TECHNICAL REPORT

ISO/TR 9494

First edition
1997-12-15

Petroleum liquids — Automatic pipeline sampling — Statistical assessment of performance of automatic samplers determining the water content in hydrocarbon liquids

Produits pétroliers liquides — Échantillonnage automatique en oléoduc — Estimation statistique des performances d'échantillonneurs automatiques pour déterminer la teneur en eau dans les hydrocarbures liquides

Reference number
ISO/TR 9494:1997(E)

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X.400 c=ch; a=400net; p=iso; o=isocs; s=central

Printed in Switzerland

Foreword

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

Tha main task of technical committees is to prepare International Standards, but in exceptional circumstances a technical committee may propose the publication of a Technical Report for one of the following types :

- type 1, when the required support cannot be obtained for the publication of an International Standard, despite repeated efforts;

- type 2, when the subject is still under technical development or where for any other reason there is the future but not immediate possibility of an agreement on an International Standard;

- type 3, when a technical committee has collected data of a different kind from that which is normally published as an International Standard (« state of the art », for example).

Technical Reports of types 1 and 2 are subject to review within three years of publication, to decide whether they can be transformed into International Standards. Technical Reports of type 3 do not necessarily have to be reviewed until the data they provide are considered to be no longer valid or useful.

ISO/TR 9494, which is a Technical Report of type 3, was prepared by Technical Committee ISO/TC 28, *Petroluem products and lubricants*, Subcommittee SC 3, *Static petroleum measurement.*

In publishing this text, the committee was aware that the terminology used in this Technical Report in connection with measurement uncertainty, and the methods used to evaluate and express measurement uncertainty, are not consistent with the *Guide to the Expression of Uncertainty in Measurement.* Neverthless it is believed that it will still serve as a helpful aid to those who have to implement ISO 3171, in particular clause 16.

It is envisaged that at the first revision of this Technical Report the opportunity will be taken to align it with the *Guide to the Expression of Uncertainty in Measurement.*

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Petroleum liquids — Automatic pipeline sampling — Statistical assessment of performance of automatic samplers determining the water content in hydrocarbon liquids

1 Scope

This Technical Report describes a mathematical method for assessing the overall uncertainty of automatic sampling systems for determining the water content in oil being transferred through pipelines.

The model estimates the overall uncertainty (tolerance) by combining statistically the individual systematic and random uncertainties of a number of individual component variables defined in an automatic 'grab' type sampling system.

The tolerances on water content determination as a function of the number of sampling grabs, the water content, and the number of water analyses performed are summarized in graphics form (see figures 6-11).

It serves as technical support for clause 16 of ISO 3171.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this Technical Report. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this Technical Report are encouraged to investigate the possibility of applying the most recent editions of the standards listed below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 3171: 1988 Petroleum liquid - Automatic pipeline sampling

RENYI. Calculation of probabilities. Dunod, 1966

3 Definitions of symbols

w, w subscripted	= Water content in the pipeline, in percent volume/volume (v/v)
P_i, q_i, S', w', w''	= Water content in the various parts of the sampler and of the analysis
T_j, T;	= Estimates of water content
V, V_i	= Volume of fluid passing through the system in the interval between two consecutive grabs

v_i = Total volume of fluid passing through the straight section from the beginning of sampling up to t_i

W = Total volume of fluid passing through the straight section

e_i = Volume of grab

D = Combined uncertainty of the random uncertainties and systematic uncertainties in "w" - half-width of a symmetrical bilateral confidence interval (with a 95 % confidence level)

n = Number of analyses

N = Number of grabs

S, R, L and P = Derived parameters

$a_s b_s$----g_s = Relative systematic uncertainty on the factors influencing the measurement "w"

$a_r b_r$----g_r = Relative random uncertainty on the factors influencing the measurement "w"

NOTE - The relative uncertainty on x is = $\dfrac{Uncertainty\ of\ x}{value\ of\ x}$

Where the relative systematic uncertainties and the relative random uncertainties are the following:

