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Validation of the strength of reference solutions used for measuring concentrations

Vérification du titre des solutions de référence utilisées pour la mesure des concentrations

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Foreword

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International Standard ISO 10980 was prepared by Technical Committee ISO/TC 85, *Nuclear energy*, Subcommittee SC 5, *Nuclear fuel technology*.

Annexes A, B and C form an integral part of this International Standard. Annexes D, E, F, G, H and J are for information only.

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Validation of the strength of reference solutions used for measuring concentrations

1 Scope

The reference solutions used for the standardization of analytical methods are the means through which the final result of the analysis is traceable to the basic units and to their standards.

The strength of these solutions should therefore be traceable to these same units with a relative accuracy of ± 0,1 % or better.

This International Standard specifies procedures for preparing reference solutions, as well as a set of procedures for ensuring the quality of their preparation and the degree of accuracy of the solution strength.

It is intended to be a working document for analytical chemists. The underlying statistical theory is therefore not presented in full details or rigorously, in order to simplify application.

Sufficient details are included in annex H, in order to implement the procedure step by step in a laboratory environment.

2 Principle

Uranium, plutonium and potassium dichromate reference solutions are prepared independently.

These reference solutions are prepared exclusively from certified reference materials or from materials which have been analysed by at least two independent methods. Exactly weighed quantities of these materials are dissolved quantitatively and the solutions thus obtained are themselves weighed exactly.

The solution strengths are calculated from weighing data and from the known composition of the source materials.

The accuracy of their preparation is checked by comparing these solutions between themselves with the help of analytical methods so that the relative difference Δ between A_c, the strength calculated for these solutions, and A_m, the mean of replicate measurements, does not exceed 0,1 %.

Two categories of reference solutions can be distinguished according to the quality of the materials used in their preparation:

- primary reference solutions;
- secondary reference solutions.

3 Primary reference solutions

Primary reference solutions are prepared from reference materials which are distributed by approved organizations certifying their composition with a relative uncertainty of 0,05 % or better, corresponding to the confidence interval for a probability level of 95 %.

The strength of these solutions shall be known with a degree of accuracy as close as possible to that which is indicated by the certificate of the original reference material.

Because these materials are very expensive, it is essential to use them economically. This is why these primary reference solutions will be used above all to calibrate or to check the strength of the secondary reference solutions.

The primary reference materials as well as the procedures to be used for preparing the primary reference solutions are given in the annexes:

Annex A: Preparation of uranium primary reference solutions;

Annex B: Preparation of plutonium primary reference solutions;

Annex C: Preparation of dichromate primary reference solution.

3.1 Purpose of the validation procedure

The purpose of the validation procedure is to ensure that no "abnormal" errors occurred during the preparation of the solution from the certified reference material. A second primary reference solution is used to verify that the two calculated strengths agree with the results obtained during the titration of one of the solutions by the other. That is:

- verification of a dichromate solution by means of a uranium solution, or inversely;
- verification of a dichromate solution by means of a plutonium solution, or inversely.

The method used for this verification should be the most precise one employed by the laboratory, for example the ISO 7097 method for uranium and the ISO 8298 one for plutonium, provided that the testing laboratory can perform these methods on pure uranium or plutonium solutions with a coefficient of variation of repeatability of 0,05 % or better and with biases less than 0,02 %.

The number of determinations to be carried out depends on the accepted risks and on the precision of the method used, as explained in 3.2.

3.2 Verification of the strength of a primary reference solution

3.2.1 Principle of the procedure

A titration solution T (for example potassium dichromate) is prepared by weighing and dilution. Its strength is calculated and recorded, T_c.

In order to check the strength of solution T, a primary standard solution (U or Pu), designed A, is prepared. Let A_c be the strength calculated for this solution.

Select an analytical method which presents no bias at all and apply it n times to A, using T as the titration solution. Call A_m the mean of the results obtained and Δ the relative difference between A_m and A_c:

$$\Delta = \frac{A_m - A_c}{A_c} \qquad \ldots (1)$$

Even if the true strength of solution T is equal to the calculated value, T_c, the value of Δ is not generally nil because of errors in the measurement and preparation of the standard solution A. Solution T shall however be accepted as long as the absolute value of Δ does not exceed a certain threshold. The value of the threshold depends on the number of measurements n and on the confidence which is desired in the subsequent analyses.

After the number of measurements n is established, the probabilities of retaining solutions which are affected by given errors Δ_0 and the confidence interval of the strength of solution T can be calculated.

If the difference $|\Delta|$ is lower than the selected threshold, the conclusion is that the strengths A_c and T_c, but also the analytical method, have the expected accuracy.

Alternatively, if the difference $|\Delta|$ exceeds the selected threshold, this can be due to an error in the strength of one or of the other solutions, or to a bias in the analytical method.

3.2.2 Choice of the number n of measurements to be carried out on the standard solution

The number n depends on several factors.

a) Preparation and measurement errors

The operations described in 3.2.1 are affected by the following errors:

1) errors in the strength T_c, due to uncertainties in the certification and preparation, and represented by the relative standard deviation σ_T/T_c;

2) errors in the strength A_c, due to uncertainties in the certification and preparation, and represented by the relative standard deviation σ_A/A_c;

3) errors in the n measurements, represented by the relative standard deviation σ_m/A_c.

The standard deviation of these errors shall be known or estimated as precisely as possible, for example, by variance analysis or by error propagation.

When n is chosen, the preparation and measurement errors result in a total error in Δ, the standard deviation of which can be calculated by:

$$\sigma_\Delta = \sqrt{\left(\frac{\sigma_T}{T_c}\right)^2 + \left(\frac{\sigma_A}{A_c}\right)^2 + \frac{1}{n}\left(\frac{\sigma_m}{A_c}\right)^2} \qquad \ldots (2)$$

(Annex E includes the derivation of equation 2.)

If the strength of T is truly equal to T_c and if the analysis method is not biased, the possible values of Δ are part of a distribution, which is assumed to be Gaussian, with mean zero and a standard deviation σ_Δ. In other words, there is a probability of 99,9 % that Δ may take any value between $-3\sigma_\Delta$ and $+3\sigma_\Delta$.

Alternatively, if the strength, T_c, includes a relative error $\Delta_0 = 0$, the distribution function of the potential values of Δ will be centred around a mean value Δ_0 (see figure D.2).

b) Choice of n

According to figure D.2, the risk of false alarm, α, and the risk of non-detection, β, vary in opposite directions. Both risks depend also upon the number of measurements, n.

Equation (3) gives the number of measurements n to perform in order to detect a true error of Δ_0, with selected values of risks α and β:

$$n = \frac{(\sigma_m/A_c)^2}{[\Delta_0^2/(L_\alpha + L_\beta)^2] - (\sigma_T/T_c)^2 - (\sigma_A/A_c)^2} \qquad \ldots (3)$$

The values of L_α and L_β are given in table 1 as a function of the risks α and β.

The value of n calculated using equation (3) is rounded up to the next highest integer.

If this value is not realistic (too high), it will be necessary to revise the choice of different parameters, especially by increasing Δ_0 and β. The efficiency and sample size curves (see annex F) are used to select the appropriate values. A numerical example is given in annex E.

Table 1

Risk α or β %	L_β	L_α
0,003	4,00	3,90
0,050	3,30	3,46
0,100	3,09	3,30
1,000	2,33	2,58
5,000	1,65	1,96
10,000	1,28	1,65
25,000	0,67	1,15
50,000	0,00	0,67

c) Comment

Since the number *n* must be positive, formula (3) can only be applied if

$$\Delta_0 > \Delta_{\text{min}} = (L_\alpha + L_\beta)\sqrt{\left(\frac{\sigma_T}{T_c}\right)^2 + \left(\frac{\sigma_A}{A_c}\right)^2} \qquad \ldots (4)$$

For a given risk of false alarm α a relative error Δ_0 in the titration solution is likely to be detected with a probability equal to at least $(100 - \beta)$ only if it is greater than Δ_{min}. See the numerical example in annex E.

3.2.3 Test procedure

After calculating *n* from equation (3), calculate the standard deviation σ_Δ using formula (2). The actual error Δ_0, which may be detected with given risks α and β, is equal to

$$\Delta_0 = (L_\alpha + L_\beta)\sigma_\Delta \qquad \ldots (5)$$

For a risk of non-detection $\beta = 100$ %, L_β is equal to zero and Δ_0 has a limiting value:

$$\lim|\Delta| = L_\alpha \sigma_\Delta \qquad \ldots (6)$$

The mean difference of the *n* measurements, Δ, is calculated for each titration solution using formula (1). If the absolute value of Δ is below or equal to $L_\alpha\sigma_\Delta$, the titration solution is accepted with the risk β of having in reality a solution with a difference equal to at least Δ_0. If $|\Delta|$ is greater than $L_\alpha\sigma_\Delta$, the solution is rejected and the risk of this rejection being unfair is equal to α.

3.2.4 Strength of reference solution

If the solution is accepted, its strength is given at the $(100 - \alpha)$ confidence level by the expression:

$$T_c\,(1 \pm L_\alpha\,\sigma_T/T_c) \qquad \ldots (7)$$

a) Example

This example is drawn from annexes E and F. If the numerical values used in annexes A and C are taken and if the analytical method presents a coefficient of variation of 0,03 %, then:

$\sigma_m/A_c = 3{,}00 \times 10^{-4}$

$\sigma_A/A_c = 2{,}74 \times 10^{-4}$ (uranium)

$\sigma_T/T_c = 1{,}14 \times 10^{-4}$ (dichromate)

If five determinations are carried out, σ_Δ may be calculated:

$\sigma_\Delta = 3{,}24 \times 10^{-4}$

Selecting a risk of unfair rejection, $\alpha = 5$ %, the rejection limit is calculated according to equation (6):

$$\lim|\Delta| = 1{,}96 \times 3{,}24 \times 10^{-4}$$

$$= 6{,}35 \times 10^{-4}$$

If the mean difference is greater than the rejection limit,

$$|\Delta| = \frac{|A_m - A_c|}{A_c} > 0{,}064\ \%$$

the solution under test must be rejected and a new solution prepared. Under these conditions there is a risk of rejecting 5 times out of 100 a solution which is actually correct.

If the difference Δ is smaller then 0,064 %, the solution is accepted, and the confidence interval for the strength is

$T_c\left(1 \pm 2{,}3 \times 10^{-4}\right)$ for the dichromate, and

$A_c\left(1 \pm 5{,}5 \times 10^{-4}\right)$ for the uranium,

depending upon which solution was to be verified.

In the above case, there is a risk β of 10 % of accepting the strengths as correct although they actually include an error greater than or equal to Δ_0:

$$\Delta_0 = (L_\alpha + L_\beta)\sigma_\Delta$$

$$= (1{,}96 + 1{,}28) \times 3{,}24 \times 10^{-4}$$

$$= 10{,}5 \times 10^{-4}$$

due to a mistake in the preparation. The risk β of non-detection comes down to 1 % if the preparation error is 0,14 % ($L_\beta = 2{,}33$).

b) Comment

In the event that both of the compared reference solutions have to be checked:

- obtaining a difference lower than the limit value validates both solutions, as well as the analytical method;
- obtaining a difference greater than the limit value necessitates preparation of a third reference solution which will be compared with one of the two previous ones. (The combined tests shall allow any ambiguity to be cleared up. If the difference remains too large, it is possible that the analytical method presents a bias which must be eliminated before the test can proceed further.)

4 Secondary reference solutions

Secondary reference solutions are prepared as follows:

- from secondary reference materials distributed by approved organizations and certified as having a precision between ± 0,05 % and ± 0,2 %; or
- from uncertified but pure materials, distributed by an approved organization.

