measure for each function, and using these measures to select a suitable polynomial degree. A common measure when the only uncertainties are associated with the y_i [case 6.6 a)] is the chi-squared statistic χ^2_{obs}, the sum of squares of the deviations of the fitted polynomial of degree n from the y_i, weighted inversely by the squared standard uncertainties associated with the y_i-values (Subclause 9.2). When covariances associated with the y_i are present [Subclause 9.3, case 6.6 b)], a modified measure is used:

$$\chi^2_{\text{obs}} = \hat{\boldsymbol{e}}^{\mathsf{T}}\boldsymbol{V}_{\boldsymbol{y}}^{-1}\hat{\boldsymbol{e}}\,, \tag{10}$$

where $\hat{e}_i = y_i - p_n\left(x_i, \hat{\boldsymbol{a}}\right)$ are the residuals for degree n corresponding to the estimate $\hat{\boldsymbol{a}}$ of $\boldsymbol{a}$. When uncertainties and possibly covariances are also associated with the x_i [cases 6.6c) and 6.6 d)], a further measure is used that takes this knowledge into consideration (see Subclauses 9.4 and 9.5). Sometimes the notation $\chi^2_{\text{obs}}\left(n\right)$ is used when it is helpful to indicate explicit dependence on degree n.

7.7.2 In most of this document, uncertainty information is considered to be provided with the data, and accordingly the only parameters to be estimated are the $n + 1$ polynomial coefficients. Exceptionally, where no uncertainty information is available, certain assumptions are made in order to proceed (Subclause 9.6). In that case, the standard deviation of the errors in the y-values is also estimated.

7.7.3 When uncertainty information is available, use is made in this document of generally accepted model-selection criteria, specifically, Akaike's Information Criterion (AIC), corrected AIC (AICc) and the Bayesian Information Criterion (BIC)[4], which apply when the calibration data errors can be regarded as drawn from normal distributions, as assumed throughout (Clause 9). For m data points and a polynomial model with $n + 1$ parameters, these criteria are:

$$\mathrm{AIC}\left(n\right) = \chi^2_{\mathrm{obs}}\left(n\right) + 2\left(n+1\right),$$

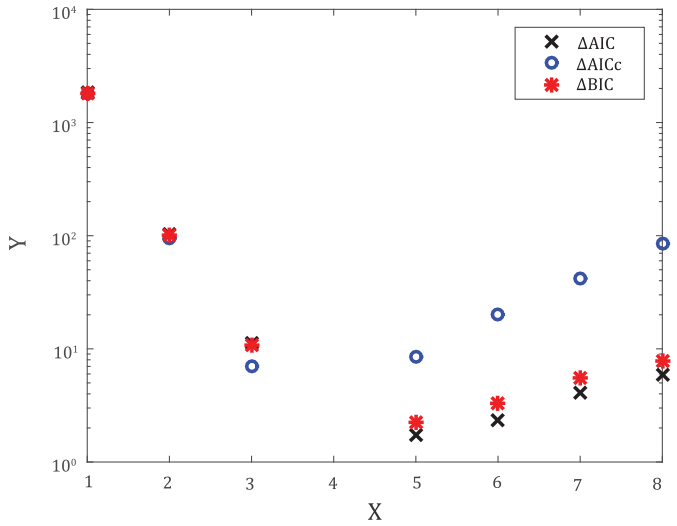
$$\mathrm{AICc}\left(n\right) = \mathrm{AIC}\left(n\right) + \frac{2\left(n+1\right)\left(n+2\right)}{m-n-2},$$

$$\mathrm{BIC}\left(n\right) = \chi^2_{\mathrm{obs}}\left(n\right) + \left(n+1\right)\ln m. \qquad (11)$$

7.7.4 All three criteria are designed to balance goodness of fit and simplicity of model. Given a number of candidate models, namely, for polynomial degrees $n = 1, \ldots, n_{\max}$, for a suitable choice of the maximum degree $n_{\max}$, the model having the smallest value of AIC (or AICc or BIC) would usually be selected. Some experiments[34] with these criteria for polynomial modelling found that AIC and BIC performed similarly, although AICc was more suitable for small data sets. Although more experience is needed before strong conclusions can be drawn, for practical polynomial calibration problems there is some evidence that the same degree of polynomial is usually selected by the three criteria when they can all be used. That is the case for the examples given in this document. However, since the computation involved in providing values for all three criteria is minimal, they could all be examined.

NOTE 1 The values of AIC for various values of n can be compared among themselves, as can the values of AICc or BIC. The values of AIC cannot be compared with those of BIC, for instance.

NOTE 2 AIC(n) and BIC(n) appear to have similar discriminatory power for polynomial models. AICc(n) has greater discriminatory power, but applies for fewer degrees (for which $n \leq m - 3$), which might be important when m, the number of calibration points, is small. Also see reference [8]. See, for instance, Figure 7, an explanation of which is given in Subclauses 7.7.5 and 7.7.6, which relates to an example of absorbed dose-optical density data that is discussed in more detail in Subclause 9.2.



Key

X polynomial degree n

Y adjusted information criterion

NOTE The values of zero for degree 4 are not shown: see Subclause 7.7.6.

Figure 7 — Adjusted information criteria versus polynomial degree for absorbed dose-optical density calibration data

NOTE 3 The polynomial degrees to be considered can be $n_{\min},\ldots,n_{\max}$, where $n_{\min}$ is the degree for which any lower degree is judged to be inadequate for the calibration data in hand. Possible reasons include high curvature or generally extreme non-linear behaviour.

7.7.5 In practice, the *adjusted* criterion $\Delta\mathrm{AIC}(n)=\mathrm{AIC}(n)-\mathrm{AIC}_{\min}$ may be used instead, where $\mathrm{AIC}_{\min}$ is the minimum of $\mathrm{AIC}(1),\ldots,\mathrm{AIC}(n_{\max})$. Criteria AICc and BIC can be adjusted similarly. Since, for a given data set, $\mathrm{AIC}_{\min}$ is a constant, the adjusted criterion is simply a shift of the original criterion, and so the adjusted values can be compared just as the original values can. Let $n=n^*$ at the minimum AIC value. Then $n=n^*$ is the optimal degree according to the criterion and $\Delta\mathrm{AIC}(n^*)=0$.

7.7.6 A plot of the values $\Delta\mathrm{AIC}(1),\ldots,\Delta\mathrm{AIC}(n_{\max})$ against n instead of, or in addition to, a table containing their values can be informative. If the values $\Delta\mathrm{AIC}(1),\ldots,\Delta\mathrm{AIC}(n_{\max})$ [with the exception of $\Delta\mathrm{AIC}(n^*)$, which is zero] span several orders of magnitude, it may be useful to plot the values against n on a logarithmic scale. In such a case the zero $\Delta\mathrm{AIC}(n^*)$, is "off the chart" since its logarithm equals $-\infty$. See Figure 7, for example.

7.7.7 Related to the χ^2_{obs} statistic is the root-mean-square residual (RMSR):

$$\mathrm{RMSR}\left(n\right) = \left[\frac{\chi^2_{\mathrm{obs}}\left(n\right)}{m-n-1}\right]^{1/2}, \tag{12}$$

which applies for $n < m-1$. As n is increased, the values of $\mathrm{RMSR}\left(n\right)$ tend to decrease initially and then to saturate when the calibration data set is suited to representation by a polynomial.

NOTE 1 The RMSR-values would often decrease once more for higher degrees when the polynomial function follows more closely the noise in the data (corresponding to over-fitting)[7].

NOTE 2 R^2 is a statistical indicator often used in practice that measures the 'proportion of the variance about the mean of the y-data explained by the fitted function'[33]. This measure and some of its generalizations only apply to the simplest uncertainty structures, such as 6.6 a) and 6.6 e), and are therefore unsuitable for general calibration purposes.

7.7.8 The values of AIC, AICc, BIC and RMSR for $n = 1,\ldots,n_{\max}$ can be used for the initial selection of an appropriate polynomial degree. Although RMSR has been traditionally used to select a suitable polynomial degree[7], it may be difficult to decide at which degree the root-mean-square residuals have saturated for practical purposes, particularly for the small data sets often arising in calibration work. Whenever possible it is therefore recommended to use one of the information criteria for this purpose, for which the decision is generally clearer. Such a chosen polynomial should always be further assessed for suitability, using visual checks (Subclause 7.5), a monotonicity check (Subclause 7.6) if appropriate or, importantly, employing knowledge of the intended application.

7.8 Validation of the calibration function

7.8.1 Consider the polynomial function of degree n selected as in Subclause 7.7. Under the assumption that the calibration data are regarded as realizations of random variables having normal distributions (not necessarily independent), the distribution for the measure for which Formula (10) constitutes a realization is χ^2_ν with $\nu = m-n-1$ degrees of freedom. Accordingly, the probability that χ^2_{obs} exceeds any particular quantile of χ^2_ν can be determined. The 95 % quantile is recommended.

7.8.2 If χ^2_{obs} for the polynomial degree indicated by one or more of the information criteria exceeds the 95 % quantile, it is considered that the polynomial calibration function cannot be regarded as explaining the data. Moreover, such a result implies that the corresponding parameter estimates $\hat{\boldsymbol{a}}$ and the associated covariance matrix $\boldsymbol{V}_{\hat{\boldsymbol{a}}}$ should be regarded as unreliable, as should any value and its associated uncertainty obtained from the function (see Subclause 7.9). In such a case, the data and associated uncertainties should be reviewed. Alternatively, and perhaps additionally, polynomials having degrees close to that selected using Subclause 7.7 could be considered. A calibration function consisting of some other mathematical form can be entertained; such a consideration is largely beyond the scope of this document, but polynomials in a transformed variable are considered in Subclause 11.

7.8.3 The chi-squared test does not distinguish between a poor functional model and a poor statistical model. Plotting the weighted residuals of the model, and, in a case where there are non-zero covariances, transformed weighted residuals, can be informative (Subclause 7.5.5).

7.9 Use of the calibration function

7.9.1 The calibration function is typically used for inverse evaluation where, given an estimate of y and its associated standard uncertainty, the corresponding value of x is estimated and its associated standard uncertainty is evaluated. See Subclause 12.2. The calibration function is also sometimes used for direct evaluation where, given an estimate of x and its associated standard uncertainty, the corresponding value of y is determined and its associated standard uncertainty is evaluated. See Subclause 12.3. In both cases the standard uncertainty associated with the estimate is evaluated using the covariance matrix $\boldsymbol{V}_{\hat{\boldsymbol{a}}}$ for $\hat{\boldsymbol{a}}$.

7.9.2 It is assumed that the conditions of measurement that held during the acquisition of the calibration data hold at the time a response value is measured for which the calibration function is used inversely to provide a stimulus value. In this regard, response values are often obtained at the same time for a number of stimulus values that correspond to standards and a number of stimulus values that correspond to 'unknowns', that is, for which stimulus values are required. An example is enzyme-linked immunosorbent assay (ELISA)[15]. Otherwise, either a new calibration might be necessary or appropriate adjustment made to take account of any change such as drift that might have occurred (and that any associated uncertainty is also handled). Similar remarks apply when the calibration function is used for direct evaluation.

NOTE Control charts can be useful for monitoring drift.