- Degree of non-homogeneity of water content, as described in clause 5 and annex A of ISO 3171: 1988 (e.g. poor dispersion)

  a_s relative systematic uncertainty

  a_r relative random uncertainty

- Distortion of the water content by the sampling system as described in clause 8 of ISO 3171: 1988 (e.g. non-isokinetic)

  b_s relative systematic uncertainty

  b_r relative random uncertainty

- Uncertainties on the volume of each grap

d_s relative systematic uncertainty (not used but see clause 9)

d_r relative random uncertainty

- Flowmeter (degree of non-proportionality), as described in clause 10 of ISO 3171: 1988 (e.g. variations in the k-factor of correction of the turbine meter)

c_s relative systematic uncertainty (not used but see clause 9)

c_r relative random uncertainty

- Distortion of water content during sampling, as described in clause 11 of ISO 3171: 1988 (e.g. by emulsification or evaporation)

h_s relative systematic uncertainty

h_r relative random uncertainty

- Distortion of water content due to sample handling and mixing, as described in clause 12 of ISO 3171: 1988 (e.g. poor homogenization in the laboratory)

f_s relative systematic uncertainty

f_r relative random uncertainty

- Distortion of water content due to transfer to laboratory glassware and analysis (e.g. tube graduation error)

g_s relative systematic uncertainty

g_r relative random uncertainty

The derived parameters are obtained from the following equations:

Sampling

$$S = a_s + b_s + h_s$$ (relative systematic uncertainty)

$$R = \frac{1}{4}(a_r^2 + b_r^2 + c_r^2 + d_r^2)$$ (relative random uncertainty)

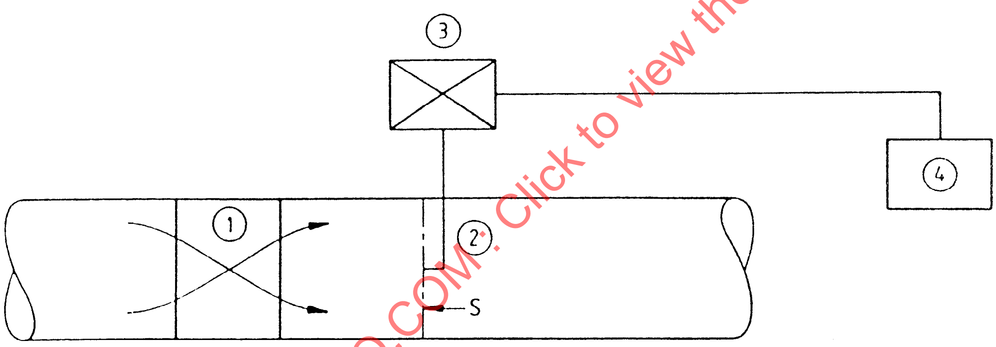
Laboratory

$$L = f_s + g_s$$ (relative systematic uncertainty)

$$P = \frac{1}{4}(f_r^2 + \frac{g^2}{n})$$ (relative random uncertainty)

4 General

The water content w of volume W fluid flowing in a pipeline is estimated by taking N samples (grabs) automatically from a section of the pipeline as illustrated in figure 1.



1- Mixer
2- Probe
3- Sampling system
4- Container (R_1)

Figure 1 - Sampling system

The probe of the sampling system is located in a section downstream from the mixer. The sampling moments are controlled by a flowmeter so that the volume of fluid passing through the section between two sampling operations is equal to V, i.e. sampling is proportional to flow.

The N samples (grabs) are collected in the same container (R_1).

The volume, v, of the fluid passing through the section is taken as a variable and w(v), the water content in the section in question, is noted.

In view of the random effects on the flowmeter, the N samples are separated by intervals of fluid volume V_i with i = 1 to N - 1 (as shown in figure 2).

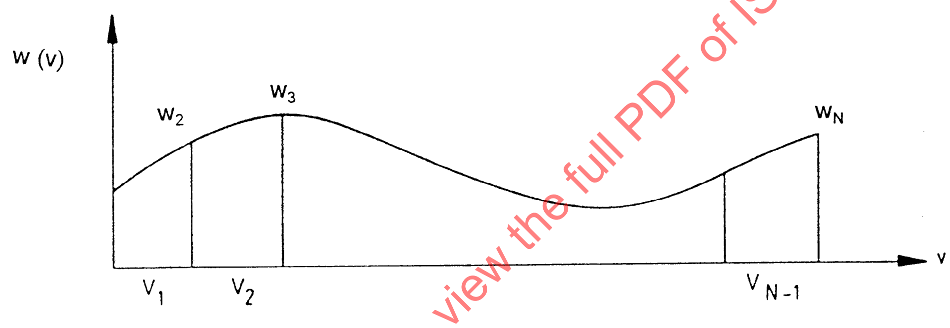


Figure 2 - Grab sequences

Thus:

$$W = \sum_{i=1}^{N-1} V_i \qquad (1)$$

taking

$$v_0 = 0 \text{ and for } i \geq 1,\ v_i = \sum_{j=1}^{i} V_j$$

$$w_i = w(v_{i=1}) \text{ for } i = 1 \text{ to } N$$

At each sampling interval sample (grab) of volume e_i is taken. Taking into account the defects of the mixer, the water content at the sampling point (probe) at this grab is P_i.