4.1 Validation of solutions prepared from certified materials

In this case the validation procedure is identical to the one recommended for the primary reference solutions (see clause 3). The permissible difference between the measured strength and the calculated one will be higher than in the case of primary reference solution. Acceptance of the solution will lead to the adoption of the strength and the degree of precision calculated from the certificate of the secondary reference material.

4.2 Standardization of solutions prepared from uncertified materials

The solution will be standardized with the aid of a primary reference solution, after making sure that there are no impurities which might interfere with the calibration method.

In addition to the possible interferences linked to the secondary reference solution itself, the possible bias of the method also has to be taken into account. If σ_b is the coefficient of variation of the method used to correct or detect the bias of the standardization, the uncertainty of the measured strength of the solution is expressed by a coefficient of variation:

$$\frac{\sigma_e}{A_m} = \sqrt{\frac{1}{n}\left(\frac{\sigma_m}{A_m}\right)^2 + \left(\frac{\sigma_T}{T_c}\right)^2 + \sigma_b^2} \qquad \ldots (8)$$

or

$$\frac{\sigma_e}{T_m} = \sqrt{\frac{1}{n}\left(\frac{\sigma_m}{T_m}\right)^2 + \left(\frac{\sigma_A}{A_c}\right)^2 + \sigma_b^2} \qquad \ldots (9)$$

depending on whether a secondary reference solution of uranium (or plutonium), or a dichromate titrant is standardized.

Note that the absence of a systematic error can be checked, at best, within the limit of uncertainty of the reference materials used for checking it.

4.3 Numerical examples

Assume that the absence of a systematic error has been verified and the test repeated numerous times with the aid of a reference solution certified with a coefficient of variation of 0,025 % and a dichromate titrant known with a coefficient of variation of 0,010 %. In this case, $\sigma_b = 0{,}026\,9 \times 10^{-2}$.

a) Standardization of a uranium solution by means of a dichromate primary solution

Assume the standard deviation values given in annexes C and E:

$\sigma_T/T_c = 1{,}14 \times 10^{-4}$

$\sigma_m/A_m = 3{,}00 \times 10^{-4}$

$\sigma_b = 2{,}69 \times 10^{-4}$

If $n = 5$, then $\sigma_e/A_m = 3{,}21 \times 10^{-4}$, and a probability of 95 % that the solution strength lies within

$A_m\left(1 \pm 6{,}3 \times 10^{-4}\right)$.

b) Calibration of a dichromate solution by means of a primary uranium solution

Assume the standard deviation values given in annexes A and E:

$\sigma_A/A_c = 2{,}74 \times 10^{-4}$

$\sigma_m/T_m = 3{,}00 \times 10^{-4}$

$\sigma_b = 2{,}69 \times 10^{-4}$

If $n = 5$, then $\sigma_e/T_m = 4{,}07 \times 10^{-4}$ and a probability of 95 % that the solution strength lies within

$T_m\left(1 \pm 8{,}0 \times 10^{-4}\right)$.

4.4 Standardization and validation with the aid of two reference solutions (two independent methods)

The solution is measured by:

a) method (1) with the aid of a reference solution S_1, the strength S_1 of which is known, either by preparation or titration, with an uncertainty estimated by the standard deviation σ_{S1}. The measurement characterized by the standard deviation σ_1 is carried out n_1 times, A_1 being the mean of the results; or

b) method (2) with the aid of a reference solution S_2, the strength S_2 of which is known, either by preparation or titration, with an uncertainty characterized by the standard deviation σ_{S2}. The measurement characterized by the standard deviation σ_2 is carried out n_2 times, A_2 being the mean of the results.

The relative difference observed is

$$\Delta = \frac{A_1 - A_2}{A_2} \qquad \ldots (10)$$

with

$$\sigma_\Delta = \sqrt{\left(\frac{\sigma_{S1}}{S_1}\right)^2 + \left(\frac{\sigma_{S2}}{S_2}\right)^2 + \frac{1}{n_1}\left(\frac{\sigma_1}{A_1}\right)^2 + \frac{1}{n_2}\left(\frac{\sigma_2}{A_2}\right)^2} \qquad \ldots (11)$$

If this difference Δ is acceptable, a weighted mean of the values A_1 and A_2 will be selected as the best estimate of the strength A. Numbers n_1 and n_2 will therefore be selected with the aim of minimizing the random component of the variance of Δ, with the minimum total number of measurements.

This is achieved when

$$n_2 = n_1[(\sigma_2/A_2)/(\sigma_1/A_1)] \qquad \ldots (12)$$

For a fixed α (the unfair rejection of $\Delta_0 = 0$) and a fixed β (the probability of accepting the equality when the true Δ has a value $\Delta_0 = 0$) n_1 can be calculated as follows:

$$n_1 = \frac{(\sigma_1/A_1)[(\sigma_1/A_1) + (\sigma_2/A_2)]}{[\Delta_0/(L_\alpha + L_\beta)]^2 - (\sigma_{S1}/S_1)^2 - (\sigma_{S2}/S_2)^2} \qquad \ldots (13)$$

n_2 is derived from equation (12). The minimum value of Δ_0 which can be chosen is:

$$\Delta_{\min} = (L_\alpha + L_\beta)\sqrt{(\sigma_{S1}/S_1)^2 + (\sigma_{S2}/S_2)^2} \qquad \ldots (14)$$

Once n_1 and n_2 have been chosen, the limit value of the acceptable difference can be calculated from equations (11) and (6):

$$\lim|\Delta| = L_\alpha \sigma_\Delta$$

1) If $|\Delta|$ is above this limit, the equality of A_1 and A_2 is rejected, there being a risk α of making an unfair rejection. In this case, the following may be called into question:

- either the preparation of the S_1 solution, or
- the preparation of the S_2 solution, or
- method (1), or
- method (2), or

— the preparation of the secondary reference solution which may contain an interfering element in one or the other of the methods.

2) If $|\Delta|$ is below this limit, the equality of A_1 and A_2 is accepted. A weighted mean of A_1 and A_2 is adopted as best estimate of the strength A:

$$A = \frac{A_1/(\sigma_{A1})^2 + A_2/(\sigma_{A2})^2}{1/(\sigma_{A1})^2 + 1/(\sigma_{A2})^2} \qquad \ldots (15)$$

with

$$(\sigma_{A1}/A_1)^2 = (\sigma_{S1}/S_1)^2 + (\sigma_1/A_1)^2/n_1 \qquad \ldots (16)$$

$$(\sigma_{A2}/A_2)^2 = (\sigma_{S2}/S_2)^2 + (\sigma_2/A_2)^2/n_2 \qquad \ldots (17)$$

The confidence limits of the best estimate are:

$$A(1 \pm L_\alpha \sigma/A) \qquad \ldots (18)$$

$$\sigma/A = \frac{1}{\sqrt{1/(\sigma_{A1}/A_1)^2 + 1/(\sigma_{A2}/A_2)^2}} \qquad \ldots (19)$$

A numerical example is given in annex G.

5 Report of the results

A written protocol shall be made of the results of the validations.

Annex H gives an example of a protocol applicable to the validation of a reference solution by titration against another reference solution.

Annex A
(normative)

Preparation of uranium primary reference solutions

A.1 Scope

This procedure describes the preparation of uranium primary reference solutions, which may be used:

— for verifying the quality of the preparation of the dichromate primary reference solution;

— for calibrating or checking the dichromate secondary reference solutions used in the U and Pu accountability assay by titration;

— for the calibration of isotopic tracer solutions used in the U assays by isotope dilution analysis.

A.2 Reference materials and reagents

All reagents shall be of recognized analytical quality and of a very high degree of purity.

A.2.1 Uranium metal, certified at ± 0,05 % or better ($\pm 2\sigma_R$) (for example: NBL 112, MU1/EC 101, MU2 or NBS 960).

A.2.2 Concentrated nitric acid.

A.2.3 Nitric acid solution, $c(HNO_3) = 6$ mol/l (approximately).

A.2.4 Nitric acid solution, $c(HNO_3) = 3$ mol/l.

A.2.5 Acetone, very pure.

A.3 Procedure

Prepare the reference solution by weighing accurately a portion of the certified uranium metal, dissolving it in nitric acid and weighing accurately the solution obtained.

Air buoyancy corrections should be done on all weighings.

The standard deviations of the masses shall be determined by carrying out a preliminary examination of the balances used and by checking them when about to be used.

A.3.1 (Acid) etching

Steep the piece(s) of uranium (A.2.1) to be dissolved in 6 mol/l nitric acid (A.2.3) until any and all visible trace of surface oxidation has been eliminated.

Rinse abundantly with distilled water, then steep in the acetone (A.2.5). Dry in the open or, better still, in a nitrogen or argon flow.

Weigh the piece(s) of uranium immediately after drying in the tared dissolution flask, using a balance which has been checked out beforehand. The mass of uranium, m_0, corrected for air buoyancy, shall be greater than 1 g and be measured within ± 0,2 mg or better.

A.3.2 Dissolution

Add concentrated nitric acid (A.2.2) to the dissolution flask in sufficient quantities to obtain complete dissolution (for example 10 ml per 0,5 g of uranium). Boil gently until all solid particles have completely disappeared and a clear solution is left. This operation shall be carried out without there being any splashing: it is preferable to use a tall narrow-necked flask, with a small funnel on top or a reflux dissolving apparatus.

After cooling, dilute with 3 mol/l nitric acid solution (A.2.4) to approximately obtain the desired concentration, by carefully rinsing the edges of the flask. If this operation cannot be carried out in the dissolution flask, transfer the solution carefully into a previously tared flask, and rinse the dissolution flask several times with the diluting acid, before making up to the desired volume.

Weigh with the best possible precision and record the net mass, M_1, of the reference solution just prepared.

Carefully seal and shake, in order to homogenize.

A.3.3 Possible dilution

Using a weight burette (or other suitable means) quantitatively transfer a known quantity (of mass m_1) of the reference solution (see A.3.2) into a previously tared flask (whose empty tare mass is M_t). m_1 shall be determined with the best possible precision.

Add the desired quantity of 3 mol/l nitric acid solution (A.2.4).

Weigh again with the best possible precision the net mass of the diluted solution, M_2.

Carefully seal and shake in order to homogenize.

A.4 Use

When needed, samples shall be taken, using a precise weighing procedure. As far as possible, the sampling shall be carried out as soon as the preparation of the solution has been completed, and the samples shall be kept in sealed flasks until required for use.

In the case where the solution is stored for a relatively long period, it is advisable to check the stability of the mass in the sealed flask. If there has been any significant change during storage, the solution should be discarded.

A.5 Solution strength

The solution strength, A_c, is given as a mass function, by the equation:

$$A_c = R \times 10^{-2} (m_0/M_1)(m_1/M_2) \qquad \text{. . . (A.1)}$$

or, in moles per gram, by

$$A_c = (1/M_A) R \times 10^{-2} (m_0/M_1)(m_1/M_2) \qquad \text{. . . (A.2)}$$

where

R is the uranium content in the certified metal, in per cent;

m_0 is the mass of uranium;

M_1 is the mass of reference solution;

m_1 is the mass of reference solution transferred to the tared flask;

M_2 is the mass of the diluted solution;

M_A is the molar mass of the uranium, in grams per mole.