8 Generic approach to determining a polynomial calibration function

8.1 Given are

a) calibration data points $\left(x_i, y_i\right),\ i = 1, \ldots, m$;

b) uncertainties and covariances associated with the x_i and y_i as appropriate; and

c) the maximum degree $n_{\max}$ (less than the number of distinct values of x_i) of polynomial to be considered.

8.2 Perform the following steps:

a) set $x_{\min}$ and $x_{\max}$, the endpoints of the stimulus interval (see Subclause 7.3);

b) form the observation vector $\boldsymbol{y} = \left[y_1, \ldots, y_m\right]^{\mathsf{T}}$;

c) form the covariance matrices $\boldsymbol{V}_{\boldsymbol{x}}$ and $\boldsymbol{V}_{\boldsymbol{y}}$ in Subclause 4.5 as necessary from the prescribed uncertainties and covariances;

d) for each polynomial degree $n = 1, \ldots, n_{\max}$:

1) form the design matrix $\boldsymbol{H}$ of dimension $m \times (n+1)$ containing the $n+1$ Chebyshev basis functions for the polynomial $p_n(x, \boldsymbol{a})$ evaluated at $t_1, \ldots, t_m$:

$$\boldsymbol{H} = \begin{bmatrix} T_0(t_1) & \cdots & T_n(t_1) \\ \vdots & \ddots & \vdots \\ T_0(t_m) & \cdots & T_n(t_m) \end{bmatrix}, \quad t_i = \frac{2x_i - x_{\min} - x_{\max}}{x_{\max} - x_{\min}}; \tag{13}$$

the elements of each row of $\boldsymbol{H}$ are generated by the recurrence relation of Formula (7);

2) depending on the uncertainty structure, apply an appropriate least-squares algorithm to $\boldsymbol{H}$ and $\boldsymbol{y}$, and $\boldsymbol{V_x}$ or $\boldsymbol{V_y}$ or both, to provide the estimate $\hat{\boldsymbol{a}}$ of the parameters $\boldsymbol{a}$ of the polynomial $p_n(x, \boldsymbol{a})$ of degree n;

3) obtain the covariance matrix $\boldsymbol{V}_{\hat{\boldsymbol{a}}}$ associated with $\hat{\boldsymbol{a}}$ (provided as a by-product of the least-squares algorithm used);

4) mark $p_n(x, \hat{\boldsymbol{a}})$ as admissible if it is monotonic over the interval $[x_{\min}, x_{\max}]$; otherwise mark it as inadmissible (Subclause 7.6). [This step may be modified when the calibration function is to be used in conjunction with a reference function (Subclause 7.6.1)];

e) if no polynomial exists that is admissible, exit the procedure with no solution: review the data and provided uncertainty information; consider alternative calibration models such as polynomials in a transformed variable or the interchange of variables (Subclause 11);

f) use one of the criteria AIC, AICc and BIC (Subclause 7.7) to select the degree n of the polynomial to be used from the set of admissible polynomials;

g) if $\chi^2_{\text{obs}}(n)$ does not exceed the 95th percentile of $\chi^2_{\text{m-n-1}}$, accept $p_n(x, \hat{\boldsymbol{a}})$ as a candidate calibration function; otherwise mark it as statistically unacceptable and exit the procedure;

h) assess the candidate calibration function for suitability. The assessment might include visual inspection of the function, its (weighted) residuals (Subclause 7.5) and some domain-specific tests.

NOTE In all examples in this document, the polynomial selected is admissible and also satisfied the condition given in 8.2 g).

8.3 Return, for the selected degree *n*:

a) the *n* + 1 coefficients in the Chebyshev representation of $p_n(x, \hat{\boldsymbol{a}})$;

b) the covariance matrix $\boldsymbol{V}_{\hat{\boldsymbol{a}}}$ associated with $\hat{\boldsymbol{a}}$.

9 Statistical models for uncertainty structures

9.1 General

9.1.1 Let the relation between a measured value x_i and the corresponding true value ξ_i, and similarly for y_i and the corresponding true value η_i, be

$$x_i = \xi_i + d_i, \quad y_i = \eta_i + e_i, \tag{14}$$

or, in terms of vectors, $\boldsymbol{\xi} = \left[\xi_1, \ldots, \xi_m\right]^{\mathsf{T}}$, $\boldsymbol{\eta} = \left[\eta_1, \ldots, \eta_m\right]^{\mathsf{T}}$, $\boldsymbol{d} = \left[d_1, \ldots, d_m\right]^{\mathsf{T}}$ and $\boldsymbol{e} = \left[e_1, \ldots, e_m\right]^{\mathsf{T}}$,

$$\boldsymbol{x} = \boldsymbol{\xi} + \boldsymbol{d}, \qquad \boldsymbol{y} = \boldsymbol{\eta} + \boldsymbol{e}. \tag{15}$$

The vectors $\boldsymbol{d}$ and $\boldsymbol{e}$ are assumed to be samples from joint normal distributions:

$$\boldsymbol{d} \in N\left(\boldsymbol{0}, \boldsymbol{V}_{\boldsymbol{x}}\right), \quad \boldsymbol{e} \in N\left(\boldsymbol{0}, \boldsymbol{V}_{\boldsymbol{y}}\right). \tag{16}$$

9.1.2 It is assumed there is negligible *model uncertainty*, that is, a polynomial of appropriate degree is capable of describing the data, in which case η_i can be replaced by $p_n\left(\xi_i, \hat{\boldsymbol{a}}\right)$, where $\hat{\boldsymbol{a}}$ is the estimate of $\boldsymbol{a}$. This assumption is tested in Subclause 7.8. The model evaluated at the data value x_i is $p_n\left(x_i, \hat{\boldsymbol{a}}\right)$. The statistical model that applies in any specific instance depends on the uncertainty structure (Clause 6). The generic approach in Clause 8 is used. The only part of that approach that depends on the uncertainty structure is the algorithm used in step 8.2 d) 2). Subclauses 9.2 to 9.6 specify an appropriate formulation of the least-squares problem for each uncertainty structure in Clause 6.6.

9.2 Response data uncertainties

For the case where the x_i are regarded as exact, standard uncertainties associated with the y_i are prescribed, and the covariances associated with the y_i are zero,

$$\boldsymbol{V}_{\boldsymbol{y}} = \mathrm{diag}\left[\mathrm{u}^2\left(y_1\right), \ldots, u^2\left(y_m\right)\right], \tag{17}$$

a diagonal matrix with the variances (squared standard uncertainties) $u^2\left(y_1\right), \ldots, u^2\left(y_m\right)$ on the main diagonal. The estimate $\hat{\boldsymbol{a}}$ of the polynomial coefficients $\boldsymbol{a}$ is given by solving the weighted least-squares (WLS) problem[17]

$$\min_{\boldsymbol{a}} \boldsymbol{e}^{\mathsf{T}} \boldsymbol{V}_{\boldsymbol{y}}^{-1} \boldsymbol{e} \equiv \min_{\boldsymbol{a}} \left[\frac{e_1^2}{u^2\left(y_1\right)} + \cdots + \frac{e_m^2}{u^2\left(y_m\right)}\right], \tag{18}$$

where $e_i \equiv e_i\left(\boldsymbol{a}\right) = y_i - p_n\left(x_i, \boldsymbol{a}\right)$[17]. Formally, the solution is given by

$$\hat{\boldsymbol{a}} = \left(\boldsymbol{H}^{\mathsf{T}} \boldsymbol{V}_{\boldsymbol{y}}^{-1} \boldsymbol{H} \right)^{-1} \boldsymbol{H}^{\mathsf{T}} \boldsymbol{V}_{\boldsymbol{y}}^{-1} \boldsymbol{y}, \tag{19}$$

where $\boldsymbol{H}$ is the matrix specified in Formula (13). In practice, the problem of Formula (18) should be solved by stable numerical methods rather than using Formula (19): see reference [11], for instance.

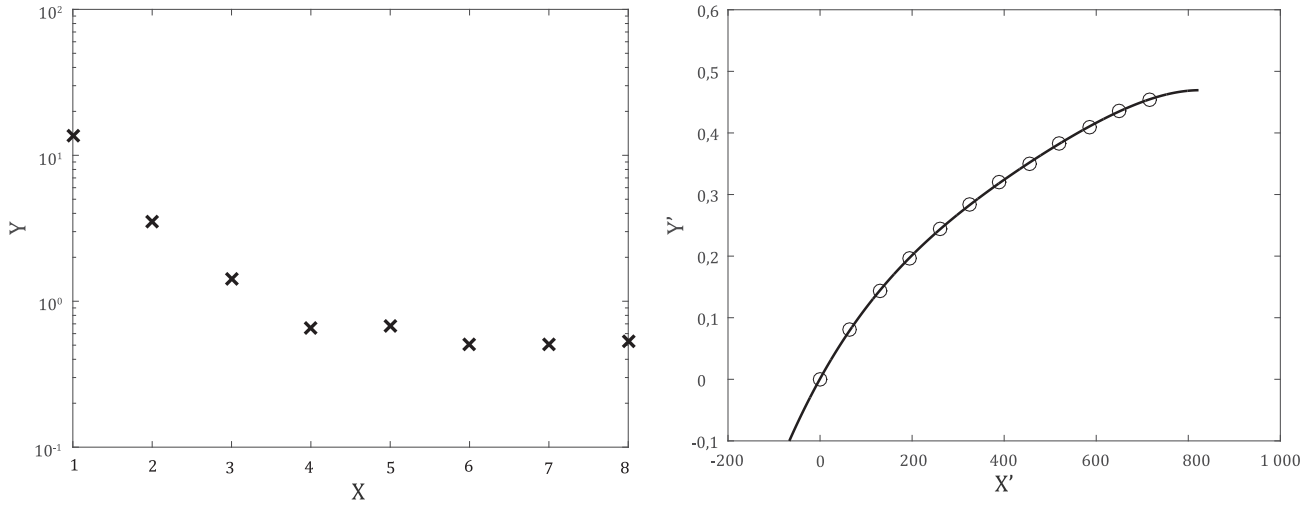
EXAMPLE Optical density as a function of absorbed dose.

Film dosimetry requires the characterization of film response with absorbed dose to film. The film calibration procedure consists of acquiring measured values of net optical density (NOD), a non-dimensional quantity, corresponding to prescribed absorbed dose values and obtaining a function that relates NOD to dose, called the sensitometric curve[3]. The *x*-values (absorbed dose *d*) are prescribed as exact numbers and provided to the measuring system before the film is irradiated. Since the radiation delivery uncertainty is very small, the uncertainties and any covariances associated with the x_i are negligible. Each corresponding y_i-value (NOD) has an associated standard uncertainty $u\left(y_i\right)$ given by aggregating several uncertainties relating to independent effects[3]. There is negligible covariance associated with the y_i-values. Typical data is given in columns 1 to 3 of Table 3.