The sampling system (with or without loop) leads to the sample not being truly representative. The water content of the material in the container is therefore not fully representative of the sample material which enters the container. The water content in the ith sample when it falls into the container (R_1) is designated q; and the water content into container (R_1) is designated w^1.

During sampling, retention of the collected volume is not perfect. The water content of the container is therefore distorted. The water content in the container (R_1) at the end of sampling is designated w^1.

The contents of (R_1) are mixed and a volume is sampled and transferred into an intermediate container (R_2).

The contents of (R_2) are mixed and n sub-samples are taken and analyzed.

A note is made of S' as the water content in (R_2), S_j as the water content in the jth sub-sample and T_j as the result of the jth analysis with j = 1 to n.

The quantity

$$T' = \frac{1}{n} \sum_{j=1}^{n} T_j \qquad (2)$$

is taken as the estimation of the water content w of the consignment.

An order of magnitude, D, for the standard deviation between T' and w as a function of N, n and various statistical parameters is allowed, i.e. a number such that:

$$Prob\ [\ |\ T' - w\ |\ < D\ ]\ \geq 0{,}95 \qquad (3)$$

The interval [T' - D, T' + D] constitutes a 95 % confidence interval

5 Statistical models

5.1 General conventions

P is taken as the true value of a physical magnitude that is to be measured by a certain method.

a) The systematic error or systematic uncertainty, S_1, represents the difference between the true value, P, and the mean of measurements, S_o, has a probability at least equal to or less than

$$S_1 = S_o - P \tag{4}$$

S_1 permits the **accuracy of the measurements to be measured**.

S_s is used to denote the absolute value of the systematic error and is sometimes referred to as the systematic deviation.

NOTE 1 - S_1 is often unknown in sign and magnitude. An upper bound of the absolute value of S_1 is therefore taken for S_s.

b) The random uncertainty, S_r, represents a number such that the absolute value of the deviation between a measurement, S', and the mean of the measurements, S_o, has a probability at least equal to or less than S_r, i.e.

$$Prob\ [\ |S' - S_o| \le S_r\ ] \ge a \tag{5}$$

If "a" is not specified, assume that it is 95 %, the value which is used below. S_r permits the **precision of the measurements to be measured**.

NOTE 2 - The characteristics of a measurement system can be defined by the repeatability, standard deviation or variance. These magnitudes are linked to the random uncertainty by the following equations.

repeatability = $\sqrt{2}$ x random uncertainty

random uncertainty = 2 x standard deviation

random uncertainty = 2 x $\sqrt{variance}$

The variance, S_3, is noted and the random uncertainty is therefore given by the following equation.

$$S_r = 2 \sqrt{S_3} \qquad (6)$$

A note is made of S_5, the number such that the deviation between a measurement, S', and the true value, P, has a probability of at least 95 % of being less than S_5, i.e.

$$Prob\ [\ |\ S' - P\ | < S_5\ ] \geq 0{,}95 \qquad (7)$$

Although S_5 has no standard designation, it is hereinafter referred to as the uncertainty on P. Thus

$$S_5 = |\ S_1\ | + 2\sqrt{S_3} \leq S_s + S_r = S_s + 2\sqrt{S_3} \qquad (8)$$

With S' denoting a random measurement of the physical magnitude P, the notation used for the following calculation of probability is as follows.

E (S') = S_o = mean of S'

var (S') = S_3 = variance of S'

It is often convenient to write S' in the form

$$S' = S_o + S_2 = P + S_1 + S_2 \qquad (9)$$

where S_2 represents the random uncertainty. Thus

$$E(S') = S_o;\ E(S_2) = 0;\ var(S') = var\ (S_2) = S_3$$

For many physical phenomena, the mean, S_o, and the random uncertainty, S_r, are proportional to the value of the physical magnitude P, i.e. it can be written

$$E\ (S') = P \times s_o;\ S_r = P \times s_r \qquad (10)$$

s_o and s_r are called the relative mean of the measurements and the relative random uncertainty.