A_c is known to have a precision of ± $2\sigma_A$. This standard deviation σ_A is obtained from the equation:

$$\frac{\sigma_A^2}{A_c^2} = \frac{\sigma_R^2}{R^2} + \frac{\sigma_{m0}^2}{m_0^2} + \frac{\sigma_{M1}^2}{M_1^2} + \frac{\sigma_{m1}^2}{m_1^2} + \frac{\sigma_{M2}^2}{M_2^2} \qquad \text{. . . (A.3)}$$

EXAMPLE:

$R = 100$ %	$\sigma_R/R = 2{,}5 \times 10^{-4}$
$m_0 = 1{,}000\ 0$ g	$\sigma_{m0} = 0{,}1$ mg
$M_1 = 80{,}000\ 0$ g	$\sigma_{M1} = 0{,}1$ mg
$m_1 = 20{,}000$ g	$\sigma_{m1} = 1$ mg
$M_2 = 500{,}000$ g	$\sigma_{M2} = 1$ mg

$$(\sigma_A/A_c)^2 = \left(2{,}5 \times 10^{-4}\right)^2 + \left(10^{-4}\right)^2 + \left(10^{-4}/80\right)^2 + \left(10^{-3}/20\right)^2 + \left(10^{-3}/500\right)^2$$

$$\sigma_A/A_c = 2{,}74 \times 10^{-4}$$

$A_c = (5{,}000\ 0 \pm 0{,}002\ 7) \times 10^{-4}$ grams of uranium per gram of solution.

Annex B
(normative)

Preparation of plutonium primary reference solutions

B.1 Scope

This procedure describes the preparation of plutonium primary reference solutions, which may be used:

- for verifying the quality of the preparation of the dichromate primary reference solution;
- for calibrating or checking the dichromate secondary reference solutions used in the U and Pu accountability assay titration;
- for the calibration of tracer solutions used in the isotope dilution assay of Pu.

B.2 Reference materials and reagents

All reagents shall be of recognized analytical quality and of a very high degree of purity.

B.2.1 Plutonium metal, certified at ± 0,05 % or better ($\pm 2\sigma_R$) (for example: MP 1/EC 201, MP2, NBL CRM 126, UK Pu 1/80990 or NBS 949).

B.2.2 Concentrated hydrochloric acid.

B.2.3 Hydrochloric acid solution, $c(\text{HCl}) = 0{,}1$ mol/l.

B.2.4 Nitric acid solution, $c(\text{HNO}_3) = 3$ mol/l.

B.2.5 Hydrofluoric acid solution, $c(\text{HF}) = 2$ mol/l.

B.3 Procedure

Prepare the reference solution by dissolving an accurately known mass of the certified plutonium metal and weighing accurately the solution obtained.

Air buoyancy corrections should be done on all weighings.

The standard deviations of the masses shall be determined by carrying out a preliminary examination of the balances used and by checking them when about to be used.

The following procedure is applicable to the reference materials MP1 and MP2. For material NBL 126, the mass of the metal piece is not certified. For a valid application of the latter, the metal piece must therefore be cleaned prior to use and weighed to ± 0,2 mg or better. The recommended procedure for using material NBL 126 is given in the certificate.

B.3.1 Opening of the glass tube

With the aid of a glass cutter make a score in the glass tube containing the plutonium sample (B.2.1), then carefully clean the scratch with a paper tissue which has been impregnated with diluted hydrochloric acid (B.2.3).

Break open the glass tube with care and empty the contents into the tared Erlenmeyer flask. Weigh in order to check that there has not been any loss during the course of this operation.

Call m_0 the mass of the plutonium unit given in the certificate.

B.3.2 Dissolution

Rinse the inside of the glass tube several times with dilute hydrochloric acid solution (B.2.3) and collect the rinsing solutions in the Erlenmeyer flask.

Add dilute hydrochloric acid solution (B.2.3) in order to just cover the piece of reference material (10 ml to 20 ml).

Add 5 ml of concentrated hydrochloric acid solution (B.2.2) and cover with a small funnel.

When the reaction has calmed down, add a further 2 ml of hydrochloric acid solution and bring gently to the boil.

If the metal is oxidized on the surface and if the dissolution is not progressing properly, add 1 ml to 2 ml of hydrofluoric acid solution (B.2.5).

After complete dissolution and cooling down, dilute with 3 mol/l nitric acid solution (B.2.4) in order to approximately obtain the desired concentration, by carefully rinsing the edges of the flask. If this operation cannot be carried out in the dissolver (or if hydrofluoric acid has to be added), transfer the solution carefully into a previously tared flask and rinse the dissolver flask several times with the diluting acid (B.2.4), before making up to the desired volume.

Measure with the best possible precision with the aid of a previously checked balance the net mass of the reference solution, M_1.

Carefully seal and shake in order to homogenize.

NOTE 1 If the reference solution is to be used for calibrating the titration in the silver oxide method, the dissolution acid should be replaced with a mixture of 8 mol/l nitric acid and 0,01 mol/l hydrofluoric acid and the dissolution carried out under reflux. Also for calibration of the Pu(VI) spectrophotometric method the dissolution acid should be replaced by 5 mol/l perchloric acid, and dissolution also carried out under reflux. Here, an equal volume of 6 mol/l nitric acid should be added to the perchloric solution before dilution with the 3 mol/l nitric acid.

B.3.3 Possible dilution

Into a tared flask, transfer a measured portion of the reference solution (see B.3.2). The net mass of the transferred portion, m_1, shall be measured with the best possible precision.

Add the desired quantity of 3 mol/l nitric acid solution (B.2.4).

Weigh again with the best possible precision; call M_2 the net mass of the diluted solution.

Carefully seal and shake to homogenize.

B.4 Use

When needed, samples of the reference solution shall be taken using an accurate weighing procedure.

In the case where the master solution is stored for a relatively long period, it is advisable to check the stability of the gross mass of the sealed flask. If there has been any significant change in mass during storage, the solution should be discarded.

B.5 Solution strength

The solution strength, A_c, is given, as a mass function, by the equation:

$$A_c = R \times 10^{-2} (m_0/M_1)(m_1/M_2) \qquad \text{. . . (B.1)}$$

or, in moles per gram, by

$$A_c = (1/M_A)R \times 10^{-2}(m_0/M_1)(m_1/M_2) \qquad \text{. . . (B.2)}$$

where

R	is the plutonium content in the certified metal, in per cent, and updated in order to take into account the decay of the isotopes of plutonium into uranium and americium;
M_A	is the molar mass of the plutonium given on the certificate, in grams per mole;
m_0	is the mass of the sample given on the certificate;
M_1	is the mass of the reference solution;
m_1	is the mass of transferred portion;
M_2	is the mass of the diluted solution.

A_c is known with a precision of $\pm 2\sigma_A$. This standard deviation is obtained from the equation:

$$\frac{\sigma_A^2}{A_c^2} = \frac{\sigma_{m0}^2}{m_0^2} + \frac{\sigma_{M1}^2}{M_1^2} + \frac{\sigma_{m1}^2}{m_1^2} + \frac{\sigma_{M2}^2}{M_2^2} \qquad \text{. . . (B.3)}$$

The uncertainty σ_{m0} is the total uncertainty in the content of the unit of reference material MP1 or MP2, marked on the certificate. It includes the uncertainty in the elemental assay, the effect of heterogeneity of the reference material, and the uncertainty on the weighing of individual units.

EXAMPLE

Consider the preparation of 80 g of a stock solution of plutonium reference solution:

$R = 100\ \%$

$m_0 = 0{,}500\ 00$ g $\qquad \sigma_{m0}/m_0 = 2{,}50 \times 10^{-4}$

$M_1 = 80{,}000\ 0$ g $\qquad \sigma_{M1} = 0{,}1$ mg

$$(\sigma_A/A_c)^2 = \left(2{,}50 \times 10^{-4}\right)^2 + \left(10^{-4}/80\right)^2$$

$$\sigma_A/A_c = 2{,}5 \times 10^{-4}$$

The concentration of the stock solution, as a mass fraction, with its 95 % confidence limits ($\alpha = 1{,}96$), is equal to

$$A_c = (6{,}250\ 0 \pm 0{,}003\ 1) \times 10^{-3}$$

Examine now the dilution of this stock solution to prepare a reference solution for the calibration of spikes used in isotope dilution analyses.

$m_1 = 2{,}000$ g $\qquad \sigma_{m1} = 0{,}10$ mg

$M_2 = 2\ 000{,}00$ g $\qquad \sigma_{M2} = 0{,}10$ g

$$(\sigma'_A/A'_c)^2 = \left(2{,}50 \times 10^{-4}\right)^2 + \left(10^{-4}/80\right)^2 + \left(10^{-4}/2\right)^2 + (0{,}10/2000)^2$$

$$\sigma'_A/A'_c = 2{,}5 \times 10^{-4}$$

The concentration of the diluted reference solution, as a mass fraction, with its 95 % confidence limits ($\alpha = 1{,}96$), is equal to

$$A'_c = (6{,}250\ 0 \pm 0{,}003\ 1) \times 10^{-6}$$

Annex C
(normative)

Preparation of potassium dichromate primary reference solutions

C.1 Scope

This procedure describes the preparation of potassium dichromate primary reference solutions, which may be used:

- for validating the preparation of U and Pu primary reference solutions used for the standardization of accountability assays by titration;
- for checking the preparation of the U and Pu primary reference solutions used for calibrating tracer solutions for isotope dilution or used for calibration of the Pu (VI) spectrophotometry;
- for standardizing or checking the U and Pu secondary reference solutions.

C.2 Reference materials and reagents

All reagents shall be of recognized analytical quality and of a very high purity.

C.2.1 Potassium dichromate, of certified purity R and associated uncertainty of less than ± 0,05 % (for example NBS 136 or NIST-SRM.136).

C.2.2 Sulfuric acid solution, $c(H_2SO_4) = 0{,}05$ mol/l (approximately).

C.3 Procedure

To prepare the reference solution, dissolve an accurately known amount of the dichromate of certified purity and weigh accurately the solution obtained.

All weights should be corrected for air buoyancy effects.

The standard deviations of the masses shall be determined by carrying out a preliminary examination of the balance used and by checking them when about to be used.

C.3.1 Weighing

In a tared flask, using a previously checked balance, weigh with the best possible precision the amount of dichromate (C.2.1) required for the desired quantity of solution (approximately 5 g of dichromate is needed for 1 litre of solution containing 0,1 equivalent per litre). Correct the net mass of dichromate, m_0, for air buoyancy (the latter corresponds to a relative correction factor of about 3×10^{-4}, for a density of dichromate of 2,676 g/cm^3). The net mass shall be measured with a relative precision of $\pm\ 10^{-4}$ or better, m_0.

NOTE 2 Before use, it may be necessary to dry the dichromate in an oven at 105 °C and then to keep it in a dessicator until the weighing. However, in all circumstances, the user should follow the procedure stated by the certifying body.

C.3.2 Dissolution

Carefully transfer weighed potassium dichromate into a tared flask (of tare mass M_0) of sufficient capacity to hold the volume of solution to be prepared.

Carefully rinse the weighing flask with sulfuric acid solution (C.2.2) and pour the rinsing solutions into the dissolution flask.

Add about half of the total desired quantity of sulfuric acid solution.

Shake manually until complete dissolution.

Make up to the desired quantity with sulfuric acid solution.

Weigh with the best possible precision; call M_1 the net mass of the reference solution.

Carefully seal and shake in order to homogenize.

C.3.3 Possible dilution

If a further dilution is necessary, proceed as follows.

Using a weight burette (or other suitable means), quantitatively transfer a known quantity (m_1) of the reference solution (see C.3.2) into a previously tared flask (having a tare mass M_t). m_1 shall be determined with the best possible precision.

Add the desired quantity of sulfuric acid solution (C.2.2). Weigh again with the best possible precision, and record the mass (M_2).

Carefully seal and shake in order to homogenize.

C.4 Use

In order to preserve the accuracy of its strength, this solution shall be dispensed with the aid of a weight burette. If the flask is kept some time before being used, it is advisable to check the stability of the gross mass of the sealed flask. If there has been any significant change in mass during storage, the solution should be discarded.