Table 3 — Absorbed dose, optical density data and weighted *y*-residuals for polynomial function of degree 4

Absorbed dose/cGy ≡ *x*	**NOD** ≡ *y*	*u*(NOD) ≡ *u*(*y*)	**Weighted *y*-residual**
0	0,000 4	0,001 7	−0,32
65	0,081 2	0,001 6	0,78
130	0,144 0	0,001 7	−0,19
195	0,195 7	0,002 0	−1,01
260	0,243 7	0,002 0	0,28
325	0,284 0	0,002 4	0,45
390	0,320 1	0,002 4	0,54
455	0,349 9	0,002 6	−0,75
520	0,382 9	0,002 6	0,16
585	0,410 0	0,002 9	−0,16
650	0,435 3	0,002 9	0,13
715	0,454 3	0,003 1	−0,01

Polynomial calibration functions with degrees from 1 to 8 were considered. Figure 8 a) shows the root-mean-square residuals RMSR(*n*) and Figure 7 the adjusted information criteria for these degrees. Table 4 gives numerically the values of $\chi^2_{\text{obs}}\left(n\right)$, AIC(*n*), AICc(*n*) and BIC(*n*) for these degrees. It is concluded that degree 4 is a reasonable choice: it gives the smallest value for all three information criteria. Degree 4 also appears to be the degree at which the root-mean-square residuals start to saturate [Figure 8 a)]. The weighted *y*-residuals for the selected polynomial are given in column 4 of Table 3. Figure 8 b) shows the data and the calibration function selected.



a) Root-mean-square residual RMSR(n) **in terms of polynomial degree** n

b) Polynomial calibration function of degree 4

Key

X polynomial degree n
Y RMSR(n)
X' stimulus variable x
Y' response variable y

Figure 8 — Relationship between absorbed dose and optical density

The corresponding Chebyshev coefficients are given in column 5 of Table 5, where the Chebyshev coefficients for degrees from 1 to 8 are given. By examining the coefficients within each row of the table it is clear they are very stable with respect to degree [compared with those that would be obtained for the monomial form [Formula (4)]. The standard uncertainties $u\left(y_i\right)$ range from 0,001 6 to 0,003 1, and it would be expected that the magnitude of negligible Chebyshev coefficients would be of comparable size or smaller. It is seen from Table 5 that for polynomial degrees 5 and higher, the Chebyshev coefficients are indeed negligible, a further indication that degree 4 is an acceptable choice. (The use of a correction polynomial of lower degree for this example is illustrated in Subclause 7.5.3.).

Table 4 — Observed chi-squared and information criteria for the dose-optical density calibration problem

Degree n	$\chi^2_{\text{obs}}\left(n\right)$	**AIC**	**AICc**	**BIC**
1	1 836,5	1 840,5	1 841,9	1 841,5
2	109,5	115,5	118,5	117,0
3	16,2	24,2	30,0	26,2
4	3,0	13,0	23,0	15,4
5	2,7	14,7	31,5	17,6
6	1,3	15,3	43,3	18,7
7	1,0	17,0	65,0	20,9
8	0,8	18,8	108,8	23,2

Table 5 — Chebyshev coefficients in polynomial functions for absorbed dose-optical density calibration problem

	Chebyshev coefficients a_i in polynomial of degree							
i	1	2	3	4	5	6	7	8
0	0,276 9	0,249 7	0,251 4	0,246 8	0,247 0	0,242 7	0,243 2	0,251 1
1	0,278 1	0,260 4	0,276 7	0,274 9	0,276 9	0,275 4	0,282 9	0,285 0
2		−0,057 0	−0,052 6	−0,060 8	−0,060 4	−0,068 4	−0,067 3	−0,053 0
3			0,014 7	0,012 8	0,014 4	0,013 2	0,019 3	0,021 1
4				−0,006 4	−0,006 1	−0,011 8	−0,011 1	−0,000 3
5					0,001 1	0,000 3	0,004 2	0,005 4
6						−0,003 2	−0,002 7	0,003 5
7							0,001 8	0,002 4
8								0,002 4

The parameter standard uncertainties and the correlation matrix, of dimension 5×5, for the selected polynomial are given in Table 6.

Table 6 — Parameter standard uncertainties and correlation matrix for the selected polynomial function of degree 4 for the absorbed dose-optical density calibration problem

Std. unc.	Correlation matrix				
0,002 7	1	0,412 7	0,966 5	0,383 9	0,902 8
0,003 2		1	0,398 3	0,889 8	0,262 3
0,004 4			1	0,413 3	0,923 6
0,002 0				1	0,323 5
0,002 4	sym.				1

9.3 Response data uncertainties and covariances

Consider the case where the x_i are regarded as exact, and standard uncertainties and covariances associated with the y_i are prescribed. The estimate $\hat{\boldsymbol{a}}$ of the polynomial coefficients $\boldsymbol{a}$ is given by solving the *generalized least-squares* (GLS) problem[17]

$$\min_{\boldsymbol{a}} \boldsymbol{e}^{\mathsf{T}} \boldsymbol{V}_{\boldsymbol{y}}^{-1} \boldsymbol{e} \tag{20}$$

where $\boldsymbol{V}_{\boldsymbol{y}}$ denotes the covariance matrix for $\boldsymbol{y} = \left[y_1, \ldots, y_m \right]^{\mathsf{T}}$ as in Subclause 4.5 and $e_i \equiv e_i\left(\boldsymbol{a}\right) = y_i - p_n\left(x_i, \boldsymbol{a}\right)$ as in Subclause 9.2. Formally, the solution is given by the same formula as Formula (19), namely,

$$\hat{\boldsymbol{a}} = \left(\boldsymbol{H}^{\mathsf{T}} \boldsymbol{V}_{\boldsymbol{y}}^{-1} \boldsymbol{H} \right)^{-1} \boldsymbol{H}^{\mathsf{T}} \boldsymbol{V}_{\boldsymbol{y}}^{-1} \boldsymbol{y}, \tag{21}$$

where $\boldsymbol{H}$ is the matrix of basis-function values [Formula (13)], as for the WLS solution, but now $\boldsymbol{V}_{\boldsymbol{y}}$ generally contains (non-zero) covariances in addition to variances (squared standard uncertainties). In practice, the problem of Formula (20) should be solved by stable numerical methods rather than using Formula (21): see reference [11] for instance.

EXAMPLE Flow meter calibration.

The calibration of a mass flow controller (MFC) having a full-scale range of 200 SCCM is carried out by characterizing its behaviour in terms of the response $z \equiv C = Q_{\mathrm{R}} \,/\, Q_{\mathrm{N}}$, where C is the calibration coefficient, Q_{R} is the flow supplied by the MFC as read by the primary flow reference (in this case MICROGAS) and $x \equiv Q_{\mathrm{N}}$ is the nominal flow.

NOTE 1 SCCM is a flow measurement term indicating $\mathrm{cm}^3\,\mathrm{min}^{-1}$ at a standard temperature and pressure. In SI units it would be expressed in terms of $\mathrm{m}^3\,\mathrm{s}^{-1}$.

NOTE 2 'Calibration coefficient' is a term used in flow measurement. It is not to be confused with the parameters or coefficients of the calibration function.

The objective of the calibration is to obtain a function from which an estimate (direct evaluation) and its associated standard uncertainty can be provided for the actual flow supplied by the instrument when a certain nominal flow is set. Values of the response, over a desired flow range, are traditionally modelled by the calibration function

$$z \equiv C = h_0 \,/\, Q_N + h_1 + h_2 Q_N + h_3 Q_N^2 \equiv h_0 \,/\, x + h_1 + h_2 x + h_3 x^2. \tag{22}$$

Calibration data consisting of values $x_i \equiv \left(Q_{\mathrm{N}}\right)_i$ of Q_N and the corresponding measured values $z_i \equiv \hat{C}_i$ of C, for $i = 1, \ldots, 7$, are given in Table 7. The values $\left(Q_{\mathrm{N}}\right)_i$ are regarded as having no uncertainty and the covariance matrix $\boldsymbol{V}_{\hat{\boldsymbol{C}}}$ associated with the values $\hat{\boldsymbol{C}}$ is obtained as follows. Each value $\hat{C}_i$ is a measured value of a quantity C_i that depends on temperature, pressure and volume measured within the primary flow reference. Since temperature, pressure and volume are measured with the same instruments for every value $\hat{C}_i$, they introduce systematic effects that lead to correlation among the $\hat{C}_i$ values, with volume making the largest relative contribution. Random effects are introduced by the measuring system, which are independent of i. The related covariance matrix hence has elements on the main diagonal that are due to both the random and the systematic effects and elsewhere due to the systematic effects. The covariance matrix, determined on this basis, as provided by the domain expert, is given in Table 8. The

corresponding standard uncertainties and correlation matrix are given in Table 9, which are more readily interpreted.

Table 7 — Data for flow meter calibration

$\boldsymbol{x}^{\mathsf{T}} \equiv \left(Q_{\mathrm{N}}\right)^{\mathsf{T}}$	10	20	35	60	90	140	200
$\hat{\boldsymbol{z}}^{\mathsf{T}} \equiv \hat{\boldsymbol{C}}^{\mathsf{T}}$	0, 975 602	1,004 602	1,012 260	1,009 808	1,003 021	0,995 182	0,993 713

Table 8 — Covariance matrix $V_{\hat{C}} / 10^{-8}$ for the flow meter calibration data

7,478	2,331	2,279	2,147	1,879	1,979	1,806
	3,396	2,251	2,120	1,856	1,955	1,783
		8,082	2,073	1,815	1,911	1,744
			6,325	1,710	1,801	1,643
				2,846	1,576	1,438
					4,820	1,514
sym.						5,131

Table 9 — Standard uncertainties $u\left(y_i\right)$ and correlation matrix for the flow meter calibration data

Std. unc.	**Correlation matrix**						
0,003	1	0,462	0,293	0,312	0,407	0,330	0,291
0,004		1	0,430	0,458	0,597	0,483	0,427
0,010			1	0,290	0,378	0,306	0,271
0,015				1	0,403	0,326	0,288
0,015					1	0,426	0,376
0,031						1	0,305
0,045	sym.						1

This formulation is not directly one of modelling by a polynomial because of the presence of the term $h_0 / Q_N \equiv h_0 / x$ in Formula (22). However, the same calibration model can, by multiplication by Q_N, be expressed as the polynomial

$$y = xz \equiv Q_N C = h_0 + h_1 Q_N + h_2 Q_N^2 + h_3 Q_N^3, \tag{23}$$

which in accordance with the provisions of this document can in turn be expressed in Chebyshev-series form.