Similarly, the relative systematic uncertainty can be defined by the equation $s_l = s_o - 1$

Thus:

$$S_l = P \times s_l \text{ and} \tag{11}$$

a) The absolute value for the relative systematic uncertainty

$$s_s = | s_l | \tag{12}$$

b) The relative variance $s_3 = s_r^2/4$ (13)

c) The relative tolerance s_5 which is such that

$$Prob \left[\left| \frac{S' - P}{P} \right| < s_5 \right] \geq 95 \ \% \tag{14}$$

Thus

$$s_5 = | s_1 | + 2\sqrt{s_3} \leq s_s + s_r = s_s + 2\sqrt{s_3} \tag{15}$$

NOTE 3 - The term 'relative' is not standard. However, these are the values often supplied in the technical specifications for equipment (e.g. flowmeter).

With S' denoting a random measurement of the physical magnitude P, S' may be expressed in the form

$$S' = P (1 + s_l + s_2) \tag{16}$$

with

$$E (S') = P (1+s_l); \ E (s_2) = 0; \ \text{var } S' = P^2 \text{ var } s_2 = P^2 \times s_3 \tag{17}$$

s_2 is referred to as the centred relative measurement uncertainty.

In view of the experimental results obtained, all the random measurements appearing in the remainder of this study are linked to their true value by an equation similar to equation (16).

If a letter (a, b, c, etc.) is chosen to represent a random effect on measurement, the indices 0, 1, 2, 3, r, 5 and s are used systematically to denote the relative mean for the measurements, the relative systematic uncertainty, the centred relative measurement uncertainty, the relative variance, the relative random uncertainty, the relative tolerance and the relative systematic deviation, respectively.

5.2 Parameters having an effect on obtaining the sample

Taking the above conventions, the following may be written using the notation from clause 4:

a) that for i = 1 to N

$$P_i = w_i (1 + a_1 + a_{2i}) \tag{18}$$

(non-homogeneity)

where

a_l is the relative systematic uncertainty and

E $(a_{2i} = 0$; var $a_{2i} = a_3$ = relative variance.

b) that for i = 1 to N

$$q_i = P_i (1 + b_1 + b_{2i}) \tag{19}$$

(distortion due to the sampling system)

where

b_1 is the relative systematic uncertainty and

E $(b_{2i} = 0$; var $b_{2i} = b_3$ = relative variance.

c) that for i = 1 to N - 1

$$V_i = V (1 + c_{1i} + c_{21}) \tag{20}$$

(flowmeter fault)

where

c_{1i} is the relative systematic uncertainty depending on the rate of operation of the flowmeter and thus dependent on i and

$E(c_{2i}) = 0$; var $c_{2i} = c_3$ = relative variance.

d) that for i = 1 to N

$$e_i = e\,(1 + d_{1i} + d_{2i}) \qquad (21)$$

(fault on the sampling volume)

where

d_{1i} is the relative systematic uncertainty depending on the velocity of the fluid and thus on i and

$E(d_{2i}) = 0$; var $d_{2i} = d_3$ = relative variance.

e) that for the container (R_1)

$$w'' = w'\,(1 + h_1 + h_2) \qquad (22)$$

(distortion due to storage in (R_1) during sampling)

where

h_s is the relative systematic uncertainty and

$E(h_2) = 0$; var $h_2 = h_3$ = relative variance.

5.3 Parameters having an effect on the analysis of the sample

Taking the above conventions, the following may be written

a) that

$$S' = w''\,(1 + f_1 + f_2) \qquad (23)$$

(transfer error)

where

f_1 is the relative systematic uncertainty and

$E(f_2) = 0$; var $f_2 = f_3$ = relative variance.

b) that for j = 1 to n

$$T_j = S' (1 + g_1 + g_{2j}) = w'' (1 + f_1 + f_2) (1 + g_1 + g_{2j}) \quad (24)$$

(fault in transfer to laboratory glassware + analysis fault)

where

g_1 is the relative systematic uncertainty and

$E(g_{2j}) = 0$; var $g_{2j} = g_3$ = relative variance.

5.4 Statistical hypotheses

Any links existing between the various relative systematic uncertainties and centred relative measurement uncertainties are now considered.