C.5 Solution strength

The solution strength, T_c, is given as a mass function, by the equation:

$$T_c = R \times 10^{-2} (m_0/M_1)(m_1/M_2) \quad \text{... (C.1)}$$

in equivalents per gram, by

$$T_c = R \times 10^{-2} (m_0/M_1)(m_1/M_2) \times 6/294{,}1846 \quad \text{... (C.2)}$$

where

R is the certified purity, in per cent;

m_0 is the mass of dichromate;

M_1 is the mass of reference solution;

m_1 is the mass of reference solution transferred to the tared flask;

M_2 is the mass of the diluted solution.

NOTE 3 If no dilution was carried out, then $m_1/M_2 = 1$.

T_c is known with a precision of $\pm 2\sigma_T$. This standard deviation σ_T is obtained from the equation:

$$\frac{\sigma_T^2}{T_c^2} = \frac{\sigma_R^2}{R^2} + \frac{\sigma_{m0}^2}{m_0^2} + \frac{\sigma_{M1}^2}{M_1^2} + \frac{\sigma_{m1}^2}{m_1^2} + \frac{\sigma_{M2}^2}{M_2^2} \quad \text{... (C.3)}$$

EXAMPLE

$R = 100$ % $\qquad \sigma_R = 10^{-2}$ %

$m_0 = 2{,}000\ 0$ g $\qquad \sigma_{m0} = 0{,}1$ mg

$M_1 = 5\ 000{,}0$ g $\qquad \sigma_{M1} = 100$ mg

$m_1/M_2 = 1$ (no dilution)

$$\frac{\sigma_T^2}{T_c} = \left(10^{-4}\right)^2 + \left(\frac{10^{-4}}{2}\right)^2 + \left(\frac{10^{-1}}{5 \times 10^3}\right)^2$$

$$= 1{,}29 \times 10^{-8}$$

$$\sigma_T/T_c = 1{,}14 \times 10^{-4}$$

$T_c = (8{,}158\ 1 \pm 0{,}001\ 8) \times 10^{-6}$ equivalent per gram.

Annex D
(informative)

α: Risk of false alarm; β: Risk of non-detection

D.1 α: risk of false alarm

In order to check the titration solution T, the absolute value of the difference Δ is compared with a threshold which will be chosen proportional to σ_Δ, i.e. of the form $L_\alpha \sigma_\Delta$ (see figure D.1).

The solution will be rejected each time that:

$$|\Delta| > L_\alpha \sigma_\Delta$$

Even if the solution is correct, rejection can take place for any value of L_α less than 3. The probability of such an unfair rejection is represented by the area of the hatched zones in figure D.1. If we call α the total probability of unfair rejection, then α is the risk of the first type, or *the risk of false alarm*.

The risk is selected in advance, generally equal to 5 % or 10 %.

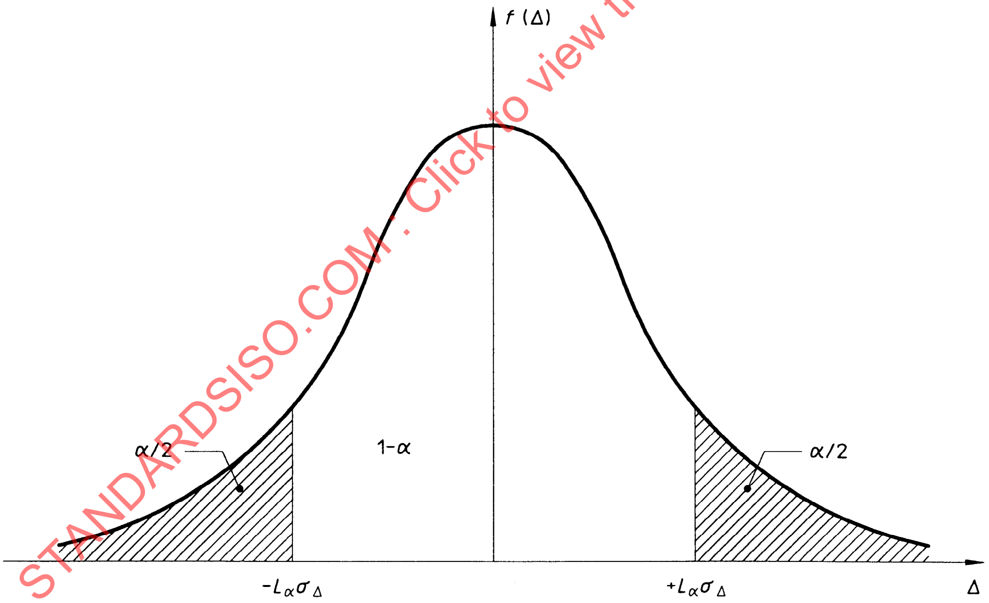


Figure D.1

D.2 β: risk of non-detection

If the strength of solution T is actually incorrect, for example greater than T_c, then the values of Δ will be on average higher than those which correspond to a correct solution; that is, the distribution curve of the incorrect solution is to the right of that of the correct solution. The two curves intersect as shown in figure D.2. There is a probability β that the absolute value of Δ is still lower than $L_\alpha \sigma_\Delta$, and that the incorrect solution will be accepted.

If the only source of error was the preparation of solution T, then Δ would be equal to Δ_0, the average value of the distribution. It is the relative error in the strength T_c which has a probability β of being undetected. The greater the error, the smaller the risk is of accepting the incorrect solution. One specifies in advance the error value Δ_0 which has a given probability β of going unnoticed. For example, it may be decided that an error Δ_0 of 10^{-3} (0,1 %) may go undetected one time out of ten ($\beta = 10$ %). On the other hand the corresponding probability of detection is $100 - \beta = 90$ %.

NOTE 4 $(100 - \beta)$ is often called the efficiency or *the power* of the test.

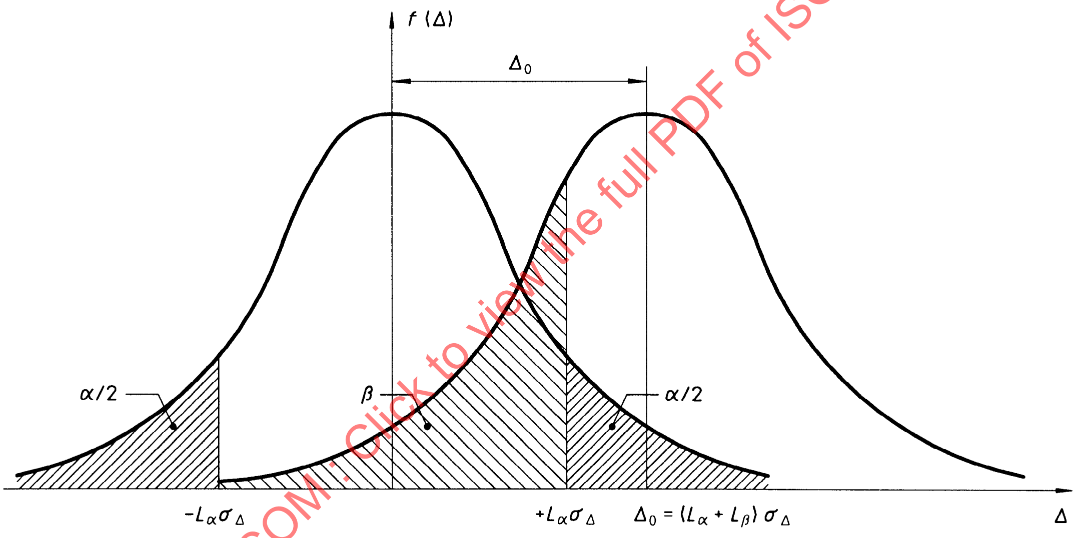


Figure D.2

Annex E
(informative)

Calculation of n and Δ_{min} — Numerical example

E.1 Source data

Assume that the standard deviations have the following values:

Strength calculated for the potassium dichromate titration solution (see annex C):

$$\frac{\sigma_T}{T_{\text{c}}} = 1{,}14 \times 10^{-4}$$

Strength of the uranium primary standard solution (see annex A):

$$\frac{\sigma_A}{A_{\text{c}}} = 2{,}74 \times 10^{-4}$$

Measurement error:

$$\frac{\sigma_{\text{m}}}{A_{\text{c}}} = 3{,}00 \times 10^{-4}$$

Select the following risks:

False alarm:

$\alpha = 5\ \%$

Non-detection:

$\beta = 10\ \%$

E.2 Calculation of Δ_{min}

$$\Delta_{\text{min}} = (L_\alpha + L_\beta)\sqrt{\left(\frac{\sigma_T}{T_{\text{c}}}\right)^2 + \left(\frac{\sigma_A}{A_{\text{c}}}\right)^2} \qquad \ldots \text{(E.1)}$$

[see equation (4)]

With the data given in clause E.1, only errors greater than

$$\Delta_{\text{min}} = (1{,}96 + 1{,}28)\sqrt{(1{,}14)^2 + (2{,}74)^2}\ \ 10^{-4}$$

$$= 0{,}096 \times 10^{-2}$$

can be detected with a probability at least equal to $(100 - \beta) = 90\ \%$.

E.3 Calculation of n

The number of measurements n to be performed to detect an error $\Delta_0 = 10^{-3}$ is calculated from

$$n = \frac{(\sigma_\mathrm{m}/A_\mathrm{c})^2}{\left[\Delta_0^2/(L_\alpha + L_\beta)^2\right] - (\sigma_T/T_\mathrm{c})^2 - (\sigma_A/A_\mathrm{c})^2} \qquad \ldots\text{(E.2)}$$

[see equation (3)]

Hence, with the same data,

$$n = \frac{(3{,}00)^2}{\left[100/(1{,}96 + 1{,}28)^2\right] - (1{,}14)^2 - (2{,}74)^2} = 12{,}5$$

This figure is rounded up to $n = 13$

If it is acceptable to retain 1 solution out of 10 with a strength in error by 0,15 % instead of 0,10 %, the number of measurements n becomes:

$$n = \frac{(3{,}00)^2}{\left[225/(1{,}96 + 1{,}28)^2\right] - (1{,}14)^2 - (2{,}74)^2} = 0{,}71$$

This is rounded up to $n = 1$.

E.4 Derivation of the equation for σ_Δ [equation (2)]

Let Δ be the relative difference between the measured strength A_m and the calculated value A_c [see equation (1)]:

$$\Delta = \frac{A_\mathrm{m} - A_\mathrm{c}}{A_\mathrm{c}}$$

$$= \frac{A_\mathrm{m}}{A_\mathrm{c}} - 1 \qquad \ldots\text{(E.3)}$$

The measured titer of the standard solution A of analyte (U or Pu) is obtained by titrating a mass M_A of solution A with a standard titrant T. Let M_T be the mass of titrant needed:

$$A_\mathrm{m} = \frac{M_\mathrm{T}}{M_\mathrm{A}} T_\mathrm{c} \qquad \ldots\text{(E.4)}$$

Thus

$$\left(\frac{\sigma_{A_\mathrm{m}}}{A_\mathrm{m}}\right)^2 = \underbrace{\left(\frac{\sigma_{T_\mathrm{c}}}{T_\mathrm{c}}\right)^2}_{\text{Systematic component}} + \underbrace{\left[\frac{\sigma_{(M_\mathrm{T}/M_\mathrm{A})}}{(M_\mathrm{T}/M_\mathrm{A})}\right]^2}_{\text{Random component } (\sigma_\mathrm{m}/A_\mathrm{m})^2}$$

For the mean of n titrations:

$$\left(\frac{\sigma_{A_\mathrm{m}}}{A_\mathrm{m}}\right)^2 = \frac{1}{n}\left(\frac{\sigma_\mathrm{m}}{A_\mathrm{m}}\right)^2 + \left(\frac{\sigma_{T_\mathrm{c}}}{T_\mathrm{c}}\right)^2 \qquad \ldots\text{(E.5)}$$

From equation (E.3):

$$\Delta' = \Delta + 1$$

$$= A_\mathrm{m}/A_\mathrm{c}$$

$$\left(\frac{\sigma_{\Delta'}}{\Delta'}\right)^2 = \left(\frac{\sigma_{A_m}}{A_m}\right)^2 + \left(\frac{\sigma_{A_c}}{A_c}\right)^2$$

From equation (E.5), and neglecting $\Delta \sim 10^{-3}$ compared to 1 (so $\Delta' \sim 1$):

$$(\sigma_{\Delta'})^2 = \frac{1}{n}\left(\frac{\sigma_m}{A_m}\right)^2 + \left(\frac{\sigma_{T_c}}{T_c}\right)^2 + \left(\frac{\sigma_{A_c}}{A_c}\right)^2 \quad \ldots \text{(E.6)}$$

[see equation (2)]

Annex F
(informative)

Efficiency and sample size curves

Annex E shows that the choice of the pair (β, Δ_0) is of considerable importance.