Thus, the data $\left(x_i, y_i\right) = \left(x_i, x_i z_i\right) \equiv \left[\left(\boldsymbol{Q}_{\mathrm{N}}\right)_i, \left(\boldsymbol{Q}_{\mathrm{N}}\right)_i \times \hat{C}_i\right]$, $i = 1, \ldots, 7$, is used to provide polynomial calibration functions in this form. In doing so, it is necessary to re-express the given uncertainty information. Since $y = xz$ and the data x-values have negligible uncertainty,

$$u\left(y_i\right) = x_i u\left(z_i\right), \qquad u\left(y_i, y_j\right) = x_i x_j u\left(z_i, z_j\right) \quad \left(i \neq j\right), \tag{24}$$

or, in terms of matrices, with $\boldsymbol{D} = \mathrm{diag}\left[x_1, \ldots, x_7\right]$:

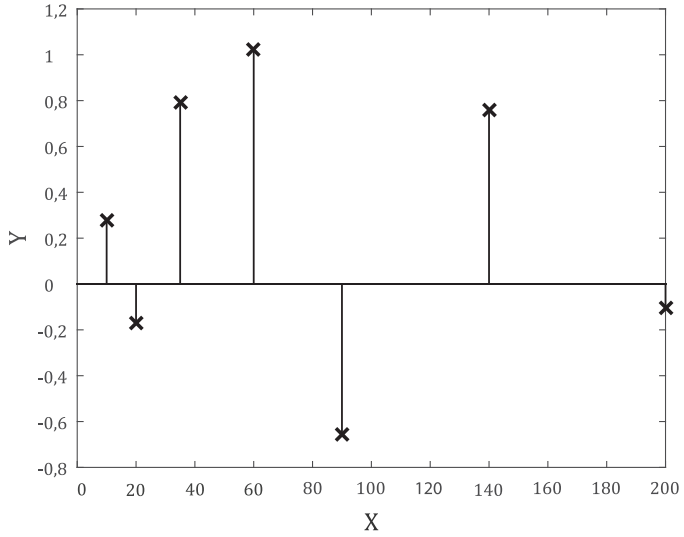
$$\boldsymbol{V}_y = \boldsymbol{D}\boldsymbol{V}_z\boldsymbol{D}. \tag{25}$$

Accordingly, polynomial calibration functions with degrees from 1 to 4 were considered, the highest degree being used to check whether degree 3 in Formula (23) is adequate. Table 10 gives numerically the values of $\chi^2_{\mathrm{obs}}\left(n\right)$, $\mathrm{AIC}\left(n\right)$, $\mathrm{AICc}\left(n\right)$ and $\mathrm{BIC}\left(n\right)$ for degree n = 1 to 4.

Table 10 — Observed chi-squared and information criteria for the flow meter calibration problem

Degree n	$\chi^2_{\mathrm{obs}}\left(n\right)$	**AIC**	**AICc**	**BIC**
1	17 171,8	17 175,8	17 178,8	17 175,7
2	3 418,2	3 424,2	3 432,2	3 424,0
3	4,3	12,3	32,3	12,1
4	4,2	14,2	74,2	13,9

From inspection of Table 10, degree 3 is a reasonable choice, giving the smallest value for all three information criteria and thus demonstrating that the traditional use of the model of Formula (22) is acceptable in this case. Moreover, degree $n = 3$ is acceptable in terms of the observed chi-squared value of 4,3 compared with the expected value of $m - n - 1 = 3$. Furthermore, a graph of the weighted residuals (Figure 9) does not indicate any systematic trend.



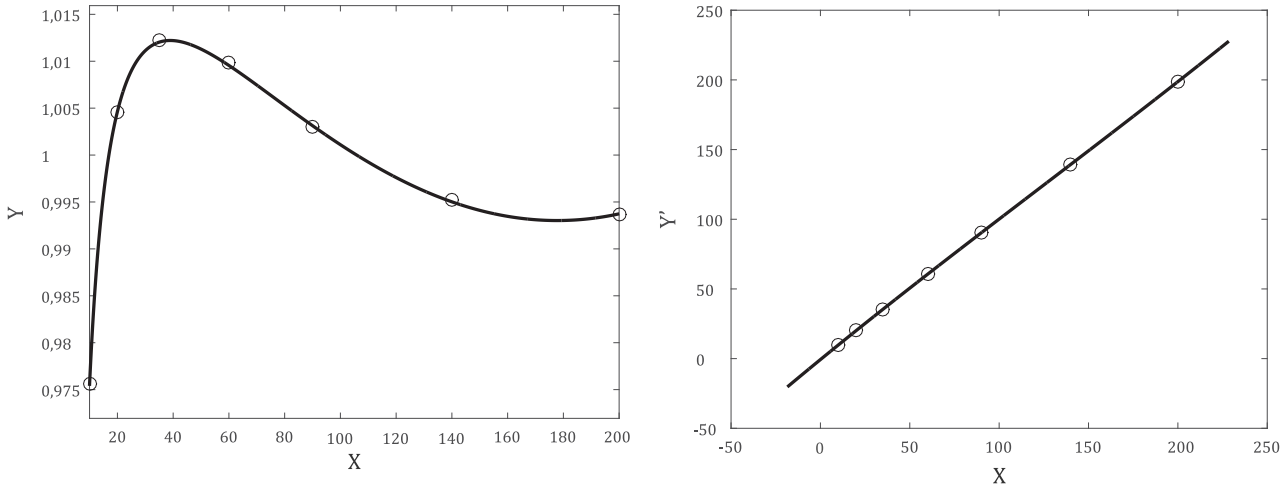
Key

X stimulus variable *x*

Y weighted *y*-residual

Figure 9 — Weighted residuals for flow meter calibration problem for polynomial function of degree 3

Figure 10 a) shows the data and the selected calibration function in terms of the original variable Q_{N}. Visually, the chosen calibration function seems to represent the data well, although there appears to be a minimum that is possibly spurious near $Q_N = 180$ SSCM. Indeed, the expected behaviour of the response variable y / x is a horizontal asymptote at the upper end of the calibration range. Presumably, increasing the resolution of the measuring system that provided the calibration data would deliver evidence of this behaviour. Additional data in that neighbourhood or other knowledge should also be informative in this regard. Figure 10 b) displays the data and chosen polynomial function in terms of the 'response variable' $Q_{\mathrm{N}}C$. From this figure it appears that the modified calibration data lie close to a straight line.



a) $z \equiv C$ **modelled by the non-polynomial function of Formula** (22) **in** $x \equiv Q_N$

b) Same calibration function expressed in polynomial form as $y = xz \equiv Q_N C$ **as a function of** x

Key

X stimulus variable x

Y response variable y/x Y' response variable y

Figure 10 — Flow meter calibration data and polynomial model

The corresponding Chebyshev coefficients for the selected polynomial of degree $n=3$ are given in column 4 of Table 11, where the Chebyshev coefficients for degrees from 1 to 4 are given. The first two coefficients, being two orders of magnitude larger than the higher-order coefficients, confirm that the calibration function in the modified variable is largely a straight line. With regard to the input uncertainties, however, the next two terms need to be taken into consideration. The parameter standard uncertainties and the correlation matrix, of dimension 4 × 4, for the selected polynomial is given in Table 12.

Table 11 — Chebyshev coefficients in polynomial calibration functions for the flow meter calibration data

	Chebyshev coefficients a_i in polynomial of degree			
i	1	2	3	4
0	105,201	103,932	104,370	104,365
1	123,893	122,018	123,308	123,303
2		–1,449	–0,646	–0,657
3			0,732	0,725
4				–0,005

Table 12 — Parameter standard uncertainties and correlation matrix for the selected polynomial function of degree 3 for the flow meter calibration data

Std. unc.	Correlation matrix			
0,020	1	0,931	0,630	0,368
0,033		1	0,818	0,667
0,018			1	0,744
0,013	sym.			1

9.4 Stimulus and response data uncertainties

9.4.1 The determination of polynomial calibration functions when both *x*- and *y*-variables have associated uncertainties is more complicated than when just the *y*-values are uncertain. When the $u\left(x_i\right)$ are regarded as negligible, the model values are simply given by evaluating $p_n\left(x,\hat{\boldsymbol{a}}\right)$ at the x_i, since the x_i are deemed equal to the "true values" ξ_i. When the $u\left(x_i\right)$ are not negligible, the ξ_i are regarded as unknown and are to be estimated together with the model parameters $\boldsymbol{a}$.

9.4.2 For the case where standard uncertainties associated with the x_i and the y_i are provided, and all covariances are zero,

$$\boldsymbol{V}_{\boldsymbol{x}} = \mathrm{diag}\left[u^2\left(x_1\right),\ldots,u^2\left(x_m\right)\right], \qquad \boldsymbol{V}_{\boldsymbol{y}} = \mathrm{diag}\left[u^2\left(y_1\right),\ldots,u^2\left(y_m\right)\right]. \tag{26}$$

9.4.3 The estimate $\hat{\boldsymbol{a}}$ of the polynomial coefficients $\boldsymbol{a}$ (and the estimate of $\boldsymbol{\xi} = \left[\xi_1,\ldots,\xi_m\right]^{\mathsf{T}}$) is given by solving the minimization problem[17]

$$\min_{\boldsymbol{a},\boldsymbol{\xi}}(\boldsymbol{d}^{\mathsf{T}}\boldsymbol{V}_{\boldsymbol{x}}^{-1}\boldsymbol{d} + \boldsymbol{e}^{\mathsf{T}}\boldsymbol{V}_{\boldsymbol{y}}^{-1}\boldsymbol{e}) \equiv \min_{\boldsymbol{a},\boldsymbol{\xi}}\left[\frac{d_1^2}{u^2\left(x_1\right)} + \cdots + \frac{d_m^2}{u^2\left(x_m\right)} + \frac{e_1^2}{u^2\left(y_1\right)} + \cdots + \frac{e_m^2}{u^2\left(y_m\right)}\right], \tag{27}$$

with

$$\boldsymbol{d} = \left[d_1,\ldots,\ d_m\right]^{\mathsf{T}},\ \boldsymbol{e} = \left[e_1,\ldots,e_m\right]^{\mathsf{T}} \tag{28}$$

where $d_i \equiv d_i\left(\xi_i\right) = x_i - \xi_i$ and $e_i \equiv e_i\left(\boldsymbol{a}\right) = y_i - p_n\left(\xi_i,\boldsymbol{a}\right)$. This problem is variously known as generalized distance regression, total least-squares and errors-in-variables.

EXAMPLE Natural gas analysis.

In gas analysis a calibration procedure typically involves measuring a series of natural gas standards (calibrants) of known composition, followed by determining for each component the detector response to the amount fractions (strictly amount-of-substance fractions) of the calibrants[32]. Thus, for each component, there is a set of amount fractions x_i and corresponding (corrected) instrument responses y_i. A calibration function provides the relationship between the instrument response and the composition of the calibrants. The instrument response and the amount fraction of a calibrant have associated uncertainties to be taken into consideration.

Calibration data and associated standard uncertainties for carbon monoxide in nitrogen are given in Table 13.

Table 13 — Data and uncertainties for carbon monoxide in nitrogen[32]

x / μmol mol^{-1}	$u(x)$ / μmol mol^{-1}	y /a.u.	$u(y)$ /a.u.
10,007 0	0,001 5	1,044 44	0,001 12
15,027 0	0,001 2	1,556 85	0,000 66
20,014 0	0,001 8	2,060 50	0,000 23
35,014 0	0,001 9	3,536 27	0,000 39
50,063 0	0,006 5	4,959 92	0,000 92
65,085 0	0,007 5	6,329 49	0,001 42
80,108 0	0,007 6	7,649 64	0,002 64
99,905 0	0,007 7	9,319 78	0,001 70
a.u. ≡ arbitrary unit			

Table 14 shows the Chebyshev coefficients in polynomial calibration functions of degrees 1 to 5 provided by generalized distance regression (GDR) for the gas analysis data. Table 15 shows the corresponding observed chi-squared values and information criteria. Note the inconsistency in the table in that the *x*-values have zeros in the fourth decimal place, whereas the corresponding values of $u(x)$ generally have non-zeros in that position. These values were provided by the practitioner in the area. A similar remark can be made about the values of R and $u(R)$ in Table 17.