It is evident that the analysis is independent of the method of obtaining the sample contained in (R_1) and that by construction, within the analysis the variables f_2 and g_{2j} are independent of each other and that the relative systematic uncertainties, f_1 and g_1, are independent of the number j of the analysis.

For a given crude, the relative systematic uncertainties, a_1, b_1, c_{1i} and d_{1i}, and the centred relative measurement uncertainties, a_{2i}, b_{2i}, c_{2i} and d_{2i}, are only linked to each other through the flow rate of fluid in the main pipeline and, if applicable, in the sampling system loop.

With regard to relative centred measurement uncertainties, the flow rate of the fluid has barely any influence except on uncertainty, a_{2i}, due to the mixer. It can therefore be assumed that the relative centred measurement uncertainties are statistically independent and that the variances of b_{2i}, c_{2i} and d_{2i} do not depend on the index i. With the mixer standard ensuring that the relative variance of this apparatus is bounded from above by a fixed number, it is possible, by replacing var a_{2i} by this number, to assume also that a_{2i} has a variance independent of i.

If the relative systematic uncertainty of the mixer, a_1, depends on the flow rate of the fluid, it is replaced by a fixed upper bound independent of the index i.

Assuming that b_1 does not depend on the flow rate of the fluid, even if an upper bound of $|b_1|$ is used, the relative systematic uncertainty of the volume sampled, d_1, depends on the flow rate of the fluid and therefore on the index i.

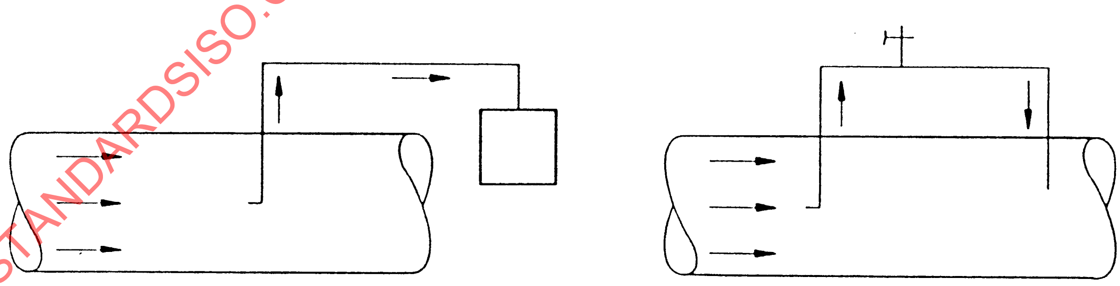
Also, the various studies on flowmeters show that the relative systematic uncertainty, c_{1i}, depends heavily on the flow rate for the fluid and therefore on the index i.

For all these reasons, it can be assumed:

a) that all the relative systematic uncertainties except those of the flowmeter and of the volume of each sample are independent of the number, i, of the sample or of the number, j, of the analysis;

b) that the variables a_{2i}, b_{2i}, c_{2i}, d_{2i}, f_2, g_{2j}, and h_2 are independent of each other and have variances independent of the indices i and j.

NOTE - The sampling systems are either direct (see figure 3) or have a circulation loop. The direct system has the disadvantage that for a long sample tube (3 m to 5 m), more than 100 samples remain in the tube, which for samples of size 2000 to 5000 represents a not inconsiderable bias. The same is not true for a sampling system with a circulation loop.



(a) Direct (b) With loop

Figure 3 - Sampling system

With V_i being random, N is arbitary.

There are two possible cases as follows:

a) The complete sampling system is installed and its characteristics are known. Then, using the formulae from 12.2 or the graphs, the mean number, N_o, of samples is determined, taking into account the desired accuracy on w. Having completed the sampling, the number of samples, N, actually taken is known. Then with N fixed and using the formulae from 12.2 or the graphs the exact accuracy obtained is determined;

b) The sampling system has yet to be installed.

For N > 1000, N may be replaced by its mean value, knowing that an error is introduced which is at most of the order of $\sqrt{\frac{1}{N}}$.

6 Study of the estimator T' of the water content of the consignment

To determine the tolerance on the estimation of w by T, i.e. a number D such that

$$\text{Prob}\{|T' - w| < D\} \geq 95\ \% \qquad (25)$$

The following procedure is followed.