When choosing n, it is therefore useful to plot the curves giving, for each value of n, the efficiency or power of the test, ($100 - \beta$), as a function of the error Δ_0 to be detected. These curves are called "efficiency curves". Alternatively it is useful to plot for a given goal detection probability, $100 - \beta$, a curve showing the number n of samples to be analyzed as a function of Δ_0. Such a curve is called a "sample size curve".

These curves can be plotted point by point using the following equation [which is equivalent to equation (5)]:

$$\Delta_0 = (L_\alpha + L_\beta)\sigma_\Delta \qquad \text{. . . (F.1)}$$

where

L_α and L_β are taken from table 1 according to the selected risks, α and β; σ_Δ (the standard deviation) is given by the following equation, which is equivalent to equation (2):

$$\sigma_\Delta = \sqrt{\left(\frac{\sigma_T}{T_c}\right)^2 + \left(\frac{\sigma_A}{A_c}\right)^2 + \frac{1}{n}\left(\frac{\sigma_m}{A_c}\right)^2} \qquad \text{. . . (F.2)}$$

The number of measurements n to perform in order to detect a true error Δ_0 with a risk α of false alarm and a risk β of non-detection, is calculated from the following equation, which is equivalent to equation (3):

$$n = \frac{(\sigma_m/A_c)^2}{\left[\Delta_0^2/(L_\alpha + L_\beta)^2\right] - (\sigma_T/T_c)^2 - (\sigma_A/A_c)^2} \qquad \text{. . . (F.3)}$$

For given risks α and β, the number n may be written as a simple function of two parameters R and E_0:

$$R^2 = (\sigma_m/A_c)^2/S^2 \qquad \text{. . . (F.4)}$$

$$E_0 = \Delta_0/S \qquad \text{. . . (F.5)}$$

where

$$S^2 = (\sigma_T/T_c)^2 + (\sigma_A/A_c)^2 \qquad \text{. . . (F.6)}$$

R^2 is the ratio of the variance of the random errors of the test method, $(\sigma_m/A_c)^2$, and the total variance of the uncertainties on the calculated values of the strengths of the reference solutions, $\left[(\sigma_T/T_c)^2 + (\sigma_A/A_c)^2\right]$;

E_0 is the ratio of the true error Δ_0 to be detected to the standard deviation S.

Equation (F.3) can be rewritten in the form of a function of E_0 for L_β:

$$L_\beta = \frac{E_0}{\left[1 + \left(n/R^2\right)^{-1}\right]^{1/2}} - L_\alpha \qquad \text{. . . (F.7)}$$

Equation (F.7) can be used to calculate L_β, from which ($100 - \beta$) may be derived in order to prepare "efficiency tables" (tables F.3 to F.5). These tables are useful for plotting "efficiency curves" (figures F.1 to F.3), for selected values of α and n/R^2.

Equation (F.3) may also be rewritten as the following equation between these normalized parameters n/R^2 and E_0:

$$\frac{n}{R^2} = \frac{1}{E_0^2 (L_\alpha + L_\beta)^{-2} - 1} \qquad \dots (F.8)$$

Equation (F.8) is convenient for calculating point by point "normalized sample size tables" (tables F.6 to F.8) from which "normalized sample size curves" (figures F.4 to F.6) may be drawn, for fixed values of the risks α and β.

EXAMPLE

Consider the case of annex A where

$$\sigma_T/T_c = 1{,}14 \times 10^{-4}$$

$$\sigma_A/A_c = 2{,}74 \times 10^{-4}$$

$$\sigma_m/A_c = 3{,}00 \times 10^{-4}$$

$$S^2 = \left(1{,}14 \times 10^{-4}\right)^2 + \left(2{,}74 \times 10^{-4}\right)^2$$

$$R^2 = \frac{\left(3{,}00 \times 10^{-4}\right)^2}{\left(1{,}14 \times 10^{-4}\right)^2 + \left(2{,}74 \times 10^{-4}\right)^2}$$

$$= 1{,}022$$

Select $\alpha = 5\ \%$ $(L_\alpha = 1{,}96)$

$\beta = 5\ \%$ $(L_\beta = 1{,}64)$

According to table F.7, a normalized number of measurements, n/R^2, equal to 9,0 must be done in order to detect a normalized error E_0 of 3,8 with the risks $\alpha = \beta = 5\ \%$. The true error Δ_0 which may be detected with the above risk is

$$\Delta_0 = E_0 \times S$$

$$= 3{,}8 \times 2{,}97 \times 10^{-4}$$

$$= 0{,}114 \times 10^{-2}$$

The actual number of measurements to be done must exceed

$$n = 9{,}0 \times R^2$$

$$= 9{,}20$$

In other words, at least 10 measurements would be required.

Table F.1 presents the results of such derivations of sample size n for increasing values of the error Δ_0 to be detected.

Table F.1 — Example of a sample size table (for $\alpha = \beta = 5$ %)

E_0	$\Delta_0 = E_0 \times S$ (× 100)	n/R^2	n calculated	n rounded
3,8	0,113	9,0	9,20	10
4,0	0,119	4,3	4,39	5
4,4	0,131	2,0	2,04	3
4,8	0,143	1,3	1,33	2
5,0	0,148	1,1	1,12	2
5,2	0,154	0,9	0,92	1

Conversely, it is possible to derive from figure F.4 how the probability of detection $100 - \beta$ varies with the magnitude of the error Δ_0 when a fixed number of measurements n are done, and a risk of false alarm α of 1 % is accepted. For instance, if 5 measurements are done:

$$n/R^2 = 4,89$$

Read E_0 for $n/R^2 = 4,89$ and various probabilities of detection, and calculate $\Delta_0 = E_0 \times S = E_0 \times 2,97 \times 10^{-4}$. Efficiency table F.2 may thus be constructed.

Table F.2 — Example of an efficiency table (for $n = 5$, $\alpha = 1$ %)

$100 - \beta$ (%)	E_0	$\Delta_0 = E_0 \times S$ (× 100)
50,0	2,83	0,084
75,0	3,60	0,107
90,0	4,23	0,126
95,0	4,65	0,138
99,0	5,38	0,160
99,9	6,22	0,185
99,995	7,13	0,212

Table F.3 — Efficiency table for a risk of false alarm of α = 1 % and L_α = 2,58

E_0	n/R^2								
	0,1	**0,2**	**0,4**	**0,9**	**1,2**	**2,0**	**4,0**	**10,0**	**50,0**
2,0									
2,2									
2,4									
2,6									
2,8								53,6	57,6
3,0							54,1	61,0	65,2
3,2						51,3	61,1	68,1	72,2
3,4						57,8	67,8	74,6	78,4
3,6					53,1	64,0	73,9	80,3	83,7
3,8				51,4	59,0	69,9	79,3	85,1	88,1
4,0				56,9	64,6	75,3	84,1	89,1	91,6
4,2				62,2	69,9	80,2	88,0	92,3	94,2
4,4				67,3	74,8	84,4	91,2	94,7	96,2
4,6				72,1	79,3	88,0	93,7	96,4	97,6
4,8				76,5	83,3	90,9	95,6	97,7	98,5
5,0			53,7	80,5	86,7	93,3	97,0	98,5	99,1
5,2			57,9	84,1	89,6	95,2	98,1	99,1	99,5
5,4			62,0	87,2	92,0	96,6	98,8	99,5	99,7
5,6			66,0	89,8	94,0	97,7	99,2	99,7	99,8
5,8			69,8	92,1	95,5	98,4	99,5	99,8	99,9
6,0			73,5	93,9	96,8	99,0	99,7	99,9	100,0
6,2			76,8	95,4	97,7	99,3	99,8	100,0	100,0
6,4		51,3	80,0	96,6	98,4	99,6	99,9	100,0	100,0
6,6		54,6	82,8	97,5	98,9	99,7	100,0	100,0	100,0
6,8		57,8	85,4	98,2	99,3	99,8	100,0	100,0	100,0
7,0		60,9	87,7	98,7	99,5	99,9	100,0	100,0	100,0
7,2		64,0	89,7	99,1	99,7	99,9	100,0	100,0	100,0
7,4		67,0	91,5	99,4	99,8	100,0	100,0	100,0	100,0
7,6		69,9	93,1	99,6	99,9	100,0	100,0	100,0	100,0
7,8		72,7	94,4	99,7	99,9	100,0	100,0	100,0	100,0
8,0		75,3	95,5	99,8	100,0	100,0	100,0	100,0	100,0

NOTE — The values are detection probabilities (100 – β) in percent corresponding to L_β values derived from the formula:

$$L_\beta = \frac{E_0}{\left(1 + R^2/n\right)^{0,5}} - L_\alpha$$

where

$$E_0 = \frac{\Delta_0}{S}$$

$$R^2 = \frac{(\sigma_m/A_c)^2}{S^2}$$

with

$$S^2 = (\sigma_T/T_c)^2 + (\sigma_A/A_c)^2$$

Table F.4 — Efficiency table for a risk of false alarm of α = 5 % and L_α = 1,96

E_0	n/R^2								
	0,1	**0,2**	**0,4**	**0,9**	**1,2**	**2,0**	**4,0**	**10,0**	**50,0**
2,0									50,8
2,2							50,3	55,5	58,6
2,4							57,4	62,9	66,1
2,6						56,5	64,3	69,8	73,0
2,8						62,8	70,7	76,1	79,2
3,0						68,8	76,5	81,6	84,4
3,2						74,3	81,6	86,2	88,6
3,4				64,8	70,9	79,3	86,0	90,0	92,0
3,6				69,8	75,7	83,6	89,6	92,9	94,5
3,8			52,8	74,4	80,1	87,3	92,5	95,2	96,4
4,0			57,1	78,6	84,0	90,4	94,7	96,8	97,7
4,2			61,2	82,4	87,3	92,9	96,3	97,9	98,6
4,4			65,2	85,7	90,1	94,8	97,6	98,7	99,2
4,6			69,1	88,6	92,4	96,3	98,4	99,2	99,5
4,8			72,8	91,0	94,3	97,5	99,0	99,5	99,7
5,0		53,2	76,2	93,0	95,8	98,3	99,4	99,7	99,9
5,2		56,5	79,4	94,7	97,0	98,9	99,6	99,9	99,9
5,4		59,7	82,3	96,0	97,8	99,3	99,8	99,9	100,0
5,6		62,8	84,9	97,1	98,5	99,5	99,9	100,0	100,0
5,8		65,8	87,3	97,9	99,0	99,7	99,9	100,0	100,0
6,0		68,8	89,4	98,5	99,3	99,8	100,0	100,0	100,0
6,2		71,6	91,2	98,9	99,5	99,9	100,0	100,0	100,0
6,4		74,3	92,8	99,3	99,7	99,9	100,0	100,0	100,0
6,6	51,2	76,8	94,1	99,5	99,8	100,0	100,0	100,0	100,0
6,8	53,6	79,3	95,3	99,7	99,9	100,0	100,0	100,0	100,0
7,0	56,0	81,5	96,2	99,8	99,9	100,0	100,0	100,0	100,0
7,2	58,3	83,6	97,0	99,9	100,0	100,0	100,0	100,0	100,0
7,4	60,7	85,5	97,7	99,9	100,0	100,0	100,0	100,0	100,0
7,6	63,0	87,3	98,2	99,9	100,0	100,0	100,0	100,0	100,0
7,8	65,2	88,9	98,6	100,0	100,0	100,0	100,0	100,0	100,0
8,0	67,4	90,4	99,0	100,0	100,0	100,0	100,0	100,0	100,0