According to the information criteria in Table 15, an appropriate degree of polynomial calibration function is $n = 3$. For this degree Figure 11 a) shows the gas analysis data and the polynomial function obtained by GDR. To the eye, the cubic function appears close to linear and the data appears to lie on that function. "Error" bars, if drawn, would be too short to be distinguishable. Figure 11 b) shows the data and the polynomial function of degree 3 after both were corrected by the polynomial of degree 1 obtained by GDR. (Subclause 7.5.3 describes the value of displaying calibration functions in this manner.) The error bars, if drawn, would now just be perceptible in the y direction on this scale, but those in the x direction would not.

Figure 12 a) shows the weighted *x*-residuals and Figure 12 b) the weighted *y*-residuals corresponding to the selected polynomial function of degree 3.

The magnitudes of the weighted residuals shown in Figure 12 for polynomial degree 3 are smaller than expected. Since there are $2m$ data and $m+n+1$ adjustable parameters, the expected value of the sum of the squares of the weighted residuals is $2m-(m+n+1)=4$, whereas the observed chi-squared value is 1,2, thus indicating that the prescribed uncertainties might have been conservatively evaluated, in fact for both variables. Such a remark is also made in reference [32].

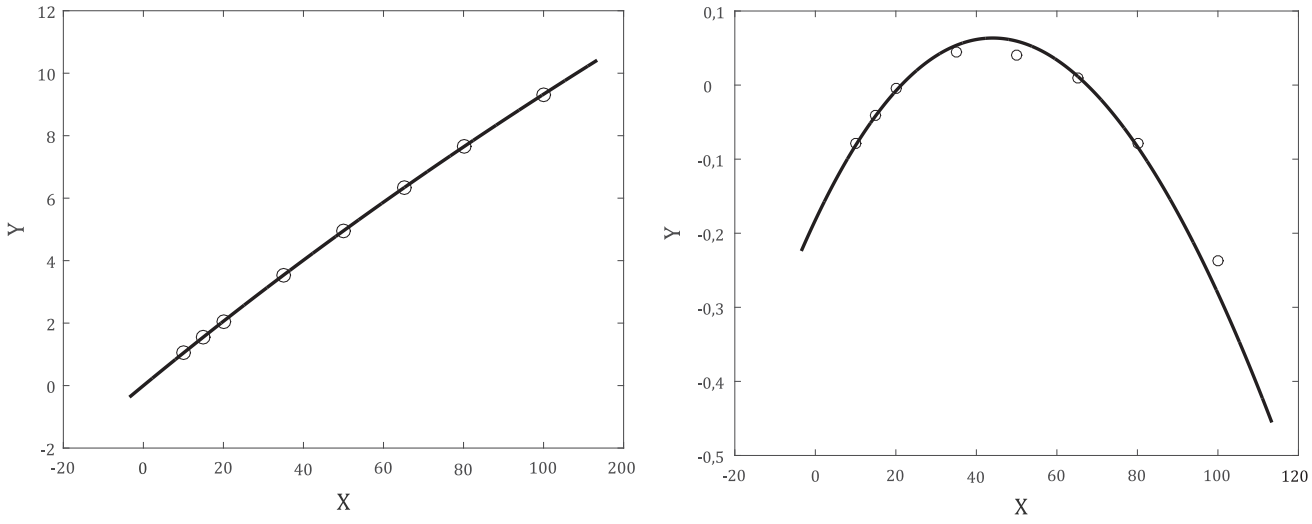
The parameter standard uncertainties and the correlation matrix, of dimension 4 × 4, for the selected polynomial are given in Table 16.

Table 14 — Chebyshev coefficients in polynomial calibration function for the gas analysis data

	Chebyshev coefficients a_i in polynomial of degree				
i	1	2	3	4	5
0	5,362 4	5,217 5	5,217 3	5,218 1	5,217 0
1	5,508 6	5,374 3	5,384 7	5,384 8	5,380 0
2		−0,198 1	−0,194 6	−0,193 2	−0,195 4
3			0,008 2	0,008 6	0,004 6
4				0,000 8	−0,000 9
5					−0,001 6

Table 15 — Observed chi-squared and information criteria for the gas analysis calibration problem

Degree n	χ^2_{obs}	AIC	AICc	BIC
1	52 179,5	52 183,5	52 185,9	52 183,6
2	46,6	52,6	58,6	52,8
3	1,2	9,2	22,5	9,5
4	0,9	10,9	40,9	11,3
5	0,4	12,4	96,4	12,9



a) Obtained by generalized distance regression

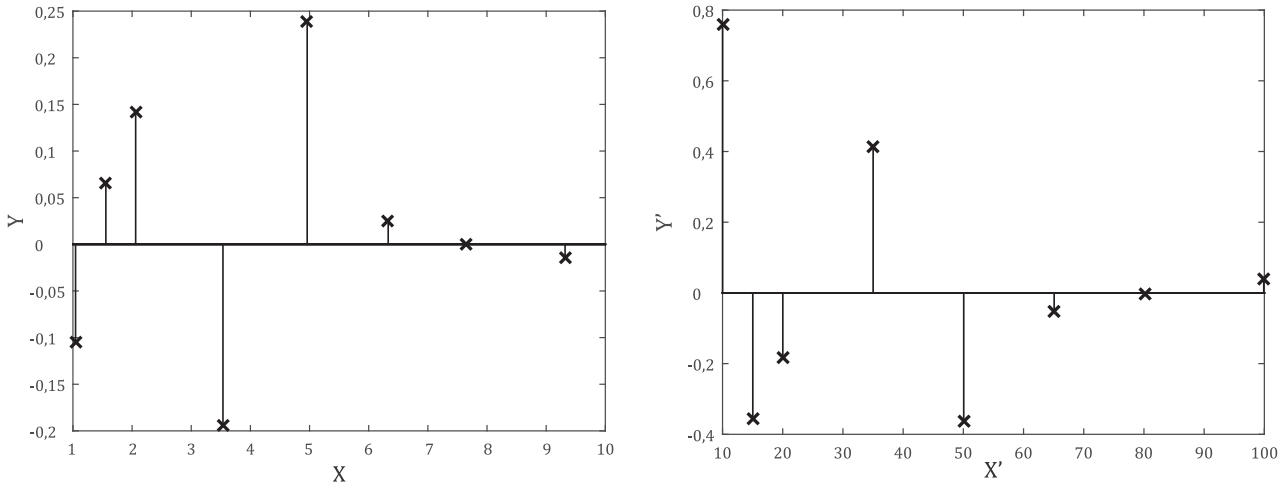
b) Data and function as corrected by a polynomial of degree 1

Key

X stimulus variable x

Y response variable y

Figure 11 — Gas analysis data and the polynomial calibration function of degree 3



a) With respect to *x*

b) With respect to *y*

Key

X	response variable *y*	X'	stimulus variable *x*
Y	weighted *x*-residual	Y'	weighted *y*-residual

Figure 12 — Weighted residuals for gas analysis calibration data for polynomial functions of degree 3

Table 16 — Parameter standard uncertainties and correlation matrix for the selected polynomial function of degree 3 **for the gas analysis calibration function**

Std. unc.	Correlation matrix			
0,000 78	1	0,479	0,668	−0,023
0,001 86		1	0,686	0,828
0,001 00			1	0,513
0,001 22	sym.			1

9.5 Stimulus and response data uncertainties and covariances

Given data $\boldsymbol{x}$ and $\boldsymbol{y}$ and the associated covariance matrices $\boldsymbol{V}_{\boldsymbol{x}}$ and $\boldsymbol{V}_{\boldsymbol{y}}$, the estimate $\hat{\boldsymbol{a}}$ of the polynomial coefficients $\boldsymbol{a}$ (and the estimate of $\boldsymbol{\xi} = \left[\xi_1, \ldots, \xi_m\right]^{\mathsf{T}}$ are given by solving the problem

$$\min_{\boldsymbol{a},\boldsymbol{\xi}} \left(\boldsymbol{d}^{\mathsf{T}}\boldsymbol{V}_{\boldsymbol{x}}^{-1}\boldsymbol{d} + \boldsymbol{e}^{\mathsf{T}}\boldsymbol{V}_{\boldsymbol{y}}^{-1}\boldsymbol{e}\right), \tag{29}$$

where $d_i \equiv d_i\left(\xi_i\right) = x_i - \xi_i$ and $e_i \equiv e_i\left(\boldsymbol{a}\right) = y_i - p_n\left(\xi_i, \boldsymbol{a}\right)$. This form of least-squares problem is also referred to as *generalized distance regression*.

EXAMPLE Resistance thermometer calibration.

The calibration of a Pt100 platinum resistance thermometer involves placing the thermometer in a thermal bath at temperatures $t_1,\ldots,t_m\ (\equiv x_1,\ldots,x_m)$ that have been measured by a reference thermometer, and measuring the corresponding m responses, namely, resistances $R_1,\ldots,R_m\ (\equiv y_1,\ldots,y_m)$, by comparing the resistance of the thermometer with the known resistance of a standard resistor. The standard uncertainties $u(t_i)$ associated with the t_i and the standard uncertainties $u(R_i)$ associated with the R_i are prescribed. The correlation coefficients $r(t_i,t_j)$ between all pairs of temperature values and correlation coefficients $r(R_i,R_j)$ between all pairs of resistance values are given. A polynomial calibration function relating the temperature t and the resistance R of the resistance thermometer is to be determined.

Table 17 shows the calibration data and the associated standard uncertainties in a case where $m=5$ and where the fifth temperature is nominally identical to the first[28]. The correlation coefficients associated with all pairs of the t_i are taken, on the advice of the domain expert, to be equal to 0,9, as are those associated with all pairs of the R_i. Thus, the covariance matrix $\boldsymbol{V_t}$ associated with $\boldsymbol{t}$ has diagonal elements $u^2(t_i)$ and off-diagonal elements $0,9u(t_i)u(t_j)$. The covariance matrix $\boldsymbol{V_R}$ is constructed similarly.

Table 18 shows the Chebyshev coefficients provided by solving the problem of Formula (29) for polynomials of degrees 1 to 3.

Table 19 shows the corresponding observed chi-squared values and the information criteria. For AICc no value is given for degree 3 since this criterion is only valid for degrees for which $m \geq n+3$ (Subclause 7.7.4). According to the values of AIC and BIC in Table 19, an appropriate degree of polynomial calibration function would be n = 2. For this degree Figure 13 a) shows the thermometer calibration data and the polynomial function obtained and Figure 13 b) this model and the data corrected by a polynomial of degree 1.