Applying the Gaussian approximation gives the equation

$$D = |E(T') - w| + 2\sqrt{\text{var}\ T'} \qquad (26)$$

In view of the statistical hypotheses made, this gives

$$T' = \frac{1}{n}\sum_{j=1}^{n} T_j = w'(1 + f_1 + f_2)(1 + h_1 + h_2)\bar{R} \qquad (27)$$

with

$$R_j = (1 + g_1 + g_{2j})\ \text{and}\ \bar{R} = \frac{1}{n}\sum_{j} R_j \qquad (28)$$

hence:

$$E(T') = E(w')(1 + h_1)(1 + f_1) E(\bar{R}) \qquad (29)$$

and

$$var\ T' = (var\ w' + E(w')^2)(var\ \bar{R}.L_3 + L_1^2\ var\ \bar{R} + L_3 E(\bar{R})^2)$$
$$+ E(\bar{R})^2.L_1^2.\ var\ w' \qquad (30)$$

with:

$$L_1 = (1 + h_1)(1 + f_1);\ L_3 = h_3 f_3 + (1 + f_1)^2 h_3 + (1 + h_1)^2 f_3 \qquad (31)$$

It is necessary to determine the means and variances of w' and $\bar{R}$ as a function of the various systematic and random uncertainties of the sampling and analysis sequence.

7 Distortion due to analysis sequence

7.1 Determination of the mean and variance

The mean and variance are determined using the following equations:

$$E(\bar{R}) = E(R_j) = 1 + g_1 \qquad (32)$$

$$var\ \bar{R} = \frac{1}{n} var\ R_j = \frac{1}{n} g_3 \qquad (33)$$

7.2 Examples

To see how the uncertainties due to the analysis and the number n of analyses affect the tolerance D of the estimation of w, it will be assumed that w" perfectly estimates w, i.e. that w" = w (which implies $h_1 = h_3 = 0$).

For the relative systematic uncertainties, relative random uncertainties and relative variances, the following normal values are taken:

$f_1 = 0{,}5\ \%$; $f_r = 1\ \%$; $f_3 = 0{,}25.10^{-4}$

$g_1 = 0{,}5\ \%$; $g_r = 8\ \%$; $g_3 = 16.10^{-4}$

The results are given in table 1.

Table 1 - Results

w	1 %		2 %	
n	1	2	1	2
$\mid E(T') - w \mid$	10^{-4}	10^{-4}	2×10^{-4}	2×10^{-4}
var T'	16×10^{-8}	8×10^{-8}	64×10^{-8}	32×10^{-8}
D	$0{,}9 \times 10^{-3}$	$0{,}64 \times 10^{-3}$	$1{,}8 \times 10^{-3}$	$1{,}28 \times 10^{-3}$

NOTE - It is desirable to carry out at least two analyses.

8 Distortion due to samples

The mean and the variance of w' are determined from the following equation:

$$E = \sum_{i=1}^{N} e_i \tag{34}$$

thus:

$$w' = \sum_{i=1}^{N} \frac{e_i}{E} q_i \tag{35}$$

and:

$$w - w' = \frac{1}{w} \int_0^w w(v)\, dv - w' = \{\frac{1}{w} \int_0^w w(v)\, dv - \sum_{i=1}^{N-1} \frac{V_i}{w} \frac{w_i + w_{i+1}}{2}\}$$

$$+ \{\sum_{i=1}^{N-1} \frac{V_i}{w} \frac{w_i + w_i+1}{2} - w'\} = A + B \qquad (36)$$

taking:

$$A = \sum_{i=1}^{N-1} \{\frac{1}{w} \int_{v_{i-1}}^{v_i} w\,(v)\, dv - \frac{V_i}{w} \frac{w_i + w_i+1}{2}\} \qquad (37)$$

$$B = \sum_{i=1}^{N-1} \frac{V_i}{w} \frac{w_i + w_{i+1}}{2} - \sum_{i=1}^{N} w_i \frac{e_i}{E} (1 + b_1 + b_{2_i})\,(1 + a_1 + a_{2_i}) \qquad (38)$$

where

A represents the deviation between the Riemann integral and the Riemann sum for the signal w (v) and;

B represents the deviation between the Riemann sum associated with the signal w (v) and the value w'.