NOTE — The values are detection probabilities (100 − β) in percent corresponding to L_β values derived from the formula:

$$L_\beta = \frac{E_0}{\left(1 + R^2/n\right)^{0,5}} - L_\alpha$$

where

$$E_0 = \frac{\Delta_0}{S}$$

$$R^2 = \frac{(\sigma_m/A_c)^2}{S^2}$$

with

$$S^2 = (\sigma_T/T_c)^2 + (\sigma_A/A_c)^2$$

Table F.5 — Efficiency table for a risk of false alarm of α = 10 % and L_α = 1,65

E_0	n/R^2								
	0,1	**0,2**	**0,4**	**0,9**	**1,2**	**2,0**	**4,0**	**10,0**	**50,0**
2,0							55,5	60,1	62,9
2,2						55,8	62,5	67,3	70,1
2,4						62,1	69,0	73,8	76,6
2,6						68,2	75,0	79,6	82,2
2,8						73,8	80,3	84,6	86,9
3,0						78,8	84,9	88,7	90,6
3,2						83,2	88,7	91,9	93,5
3,4			56,6	75,5	80,5	87,0	91,8	94,4	95,7
3,6			60,8	79,6	84,3	90,1	94,1	96,2	97,2
3,8			64,8	83,3	87,6	92,7	96,0	97,5	98,2
4,0			68,7	86,5	90,4	94,7	97,3	98,5	98,9
4,2		52,6	72,4	89,2	92,6	96,2	98,2	99,1	99,4
4,4		55,8	75,8	91,6	94,5	97,4	98,9	99,4	99,6
4,6		59,0	79,0	93,5	95,9	98,2	99,3	99,7	99,8
4,8		62,1	82,0	95,1	97,1	98,8	99,6	99,8	99,9
5,0		65,2	84,7	96,3	97,9	99,2	99,8	99,9	99,9
5,2		68,2	87,0	97,3	98,6	99,5	99,9	99,9	100,0
5,4		71,0	89,2	98,0	99,0	99,7	99,9	100,0	100,0
5,6	51,5	73,8	91,0	98,6	99,3	99,8	100,0	100,0	100,0
5,8	53,9	76,3	92,6	99,0	99,6	99,9	100,0	100,0	100,0
6,0	56,3	78,8	94,0	99,3	99,7	99,9	100,0	100,0	100,0
6,2	58,7	81,1	95,2	99,5	99,8	100,0	100,0	100,0	100,0
6,4	61,0	83,2	96,1	99,7	99,9	100,0	100,0	100,0	100,0
6,6	63,3	85,2	97,0	99,8	99,9	100,0	100,0	100,0	100,0
6,8	65,5	87,0	97,6	99,9	100,0	100,0	100,0	100,0	100,0
7,0	67,7	88,6	98,2	99,9	100,0	100,0	100,0	100,0	100,0
7,2	69,9	90,1	98,6	99,9	100,0	100,0	100,0	100,0	100,0
7,4	71,9	91,5	98,9	100,0	100,0	100,0	100,0	100,0	100,0
7,6	73,9	92,7	99,2	100,0	100,0	100,0	100,0	100,0	100,0
7,8	75,8	93,7	99,4	100,0	100,0	100,0	100,0	100,0	100,0
8,0	77,7	94,7	99,6	100,0	100,0	100,0	100,0	100,0	100,0

NOTE — The values are detection probabilities (100 − β) in percent corresponding to L_β values derived from the formula:

$$L_\beta = \frac{E_0}{\left(1 + R^2/n\right)^{0,5}} - L_\alpha$$

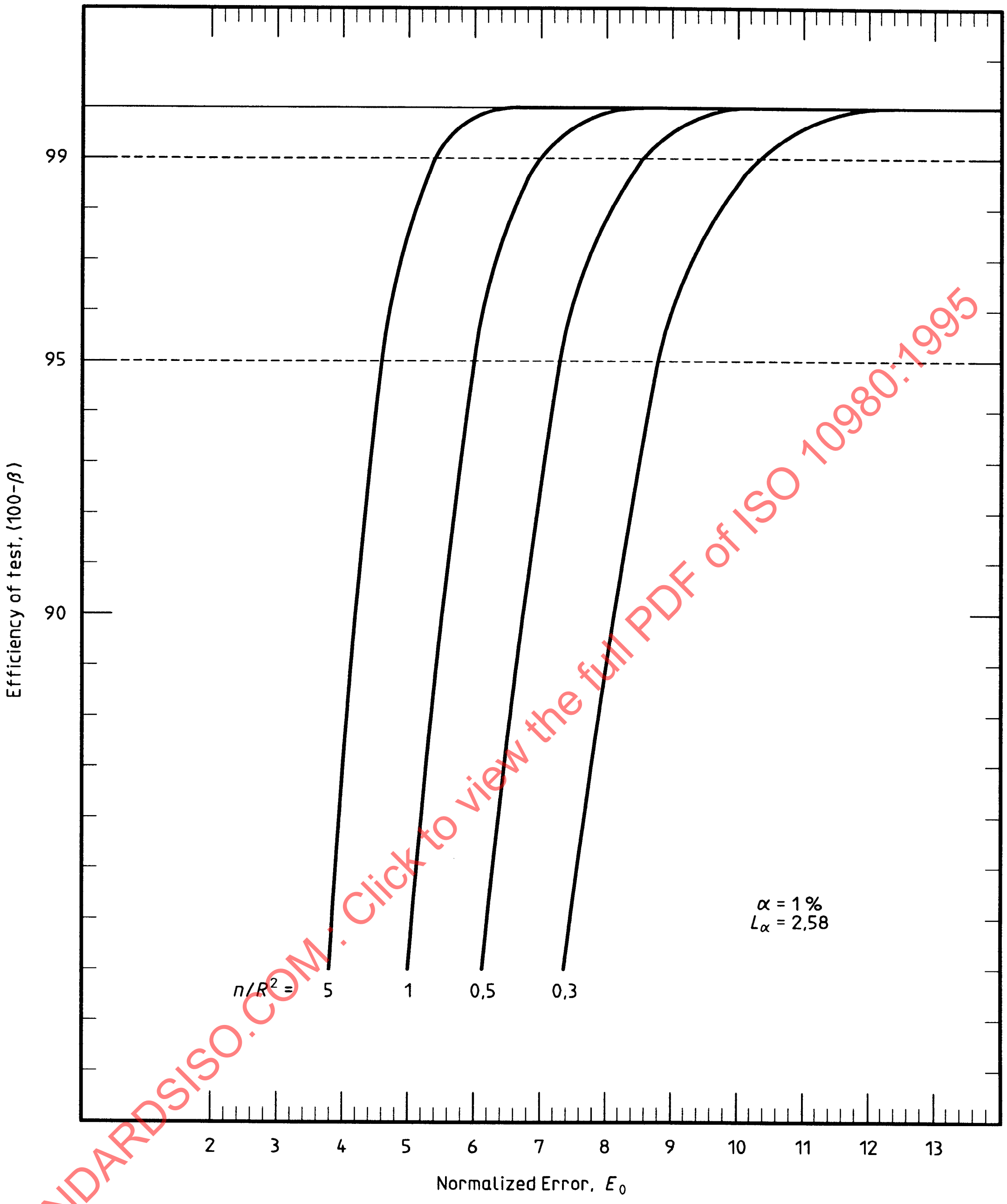
where

$$E_0 = \frac{\Delta_0}{S}$$

$$R^2 = \frac{(\sigma_m/A_c)^2}{S^2}$$

with

$$S^2 = (\sigma_T/T_c)^2 + (\sigma_A/A_c)^2$$



$$L_\beta = \frac{E_0}{\left(1 + R^2/n\right)^{0,5}} - L_\alpha$$

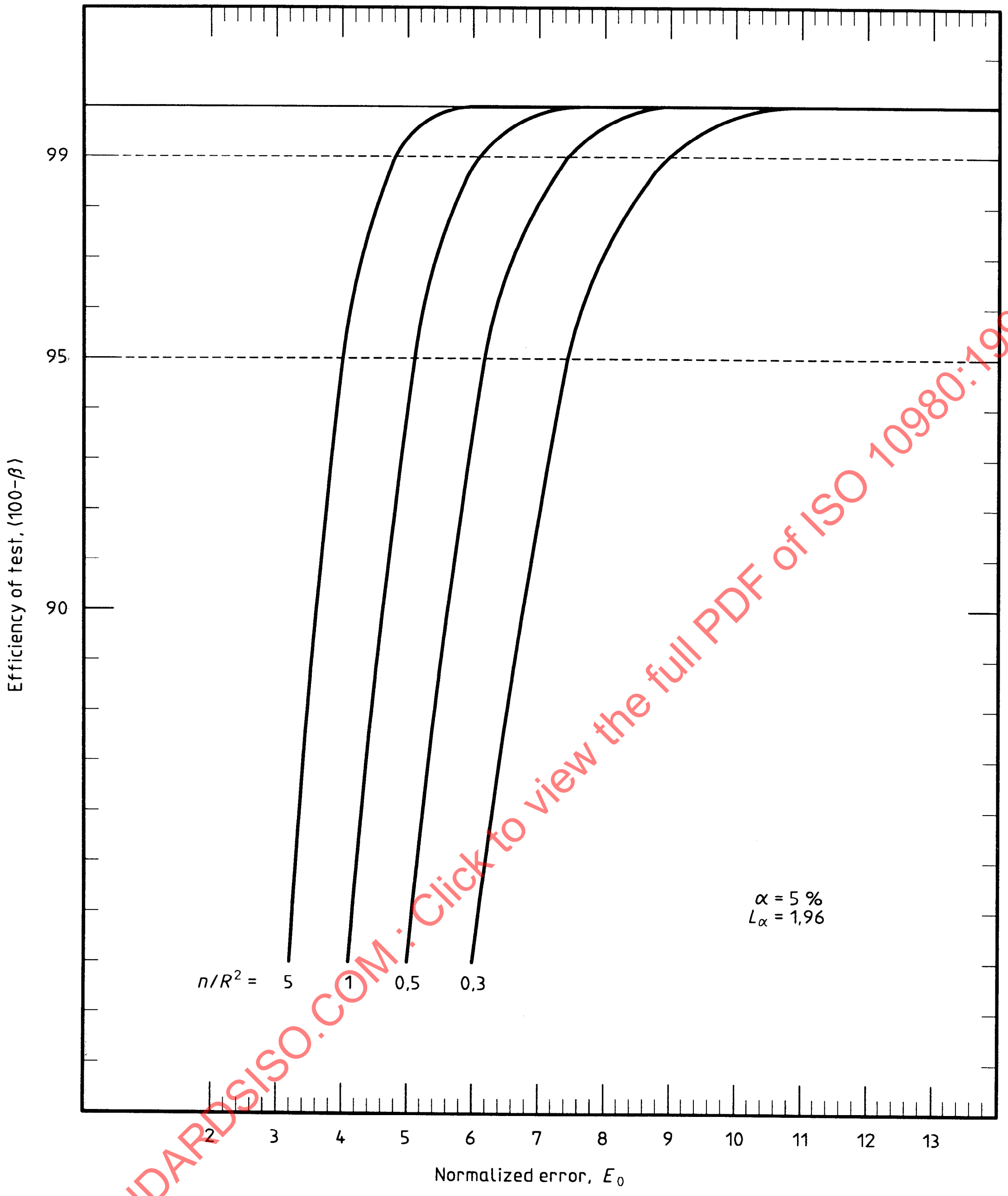
$$E_0 = \frac{\Delta_0}{S}$$

$$R^2 = \frac{(\sigma_{\mathrm{m}}/A_{\mathrm{c}})^2}{S^2}$$

where

$$S^2 = (\sigma_T/T_{\mathrm{c}})^2 + (\sigma_A/A_{\mathrm{c}})^2$$

Figure F.1 — Efficiency curves for a risk of false alarm of α = 1 % and a normalized sample size of n/R^2