Table 17 — Measured temperature and resistance values and associated standard uncertainties[28]

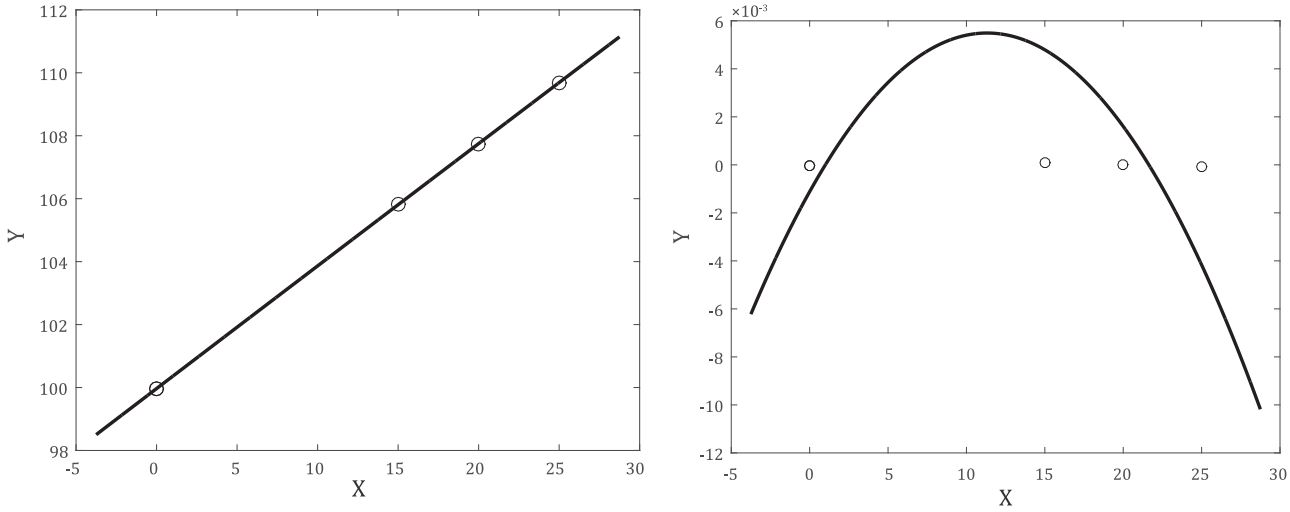
t/°C	$u(t)$/°C	R/Ω	$u(R)$/Ω
0,000	0,005	99,966 50	0,000 25
14,998	0,005	105,807 50	0,000 25
19,999	0,005	107,748 90	0,000 25
24,998	0,005	109,688 70	0,000 25
0,000	0,005	99,966 50	0,000 25

Table 18 — Chebyshev coefficients in polynomial functions for the resistance thermometer data

	Chebyshev coefficients a_i in polynomial of degree		
i	1	2	3
0	104,830 1	104,828 7	104,829 0
1	6,321 2	6,319 3	6,320 7
2		−0,006 8	−0,007 6
3			0,002 0

Table 19 — Observed chi-squared and information criteria for the resistance thermometer calibration problem

Degree n	χ^2_{obs}	AIC	AICc	BIC
1	119,4	123,4	129,4	122,6
2	1,4	7,4	31,4	6,2
3	0,0	8,0		6,4



a) Polynomial function of degree 2

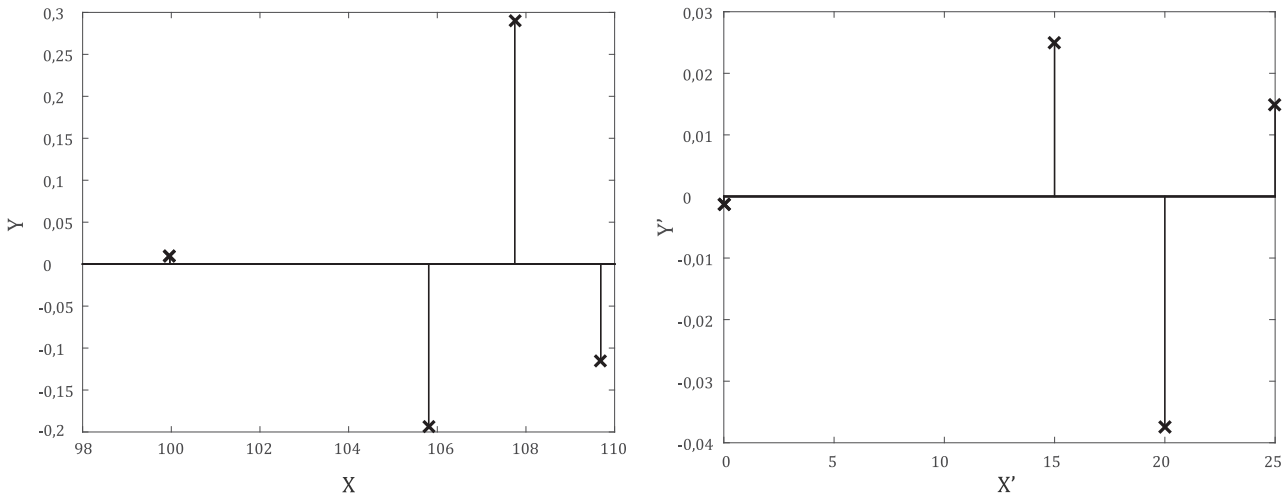
b) Data and function as corrected by a polynomial of degree 1

Key

X stimulus variable x

Y response variable y

Figure 13 — Thermometer calibration data and polynomial calibration functions



a) With respect to *x*

b) With respect to *y*

Key

X	response variable *y*	X'	stimulus variable *x*
Y	weighted *x*-residual	Y'	weighted *y*-residual

Figure 14 — Weighted residuals for the thermometer calibration data for polynomial functions of degree 2

Figure 14 shows the weighted *x*-residuals and *y*-residuals for the polynomial function of degree 2. Since all the weighted residuals have magnitude much less than unity, it would appear that the provided standard uncertainties are conservative. The parameter standard uncertainties and the correlation matrix, of dimension 3 × 3, for the polynomial function are given in Table 20.

Table 20 — Parameter standard uncertainties and correlation matrix for the selected polynomial function of degree 2 **for the resistance thermometer calibration problem**

Std. unc.	Correlation matrix		
0,001 89	1	0,015	0,068
0,000 47		1	0,380 8
0,000 63	sym.		1

9.6 Unknown data uncertainties

9.6.1 This Subclause is exceptional in that a different treatment is necessitated compared with cases in which uncertainty information is available. When no such information is provided, further assumptions need to be made about the data. The assumptions made in this document are that (a) the x_i are exact, that is, they have no associated uncertainty, and (b) the y_i have independent and identically distributed errors

$$e_i \sim \mathrm{N}\left(0, \sigma^2\right) \tag{30}$$

for some unknown variance σ^2.

9.6.2 For a specific polynomial of degree n, estimates $\hat{\boldsymbol{a}}$ of the parameters $\boldsymbol{a}$ are provided by ordinary least squares (OLS)[17] in which $\boldsymbol{e}^{\mathsf{T}}\boldsymbol{e}$, the sum of the squares of the e_i, is minimized. χ^2_{obs} is then formed from the resulting residuals $\hat{e}_i = y_i - p_n\left(x_i, \hat{\boldsymbol{a}}\right)$, $i = 1, \ldots, m$:

$$\chi^2_{\text{obs}} = \hat{\boldsymbol{e}}^{\mathsf{T}}\hat{\boldsymbol{e}} = \sum_{i=1}^{m} \hat{e}_i^2, \tag{31}$$

where $\hat{\boldsymbol{e}} = [\hat{e}_1, \ldots, \hat{e}_m]^{\mathsf{T}}$, and σ is estimated by

$$\hat{\sigma} = \left(\frac{\chi^2_{\text{obs}}}{m - n - 1} \right)^{1/2} . \tag{32}$$

9.6.3 The use of Formula (31) to estimate σ is tantamount to solving the problem

$$\min_{\boldsymbol{a}} \boldsymbol{e}^{\mathsf{T}}\boldsymbol{V}_{\boldsymbol{y}}^{-1}\boldsymbol{e} \equiv \min_{\boldsymbol{a}} \left[\frac{e_1^2}{u^2\left(y_1\right)} + \cdots + \frac{e_m^2}{u^2\left(y_m\right)} \right] \tag{33}$$

with $u^2\left(y_i\right) = \hat{\sigma}^2$, the solution of which is identical to that of minimizing $\boldsymbol{e}^{\mathsf{T}}\boldsymbol{e}$.

9.6.4 A choice of polynomial degree is made by the user, for example, by examining the RMSR-values for a sequence of values of n. The RMSR-values in this case are the estimates $\hat{\sigma}$. Then the $u\left(y_i\right)$ are set equal to $\hat{\sigma}$ and the guidance of Subclause 9.2 employed.

NOTE This way of working is not recommended when uncertainty information about the calibration data set is available initially.

EXAMPLE Isotope-based quantitation.

In isotope-based quantitation, the measurand (the quantity intended to be measured) is the isotope amount ratio of a substance of interest (the analyte) in an 'unknown' sample. This ratio is evaluated using a calibration function that gives the relationship between isotope amount ratio and mass ratio determined from a data set consisting of several pairs of values. Each pair corresponds to a 'known' sample, for which a value of R_{AB}, the isotope ratio of the mixture, is observed corresponding to a value of q, the mass ratio of the sample (analyte) A and the isotopically-labelled internal standard B[29].

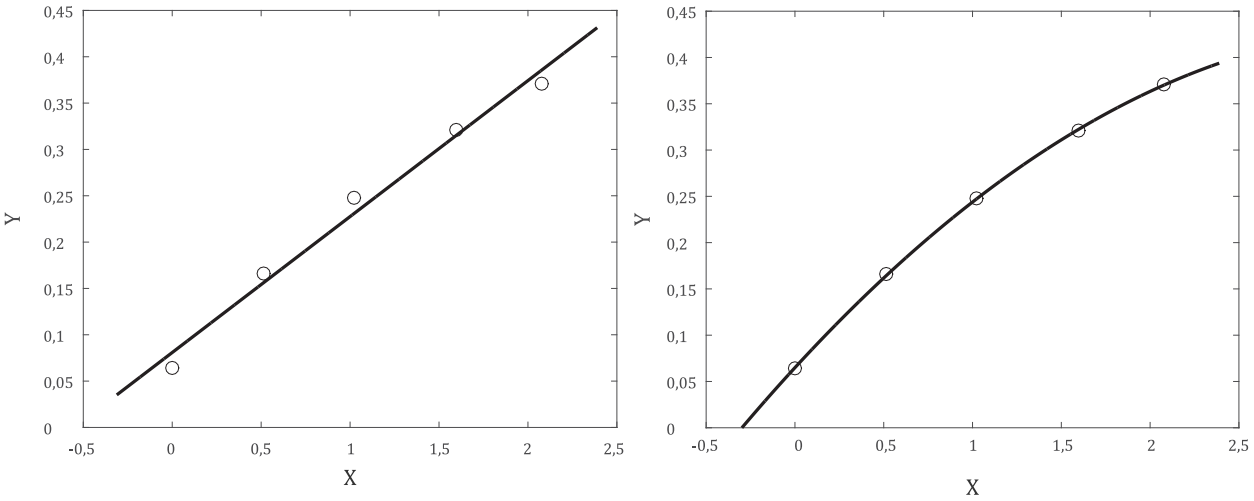
Table 21 shows five calibration points $\left(x_i, y_i\right)$, also indicated in Figure 15, where x corresponds to mass ratio q and y to isotope ratio R_{AB}. Since no uncertainty information was provided, the approach of this Subclause is used.

Table 21 — Data for isotope dilution calibration

$\hat{\boldsymbol{x}}^{\mathsf{T}} \equiv \hat{\boldsymbol{q}}^{\mathsf{T}}$	0,000	0,512	1,024	1,598	2,078
$\hat{\boldsymbol{y}}^{\mathsf{T}} \equiv \hat{\boldsymbol{R}}_{\mathrm{AB}}^{\mathsf{T}}$	0,064	0,166	0,247	0,321	0,371

Polynomial calibration functions with degrees from 1 to 3 were considered. Values obtained for RMSR, or $\hat{\sigma}$, for these degrees were respectively 1,27, 0,013 5 and 0,000 059. Degree 2 with $\hat{\sigma} = 0,0135$ was selected. The $\hat{\sigma}$-value 0,000 059 for degree 3 was considered pathologically small for the problem, with the polynomial function following the noise in the data.