Thus:

$$E\,(w') = w - E\,(A) - E\,(B) \qquad (39)$$

and:

$$var\,(w - w') = var\ w' \leq \{\sqrt{var\ A} + \sqrt{var\ B}\}^2 \qquad (40)$$

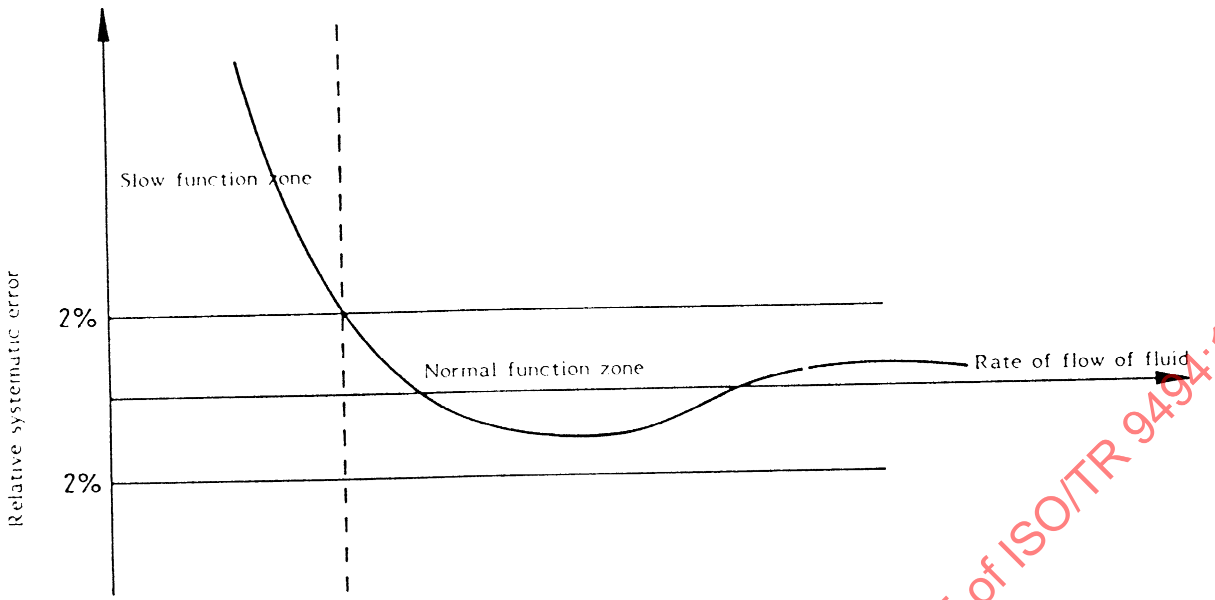


Figure 4 - Relative systematic error function for a flowmeter

Given the behaviour for the relative systematic uncertainty of a flowmeter as a function of the flow rate of the fluid (see figure 4), the following distinctions can be made:

- a 'normal' rate of operation

  |relative systematic uncertainty| < threshold (rapid flow rate)

- a 'slow' rate of operation

  |relative systematic uncertainty| < threshold (slow flow rate)

The choice of threshold depends on the type of flowmeter used (high performance: $c_r \simeq 1$ %, average performance: $c_r \simeq 1$ %, technical metering: $c_r \simeq 5$ %), this being selected according to the desired tolerance. Generally, high performance flowmeters or ultrasonic flowmeters are used for tolerances of less than 2 % and technical metering is used for tolerances of greater than 2 %.

A note is made of I_1, the collected samples taken at normal rate for the flowmeter, and of I_2, the collected samples taken at slow rate.

9 Supplementary studies

9.1 Uncertainty on the flowmeter

The total volume of fluid passing through the straight section, W, is given by the equation

$$W = \sum_i V (1 + c_{1o} + c_{2i})$$

hence:

$$W = E(W) = \sum_i V (1 + c_{1i}) \qquad (41)$$

Statistically, w_i and V_i are independent (level of w_i independent of the uncertainties on V_i).

Thus, in view of the size of N:

$$\sum_i \frac{w_i V_i}{N} = E\{\frac{\sum w_i}{N}\} . E\{\frac{\sum V_i}{N}\}(1 + \frac{Z(N)}{\sqrt{N}}) = \frac{\sum w_i}{N} \times \frac{W}{N} (1 + \frac{Z'(N)}{\sqrt{N}}) \qquad (42)$$

Where Z (N) and Z' (N) are two numbers bounded by a fixed number (see Renyi. Calculation of probabilities Dunod 1966).