$$L_\beta = \frac{E_0}{\left(1 + R^2/n\right)^{0,5}} - L_\alpha$$

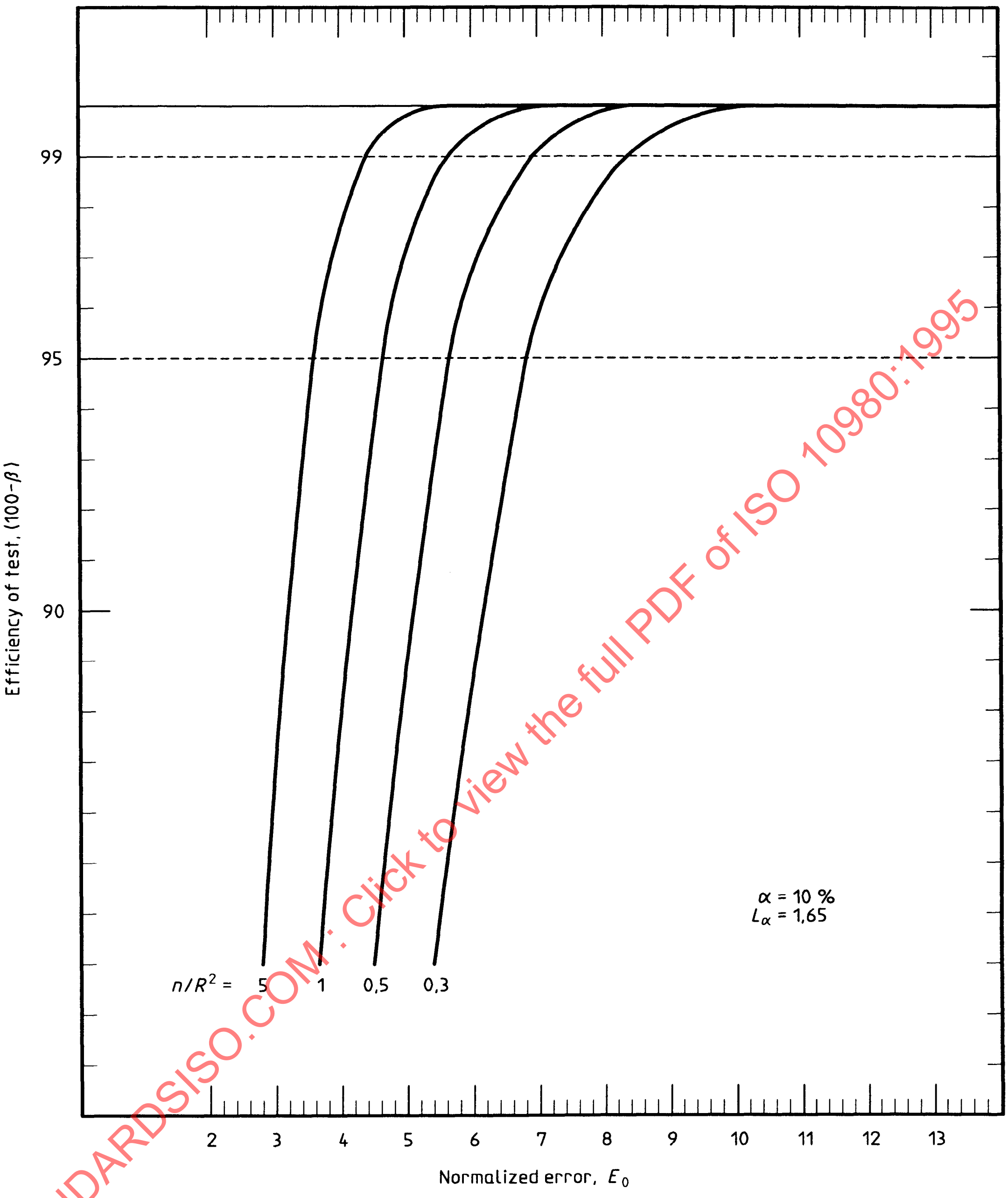
$$E_0 = \frac{\Delta_0}{S}$$

$$R^2 = \frac{\left(\sigma_\mathrm{m}/A_\mathrm{c}\right)^2}{S^2}$$

where

$$S^2 = \left(\sigma_T/T_\mathrm{c}\right)^2 + \left(\sigma_A/A_\mathrm{c}\right)^2$$

Figure F.2 — Efficiency curves for a risk of false alarm of α = 5 % and a normalized sample size of n/R^2



$$L_\beta = \frac{E_0}{\left(1 + R^2/n\right)^{0,5}} - L_\alpha$$

$$E_0 = \frac{\Delta_0}{S}$$

$$R^2 = \frac{(\sigma_m/A_c)^2}{S^2}$$

where

$$S^2 = (\sigma_T/T_c)^2 + (\sigma_A/A_c)^2$$

Figure F.3 — Efficiency curves for a risk of false alarm of α = 10 % and a normalized sample size of n/R^2

Table F.6 — Normalized sample size table for a risk of false alarm of α = 1 % and L_α = 2,58

E_0	100 − β								
	50,0	**75,0**	**90,0**	**95,0**	**99,0**	**99,5**	**99,9**	**99,95**	**99,995**
2,0									
2,2									
2,4									
2,6	53,42								
2,8	5,51								
3,0	2,81								
3,2	1,84								
3,4	1,35	10,66							
3,6	1,05	4,42							
3,8	0,85	2,73							
4,0	0,71	1,95	13,34						
4,2	0,60	1,49	5,40						
4,4	0,52	1,20	3,33	11,55					
4,6	0,46	1,00	2,37	5,33					
4,8	0,40	0,85	1,82	3,41					
5,0	0,36	0,73	1,47	2,48	24,76				
5,2	0,33	0,64	1,22	1,93	7,98	53,42			
5,4	0,29	0,57	1,04	1,57	4,68	10,14			
5,6	0,27	0,51	0,90	1,32	3,28	5,51			
5,8	0,25	0,46	0,79	1,13	2,50	3,74	20,89		
6,0	0,23	0,42	0,70	0,98	2,01	2,81	8,24	21,64	
6,2	0,21	0,38	0,63	0,86	1,67	2,23	5,07	8,54	
6,4	0,19	0,35	0,57	0,77	1,42	1,84	3,62	5,25	
6,6	0,18	0,32	0,52	0,69	1,23	1,56	2,80	3,76	24,06
6,8	0,17	0,30	0,47	0,63	1,08	1,35	2,27	2,91	9,47
7,0	0,16	0,28	0,44	0,57	0,96	1,18	1,90	2,36	5,83
7,2	0,15	0,26	0,40	0,52	0,86	1,05	1,63	1,97	4,17
7,4	0,14	0,24	0,37	0,48	0,78	0,94	1,42	1,69	3,23
7,6	0,13	0,22	0,35	0,45	0,71	0,85	1,25	1,47	2,62
7,8	0,12	0,21	0,32	0,41	0,65	0,77	1,12	1,30	2,20
8,0	0,12	0,20	0,30	0,39	0,60	0,71	1,01	1,16	1,89
E_0	0,00	0,68	1,28	1,64	2,33	2,58	3,09	3,29	3,89
					L_β				

NOTE —

$$\frac{n}{R^2} = \frac{1}{E_0^2(L_\alpha + L_\beta)^{-2} - 1}$$

$$E_0 = \frac{\Delta_0}{S}$$

$$R^2 = \frac{(\sigma_m/A_c)^2}{S^2}$$

where

$$S^2 = (\sigma_T/T_c)^2 + (\sigma_A/A_c)^2$$

Table F.7 — Normalized sample size table for a risk of false alarm of α = 5 % and L_α = 1,96

E_0	100 − β								
	50,0	**75,0**	**90,0**	**95,0**	**99,0**	**99,5**	**99,9**	**99,95**	**99,995**
2,0	24,25								
2,2	3,85								
2,4	2,00								
2,6	1,32								
2,8	0,96	7,74							
3,0	0,74	3,38							
3,2	0,60	2,11							
3,4	0,50	1,50	10,02						
3,6	0,42	1,15	4,29						
3,8	0,36	0,93	2,67	9,00					
4,0	0,32	0,77	1,91	4,33					
4,2	0,28	0,65	1,47	2,80					
4,4	0,25	0,56	1,19	2,04	18,55				
4,6	0,22	0,49	0,99	1,59	6,58	35,19			
4,8	0,20	0,43	0,84	1,29	3,93	8,35			
5,0	0,18	0,38	0,73	1,08	2,77	4,65			
5,2	0,17	0,35	0,64	0,93	2,12	3,18	16,59		
5,4	0,15	0,31	0,56	0,80	1,70	2,40	6,97	17,25	
5,6	0,14	0,28	0,50	0,71	1,41	1,91	4,35	7,26	
5,8	0,13	0,26	0,45	0,63	1,20	1,57	3,13	4,54	
6,0	0,12	0,24	0,41	0,56	1,04	1,33	2,43	3,27	19,39
6,2	0,11	0,22	0,38	0,51	0,92	1,15	1,97	2,53	8,14
6,4	0,10	0,20	0,35	0,46	0,81	1,01	1,65	2,06	5,09
6,6	0,10	0,19	0,32	0,43	0,73	0,90	1,41	1,72	3,67
6,8	0,09	0,18	0,29	0,39	0,66	0,80	1,23	1,48	2,85
7,0	0,09	0,17	0,27	0,36	0,60	0,72	1,09	1,29	2,32
7,2	0,08	0,15	0,25	0,33	0,55	0,66	0,97	1,14	1,94
7,4	0,08	0,15	0,24	0,31	0,50	0,60	0,87	1,01	1,67
7,6	0,07	0,14	0,22	0,29	0,47	0,55	0,79	0,91	1,46
7,8	0,07	0,13	0,21	0,27	0,43	0,51	0,72	0,83	1,29
8,0	0,06	0,12	0,20	0,25	0,40	0,47	0,66	0,76	1,15
E_0	0,00	0,68	1,28	1,64	2,33	2,58	3,09	3,29	3,89
					L_β				

NOTE —

$$\frac{n}{R^2} = \frac{1}{E_0^2 (L_\alpha + L_\beta)^{-2} - 1}$$

$$E_0 = \frac{\Delta_0}{S}$$

$$R^2 = \frac{(\sigma_m / A_c)^2}{S^2}$$

where

$$S^2 = (\sigma_T / T_c)^2 + (\sigma_A / A_c)^2$$

Table F.8 — Normalized sample size table for a risk of false alarm of α = 10 % and L_α = 1,65