Figure 15 b) shows the selected polynomial calibration function of degree 2. In contrast, Figure 15 a) shows the polynomial calibration function of degree 1: a clear trend is apparent in the deviations of the data from the model. The Chebyshev coefficients for the polynomial function of degree 2 are given in Table 22.



a) Degree 1 **b) Degree** 2

Key

X stimulus variable *x*

Y response variable *y*

Figure 15 — Isotope dilution data and polynomial calibration function

Table 22 — Chebyshev coefficients in polynomial function of degree 2 **for the isotope dilution calibration problem**

Degree	Chebyshev coefficient
0	0,222 5
1	0,198 4
2	−0,027 1

The parameter standard uncertainties and the correlation matrix, of dimension 3×3, for the selected polynomial are given in Table 23.

Table 23 — Parameter standard uncertainties and correlation matrix for the selected polynomial function of degree 2 for the isotope dilution calibration problem

Std. unc.	Correlation matrix		
0,007 78	1	−0,011 0	0,630 8
0,011 00		1	−0,011 5
0,012 35	sym.		1

10 Polynomials satisfying specified conditions

10.1 A polynomial calibration function may be required to pass through the origin or to pass through a stipulated point with a given gradient or satisfy exactly other derivative conditions. Conditions that fall within the scope of this document are that at each of a number of specified values of *x*, the polynomial is required to take a stipulated value and a number (that may be zero) of the leading derivatives of the polynomial take specified values.

10.2 Let $\mu\left(x\right)$ denote the polynomial of lowest degree uniquely satisfying the conditions. Let $\nu\left(x\right)$ be a "zeroizing" polynomial that (i) takes the value zero at the specified values of x and (ii) when there is a number of leading derivatives specified at some or all of these values of x its corresponding derivatives take the value zero there. Then the polynomial calibration function takes the form[7]

$$\mu\left(x\right) + \nu(x) p_n\left(x, \boldsymbol{a}\right). \tag{34}$$

The degree of the resulting polynomial will be $n + n_\nu$, where n_ν is the degree of ν. Define modified *y*-values

$$\tilde{y}_i = y_i - \mu\left(x_i\right), \quad i = 1, \ldots, m, \tag{35}$$

and, instead of the basis functions $T_r\left(t\right)$, use $\nu\left(x\right)T_r\left(t\right)$. The computation then proceeds as in clauses 9.2 to 9.6 as appropriate.

EXAMPLE 1 Polynomial calibration function passing through the origin.

A polynomial calibration function is required to pass through the origin. Thus,

$$\mu\left(x\right) = 0, \quad \nu\left(x\right) = x\,.$$

EXAMPLE 2 Polynomial satisfying simple conditions at $x = 0$ and $x = 10$.

A polynomial calibration function is required to pass through the origin and to have a first derivative of zero there, and at $x = 10$ to take the value 3. Accordingly,

$$\mu\left(x\right) = 0,03x^2, \quad \nu\left(x\right) = x^2\left(x - 10\right).$$

11 Transforming and interchanging variables

11.1 Sometimes polynomials (of modest degree) in the "natural" variable x are inadequate as calibration functions. In such a case other functions can be used, perhaps those that are non-linear in the parameters. This Subclause considers a class of calibration functions that is restricted, but to which the provisions of earlier Subclauses in this document apply. Also considered is the interchanging of variables, which can be helpful in some instances. In all cases, it is necessary to transform the given uncertainty information accordingly.

11.2 When knowledge is available about the functional relationship underpinning the calibration data, possibly obtained from the data itself, transformations of the independent variable or the dependent variable or both can be considered to render the behaviour more amenable to representation by a polynomial. Such transformations may be helpful when the behaviour in one region is radically different from that in another.

11.3 A transformation of the independent variable x can be carried out before computing candidate polynomial calibration functions:

$$\tilde{x} = \phi\left(x\right), \tag{36}$$

where ϕ is a strictly monotonic function of x. Instances of ϕ are

$$x^{\alpha}, \quad \ln\left(x+\alpha\right), \quad \frac{1}{x+\alpha}, \tag{37}$$

for some specified constant α. The calibration function is then in general no longer a function of the original variable x, but of the transformed variable $\tilde{x}$: $p_n\left(\tilde{x}, \boldsymbol{a}\right) \equiv p_n\left(\phi\left(x\right), \boldsymbol{a}\right)$. An advantage of a carefully selected transformation function is that a polynomial of lower degree may more adequately describe the calibration data.

EXAMPLE Steeply rising calibration function.

A steep rise or fall at the left-hand end of the x-interval containing the data, for example, may better be treated by constructing a polynomial calibration function in terms of $\ln\left(x+\alpha\right)$ for some suitable value of the constant α.

11.4 The dependent variable can also be transformed when it is advantageous to do so:

$$\tilde{y} = \psi\left(y\right), \tag{38}$$

where ψ is a strictly monotonic function of y.

11.5 The data values x_i and y_i are transformed accordingly before computing candidate polynomial calibration functions:

$$\tilde{x}_i = \phi\left(x_i\right), \qquad \tilde{y}_i = \psi\left(y_i\right). \tag{39}$$

When standard uncertainties $u(x_i)$ or $u(y_i)$ are specified, it is necessary to obtain the corresponding standard uncertainties in the transformed variables:

$$u(\tilde{x}_i) = \left|\frac{\partial\phi}{\partial x}\right|_{x=x_i} u(x_i), \quad u(\tilde{y}_i) = \left|\frac{\partial\psi}{\partial y}\right|_{y=y_i} u(y_i). \tag{40}$$

When $\boldsymbol{V}_{\boldsymbol{x}}$, the covariance matrix associated with the x_i, is provided, by applying ISO/IEC Guide 98-3:2008/Suppl. 2:2011, the covariance matrix associated with the $\tilde{x}_i$ is

$$\boldsymbol{V}_{\tilde{\boldsymbol{x}}} = \boldsymbol{D}\boldsymbol{V}_{\boldsymbol{x}}\boldsymbol{D}, \tag{41}$$

where $\boldsymbol{D}$ is the diagonal matrix of dimension $m \times m$ with ith diagonal element equal to $\partial\phi / \partial x$ evaluated at x_i. A similar statement applies to the $\tilde{y}_i$.

11.6 In the exceptional case where no uncertainty information is provided (Subclause 9.6), in which case the $u(y_i)$ are taken as equal to a constant, the transformed standard uncertainty associated with $u(\tilde{y}_i)$ should be taken as proportional to $|\partial\psi / \partial y|$ evaluated at y_i.

11.7 Sometimes interchanging the stimulus and response variables may make the resulting data more amenable to representation by a polynomial. The uncertainty structure is "interchanged" accordingly. Suppose a polynomial calibration problem has an uncertainty structure where the x_i-values are regarded as exact and the y_i-values have associated uncertainties and possibly covariances. That problem can be solved by WLS or GLS (Subclauses 9.2, 9.3). Upon reversal of the roles of x and y, the new problem has exact y-values and the x-values have associated uncertainties, and can be solved by GDR (subclauses 9.4, 9.5). For problems with unspecified data uncertainties, the consideration of Subclause 9.6 apply before and after an interchange of variables.

11.8 A possible advantage of working with interchanged variables is that stimulus is expressed explicitly as a polynomial in the response variable, which facilitates direct use of a determined calibration function to obtain stimulus values corresponding to prescribed response values.

12 Use of the polynomial calibration function

12.1 General

This clause considers the inverse and direct evaluation of a computed polynomial calibration function and the evaluation of the associated standard uncertainty.

12.2 Inverse evaluation

12.2.1 The computed polynomial calibration function $p_n(x, \hat{\boldsymbol{a}})$ is used to obtain the value x_0 of the stimulus x corresponding to a specified value y_0 of the response y. The standard uncertainty $u(x_0)$ for x_0 given the standard uncertainty $u(y_0)$ for y_0 is also determined. $u(x_0)$ will also depend on the

covariance matrix $\boldsymbol{V}_{\hat{\boldsymbol{a}}}$ for the estimated calibration parameters $\hat{\boldsymbol{a}}$. It is assumed that y_0 is obtained independently of the data used to provide the calibration function.

12.2.2 Given $y = y_0$ and $\boldsymbol{a} = \hat{\boldsymbol{a}}$, the equation

$$F\left(x\right) \equiv y_0 - p_n\left(x, \hat{\boldsymbol{a}}\right) = 0 \tag{42}$$

is solved for $x = x_0$. If y_0 lies between the values $p_n\left(x_{\min}, \hat{\boldsymbol{a}}\right)$ and $p_n\left(x_{\max}, \hat{\boldsymbol{a}}\right)$, x_0 will lie between $x_{\min}$ and $x_{\max}$. Monotonicity ensures there is at most one solution. Since x_0 is a zero of $F\left(x\right)$, recognized iterative methods for a zero of a function can be used[10][14].

NOTE The bisection method is a simple and robust iterative method: each iteration halves the length of the interval containing the zero. The starting interval can be taken as $\left[x_{\min}, x_{\max}\right]$. With bisection, after 10 iterations the length of the interval containing x_0 is approximately $\left(x_{\max} - x_{\min}\right) / 10^3$ and, after 20 iterations, about $\left(x_{\max} - x_{\min}\right) / 10^6$.

12.2.3 Regarding uncertainty propagation, Formula (42) is regarded as an implicit univariate measurement model (see ISO/IEC Guide 98-3:2008/Suppl. 2:2011 and reference [12]) having the input quantities y_0 and $\hat{\boldsymbol{a}}$ and a single output quantity x_0. The law of propagation of uncertainty gives, with derivation in Annex B,

$$u^2\left(x_0\right) = \frac{1}{q^2}\left[u^2\left(y_0\right) + \boldsymbol{g}^{\mathsf{T}}\boldsymbol{V}_{\hat{\boldsymbol{a}}}\boldsymbol{g}\right], \tag{43}$$

where

$$q = \frac{2}{x_{\max} - x_{\min}} \sum_{r=1}^{n} \hat{a}_r T_r'\left(t_0\right), \tag{44}$$

$$t_0 = \frac{2x_0 - x_{\min} - x_{\max}}{x_{\max} - x_{\min}} \tag{45}$$

and

$$\boldsymbol{g} = \left[T_0\left(t_0\right), \ldots, T_n\left(t_0\right)\right]^{\mathsf{T}}. \tag{46}$$

EXAMPLE Inverse evaluation for the absorbed dose-optical density example.

Consider inverse evaluation for the absorbed dose-optical density example of Subclause 9.2. Suppose as the response value a NOD value of $y_0 = 0{,}390\,5$ is measured, with an associated standard uncertainty of 0,002 7. The solution of equation (42) for stimulus value $x = x_0$ using

that value of y_0 gives the corresponding absorbed dose as 538,0 cGy. The use of Formula (43) with the obtained covariance matrix $\boldsymbol{V}_{\hat{\boldsymbol{a}}}$ gives the associated standard uncertainty as $u\left(x_0\right)$ = 7,1 cGy.