E_0	100 − β								
	50,0	**75,0**	**90,0**	**95,0**	**99,0**	**99,5**	**99,9**	**99,95**	**99,995**
2,0	2,09								
2,2	1,27								
2,4	0,89	14,25							
2,6	0,67	3,91							
2,8	0,53	2,19							
3,0	0,43	1,49	19,80						
3,2	0,36	1,11	5,12						
3,4	0,31	0,87	2,86	14,71					
3,6	0,26	0,71	1,95	5,07					
3,8	0,23	0,59	1,46	2,99					
4,0	0,20	0,51	1,15	2,09	68,22				
4,2	0,18	0,44	0,94	1,59	8,43				
4,4	0,16	0,39	0,79	1,27	4,39	11,55			
4,6	0,15	0,34	0,68	1,05	2,92	5,33			
4,8	0,13	0,30	0,59	0,89	2,17	3,41	36,18		
5,0	0,12	0,27	0,52	0,76	1,71	2,48	8,69	37,71	
5,2	0,11	0,25	0,46	0,67	1,40	1,93	4,85	9,07	
5,4	0,10	0,23	0,42	0,59	1,18	1,57	3,33	5,07	
5,6	0,09	0,21	0,38	0,53	1,01	1,32	2,51	3,48	43,00
5,8	0,09	0,19	0,34	0,47	0,88	1,13	2,00	2,62	10,24
6,0	0,08	0,18	0,31	0,43	0,78	0,98	1,65	2,09	5,73
6,2	0,08	0,16	0,29	0,39	0,70	0,86	1,40	1,73	3,93
6,4	0,07	0,15	0,26	0,36	0,63	0,77	1,21	1,47	2,97
6,6	0,07	0,14	0,24	0,33	0,57	0,69	1,06	1,27	2,37
6,8	0,06	0,13	0,23	0,31	0,52	0,63	0,94	1,11	1,97
7,0	0,06	0,12	0,21	0,28	0,47	0,57	0,84	0,99	1,67
7,2	0,06	0,12	0,20	0,26	0,44	0,52	0,76	0,89	1,45
7,4	0,05	0,11	0,19	0,25	0,40	0,48	0,69	0,80	1,27
7,6	0,05	0,10	0,17	0,23	0,38	0,45	0,63	0,73	1,13
7,8	0,05	0,10	0,16	0,22	0,35	0,41	0,58	0,67	1,02
8,0	0,04	0,09	0,15	0,20	0,33	0,39	0,54	0,61	0,92
E_0	0,00	0,68	1,28	1,64	2,33	2,58	3,09	3,29	3,89
					L_β				

NOTE —

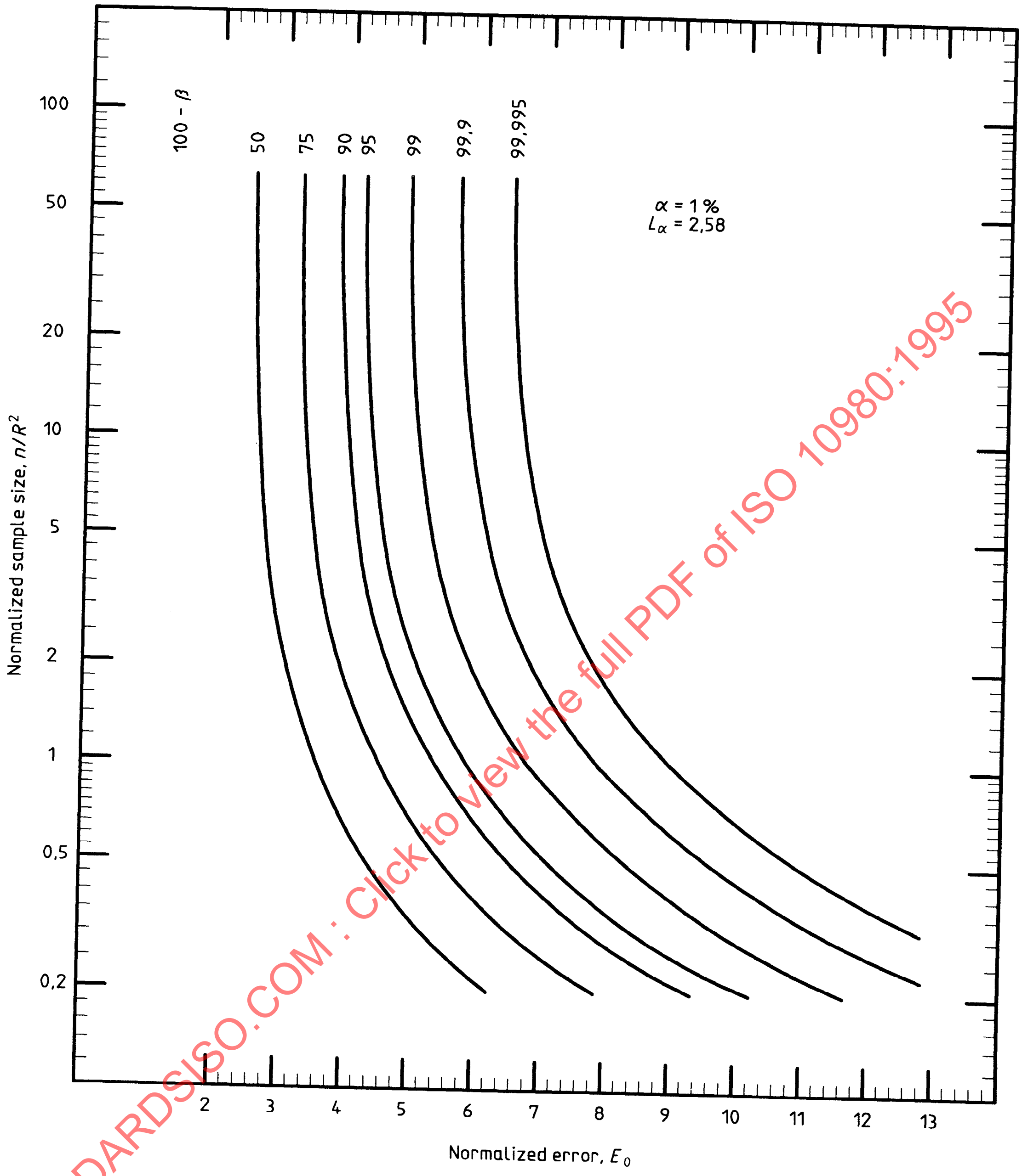
$$\frac{n}{R^2} = \frac{1}{E_0^2 (L_\alpha + L_\beta)^{-2} - 1}$$

$$E_0 = \frac{\Delta_0}{S}$$

$$R^2 = \frac{(\sigma_m / A_c)^2}{S^2}$$

where

$$S^2 = (\sigma_T / T_c)^2 + (\sigma_A / A_c)^2$$



$$\frac{n}{R^2} = \frac{1}{E_0^2 (L_\alpha + L_\beta)^{-2} - 1}$$

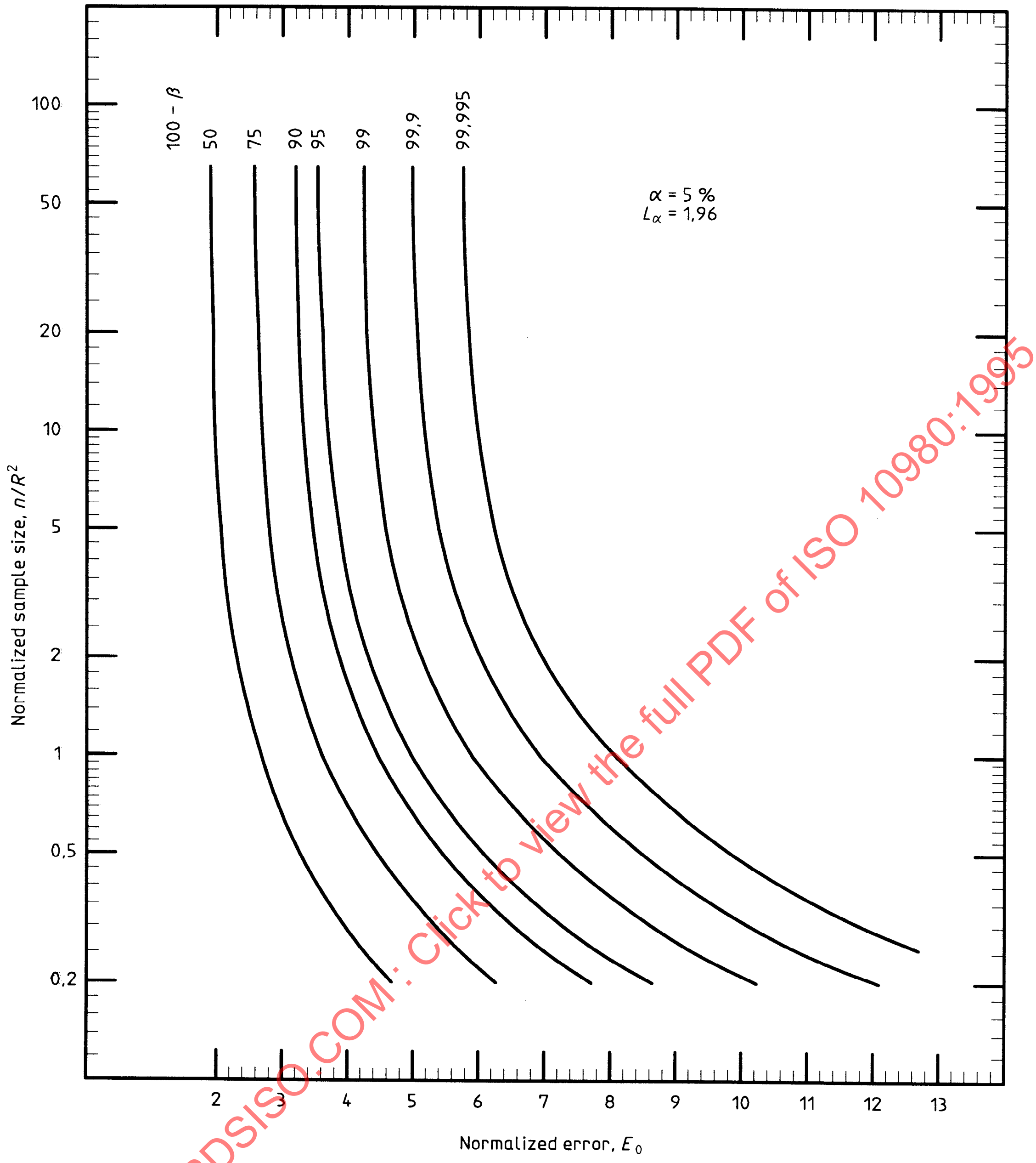
$$E_0 = \frac{\Delta_0}{S}$$

$$R^2 = \frac{(\sigma_m / A_c)^2}{S^2}$$

where

$$S^2 = (\sigma_T / T_c)^2 + (\sigma_A / A_c)^2$$

Figure F.4 — Normalized sample size curves for a risk of false alarm of α = 1 % (and selected detection probabilities 100 − β, in percent)



$$\frac{n}{R^2} = \frac{1}{E_0^2 (L_\alpha + L_\beta)^{-2} - 1}$$

$$E_0 = \frac{\Delta_0}{S}$$

$$R^2 = \frac{(\sigma_\mathrm{m}/A_\mathrm{c})^2}{S^2}$$

where

$$S^2 = (\sigma_T/T_\mathrm{c})^2 + (\sigma_A/A_\mathrm{c})^2$$

Figure F.5 — Normalized sample size curves for a risk of false alarm of α = 5 % (and selected detection probabilities 100 − β, in percent)