12.3 Direct evaluation

12.3.1 The computed polynomial calibration function $p_n\left(x, \hat{\boldsymbol{a}}\right)$ is used to obtain the value y_0 of the response variable y corresponding to a specified value x_0 of the stimulus variable x. The standard uncertainty $u\left(y_0\right)$ for y_0 given the standard uncertainty $u\left(x_0\right)$ for x_0 is also determined. In addition to its dependence on $u\left(x_0\right)$, $u\left(y_0\right)$ will also depend on the covariance matrix $\boldsymbol{V}_{\hat{\boldsymbol{a}}}$ for the estimated calibration parameters $\hat{\boldsymbol{a}}$. It is assumed that x_0 is obtained independently of the data used to provide the calibration function.

12.3.2 The response value y_0 corresponding to stimulus value x_0 is given by direct evaluation:

$$y_0 = p_n\left(x_0, \hat{\boldsymbol{a}}\right) \tag{47}$$

using the evaluation procedure given in Table 1 in Subclause 7.4.

12.3.3 Applying LPU, the standard uncertainty $u\left(y_0\right)$ associated with y_0, using the notation of Subclause 12.2.3, is given by

$$u^2\left(y_0\right) = \boldsymbol{g}^{\mathsf{T}} \boldsymbol{V}_{\hat{\boldsymbol{a}}} \boldsymbol{g} + q^2 u^2\left(x_0\right) \tag{48}$$

EXAMPLE Direct evaluation for the flow meter calibration example.

Consider direct evaluation for the flow meter calibration example of Subclause 9.3. Following calibration, let $\hat{C}_0$ be the measured calibration coefficient corresponding to nominal flow $\left(Q_N\right)_0$. Then the estimate of the flow supplied by the instrument is given by $\left(\hat{Q}_{\mathrm{R}}\right)_0 = \left(Q_{\mathrm{N}}\right)_0 \hat{C}_0$ with associated uncertainty $u\left[\left(\hat{Q}_{\mathrm{R}}\right)_0\right] = \left(Q_{\mathrm{N}}\right)_0 u\left(\hat{C}_0\right)$, where $u\left(\hat{C}_0\right)$ can be obtained by applying LPU to the calibration model. Suppose a nominal flow (stimulus) value of $x_0 \equiv \left(Q_N\right)_0$ = 85 SCCM is specified, for which the associated standard uncertainty $u\left[\left(\hat{Q}_N\right)_0\right]$ is zero. The use of Formula (47) for this value of x gives the corresponding value y_0 of y as $x_0 z_0 \equiv Q_{\mathrm{N}} \hat{C}_0$ as 85,357 SCCM, from which $z_0 \equiv \hat{C}_0 = 1,004\,194$. The use of Formula (48) with the obtained covariance matrix $\boldsymbol{V}_{\hat{\boldsymbol{a}}}$ (see Table 12) gives the standard uncertainty associated with $z_0 \equiv \hat{C}_0$ as $u\left(z_0\right) = 0,013\,4$, from which $u\left(x_0\right) = u\left(Q_{\mathrm{N}}\right) = 0,000\,157$ SCCM.

Annex A
(informative)

Checking the monotonicity of a polynomial

Consider the polynomial $p_n\left(x\right) \equiv P_n\left(t\right)$, whose suitability as a calibration function is considered in Subclause 7.6. The first derivative $Q_{n-1}\left(t,\boldsymbol{b}\right) \equiv P_n'\left(t,\boldsymbol{a}\right)$ of $P_n\left(t,\boldsymbol{a}\right)$ can be expressed in Chebyshev series form as

$$Q_{n-1}\left(t,\boldsymbol{b}\right) = b_0 T_0\left(t\right) + \cdots + b_{n-1} T_n\left(t\right) = \sum_{r=0}^{n-1} b_r T_r\left(t\right). \tag{A.1}$$

The b_r are obtained from the a_r using the recurrence relation (see reference [6], page 11)

$$b_n = b_{n-1} = 0, \qquad b_r = b_{r+2} + 2\left(r+1\right)a_{r+1}, \quad r = n-1,\ldots,0\,. \tag{A.2}$$

For $p_n\left(x,\boldsymbol{a}\right)$ to be monotonic in $\left[x_{\min}, x_{\max}\right]$ or, equivalently, for $P_n\left(t,\boldsymbol{a}\right)$ to be monotonic in $\left[-1,1\right]$, $Q_{n-1}\left(t,\boldsymbol{b}\right)$ must possess no zero in this interval. The zeros of the polynomial $Q_{n-1}\left(t,\boldsymbol{b}\right)$ are the eigenvalues of the *colleague matrix* (see Reference [31], page 134) of dimension $\left(n-1\right)\times\left(n-1\right)$:

$$\begin{bmatrix} 0 & 1 & & & & \\ \frac{1}{2} & 0 & \frac{1}{2} & & & \\ & \frac{1}{2} & 0 & \frac{1}{2} & & \\ & & \ddots & \ddots & \ddots & \\ & & & & & \frac{1}{2} \\ & & & & \frac{1}{2} & 0 \end{bmatrix} - \frac{1}{2b_{n-1}} \begin{bmatrix} 0 \\ \vdots \\ 0 \\ 1 \end{bmatrix} \begin{bmatrix} b_0 & b_1 & \cdots & b_{n-2} \end{bmatrix}, \tag{A.3}$$

in which entries that are not displayed are zero. This matrix can be assembled straightforwardly and standard software can be used to obtain its eigenvalues, which can then be checked whether they lie outside the interval $\left[-1,1\right]$, in which case the corresponding polynomial is admissible. Before the application of the statistical criterion in Subclause 7.7, a candidate polynomial that is not monotonic over $\left[-1,1\right]$ should generally be marked as inadmissible and not considered further. An exception would be when the obtained polynomial is a correction polynomial to augment a reference function so as to yield a monotonic calibration function (Subclause 7.6).

Annex B
(informative)

Standard uncertainty associated with a value obtained by inverse evaluation

This annex derives Formula (43) in Subclause 12.2.3 for the standard uncertainty associated with a value obtained by inverse evaluation. For specified Chebyshev coefficients $\hat{\boldsymbol{a}}$ and given a response value y_0, the polynomial equation

$$h\left(x_0; y_0, \boldsymbol{a}\right) \equiv y_0 - P_n\left(t_0, \boldsymbol{a}\right) = 0 \tag{B.1}$$

with

$$\boldsymbol{a} = \hat{\boldsymbol{a}}, \qquad t_0 = \frac{2x_0 - x_{\min} - x_{\max}}{\Delta x}, \qquad \Delta x = x_{\max} - x_{\min}, \tag{B.2}$$

is solved for x_0 as in Subclause 12.2. Knowing the covariance matrix $\boldsymbol{V}_{\hat{\boldsymbol{a}}}$, and given the standard uncertainty $u\left(y_0\right)$ associated with y_0, the standard uncertainty $u\left(x_0\right)$ associated with x_0 can be evaluated as follows. The above equation $y_0 - P_n\left(t_0, \boldsymbol{a}\right) = 0,$ which is an implicit measurement model (see ISO/IEC Guide 98-3:2008/Suppl. 2:2011) having partial derivatives

$$\frac{\partial h}{\partial y_0} = 1, \qquad \frac{\partial h}{\partial \boldsymbol{a}} = -\frac{\partial P_n}{\partial \boldsymbol{a}}, \qquad \frac{\partial h}{\partial x_0} = \frac{\partial h}{\partial t_0}\frac{\partial t_0}{\partial x_0} = -\frac{2}{\Delta x}P_n'\left(t_0\right) = -\frac{2}{\Delta x}\sum_{r=0}^{n} a_r T_r'\left(t_0\right) = -q \tag{B.3}$$

is obtained by using Formula (9). Further use of that formula gives, say,

$$\frac{\partial P_n}{\partial \boldsymbol{a}} = \left[T_0\left(t_0\right) \cdots T_n\left(t_0\right)\right] = \boldsymbol{g}^{\mathsf{T}}. \tag{B.4}$$

Applying the generalized law of propagation of uncertainty (see ISO/IEC Guide 98-3:2008/Suppl. 2:2011), with the variable $\boldsymbol{x}^{\mathsf{T}}$ there corresponding to $\left[y_0, \boldsymbol{a}^{\mathsf{T}}\right]$ and y there corresponding to x_0, the sensitivity matrix of dimension $1 \times \left(n+2\right)$ for $\left[y_0, \boldsymbol{a}^{\mathsf{T}}\right]^{\mathsf{T}}$ is

$$\boldsymbol{S}_{\left[y_0, \boldsymbol{a}^{\mathsf{T}}\right]^{\mathsf{T}}} = \left[\frac{\partial h}{\partial y_0} \quad -\left(\frac{\partial P_n}{\partial \boldsymbol{a}}\right)^{\mathsf{T}}\right] = \left[1 \quad -\boldsymbol{g}^{\mathsf{T}}\right] \tag{B.5}$$

and the sensitivity matrix of dimension 1×1 (a scalar) for x_0 is

$$\boldsymbol{S}_{x_0} = \frac{\partial h}{\partial x_0} = -q. \tag{B.6}$$

Thus, the sensitivity matrix of dimension $1 \times \left(n+2\right)$ (see ISO/IEC Guide 98-3:2008/Suppl. 2:2011) is

$$\boldsymbol{S} = \boldsymbol{S}_{x_0}^{-1}\boldsymbol{S}_{\left[y_0,\boldsymbol{a}^{\mathsf{T}}\right]^{\mathsf{T}}} = -\frac{1}{q}\left[1 \quad -\boldsymbol{g}^{\mathsf{T}}\right]. \tag{B.7}$$

Hence, denoting the covariance matrix of dimension $\left(n+2\right)\times\left(n+2\right)$ associated with $\left[y_0,\hat{\boldsymbol{a}}^{\mathsf{T}}\right]^{\mathsf{T}}$ by $\boldsymbol{V}_{\left[y_0,\hat{\boldsymbol{a}}^{\mathsf{T}}\right]^{\mathsf{T}}}$, the standard uncertainty $u\left(x_0\right)$ associated with x_0 (using ISO/IEC Guide 98-3:2008/Suppl. 2:2011), is derived from

$$u^2\left(x_0\right) = \boldsymbol{S}\boldsymbol{V}_{\left[y_0,\hat{\boldsymbol{a}}^{\mathsf{T}}\right]^{\mathsf{T}}}\boldsymbol{S}^{\mathsf{T}} = \frac{1}{q^2}\left[1 \quad -\boldsymbol{g}^{\mathsf{T}}\right]\begin{bmatrix} u^2\left(y_0\right) & \boldsymbol{0}^{\mathsf{T}} \\ \boldsymbol{0} & \boldsymbol{V}_{\hat{\boldsymbol{a}}} \end{bmatrix}\begin{bmatrix} 1 \\ -\boldsymbol{g} \end{bmatrix} = \frac{1}{q^2}\left[u^2\left(y_0\right) + \boldsymbol{g}^{\mathsf{T}}\boldsymbol{V}_{\hat{\boldsymbol{a}}}\boldsymbol{g}\right], \tag{B.8}$$

hence establishing Formula (43) in Subclause 12.2.3.

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