Take:

$$\sum_i w_i V_i = (\sum_i w_i)\frac{W}{N} (1 + \frac{Z'(N)}{\sqrt{N}}) \qquad (43)$$

This gives:

$$p_1 = \frac{card\ I_1}{N} = \text{proportion of samples at normal rate}$$

$$p_2 = \frac{card\ I_2}{N} = \text{proportion of samples at slow rate}$$

take:

δ_1 as being mean for the relative systematic uncertainties at normal rate

$$+ \frac{1}{card\ I_1} \sum_{i\ \varepsilon\ I_1} c_{1_i} = \frac{1}{Np1} \sum_{i\ \varepsilon\ I\ 1} c_{1_i} \qquad (44a)$$

δ_2 as being = mean for the relative systematic uncertainties at slow rate

$$+ \frac{1}{card\ I_2} \sum_{i\ \varepsilon\ I_2} c_{1_i} = \frac{1}{Np2} \sum_{i\ \varepsilon\ I\ 2} c_{1_i} \qquad (44b)$$

again take:

$$\delta_3 = p_1\ \delta_1 + p_2\ \delta_2 \qquad (45)$$

then:

$$\sum_i c_{1i} = N\ \delta_3 \qquad (46)$$

and:

$$W = (VN\ (1 + \delta_3) \qquad (47)$$

NOTE - In practice, δ_1 and δ_3 are unknown, but an upper bound δ'_1 of $|\delta_1|$ and an upper bound δ'_2 of $|\delta_2|$ are known.

$|\delta_3|$ is thus derived from above by:

$$\delta'_3 = p_1\, \delta'_1 + p_2\, \delta'_2$$

(The value for the threshold is always an upper bound of $|\delta_i|$).

For example if $p_1 > 90$ % with $\delta'_1 = 2$ % and $p_2 < 10$ % with $\delta'_2 = 10$ %, this results in

$$|\delta_3| \leq 2{,}8\ \%$$

9.2 Uncertainties on the grab

Take:

$$E_i = e_i/E$$

thus:

$$\sum_i E_i = 1$$

and

$$E_i = \frac{1}{N} \cdot \frac{1 + d_{1_i} + d_{2_i}}{1 + \bar{d} + \bar{d}_2} \sim \frac{1}{N}(1 + d_{1_i} - \bar{d} + d_{2_i} - \bar{d}_2) \qquad (48)$$

with:

$$\bar{d} = \frac{1}{N}\sum_i d_{1_i} \ and\ \bar{d}_2 = \frac{1}{N}\sum_i d_{2_i}$$

hence:

$$E\ (E_i) \simeq \frac{1}{N} \ and\ var\ E_i \simeq \frac{1}{N^2}\ var\ (d_{2_i} - \bar{d}_2) \simeq \frac{d_3}{N^2} \qquad (49)$$

It can be shown, as above, by assuming that the uncertainties on e_i are independent of the level of w_i and in view of the size of N, that

$$\sum_i \frac{w_i E_i}{N} = E(\frac{\sum w_i}{N})\ E(\frac{\sum E_i}{N})\ (1 + \frac{Z(N)}{\sqrt{N}}) = \sum_i \frac{w_i}{N}\ (1 + \frac{Z'(N)}{\sqrt{N}}) \qquad (50)$$

and

$$\sum = \frac{w_i E_i}{N} = (\frac{\sum w_i E_i}{N})\ (1 + \frac{Z''(N)}{\sqrt{N}}) \qquad (51)$$

where Z (N), Z'(N) and Z" (N) are absolute values bounded from above by a fixed number (the inter-relationship between the variables E_i does not alter the result).

10 Distortion due to the instants in time when samples are taken

A direct upper-bounding $\int_a^{a+u} w(v)\,dv - u\ \frac{w(a) + w(a+u)}{2}$ is too severe.

The difference Y (a) - Z (a) is randomised with

$$Y(a) = \int_a^{a+u} w(v)\,dv \text{ and } Z(a) = u\ \frac{w(a) + w(a+u)}{2} \qquad (52)$$

assuming that a varies uniformly on {0, W-u}. This gives

$$E(Z(a)) = uw \qquad (53)$$

and

$$E\ \{Y(a)\} = \frac{1}{w}\ \int_0^{W-u} (\int_a^{a+u} w(v)\,dv)\,da = uw + \rho\frac{u^2}{W} \text{ with } \rho \varepsilon \{0,1\} \qquad (54)$$

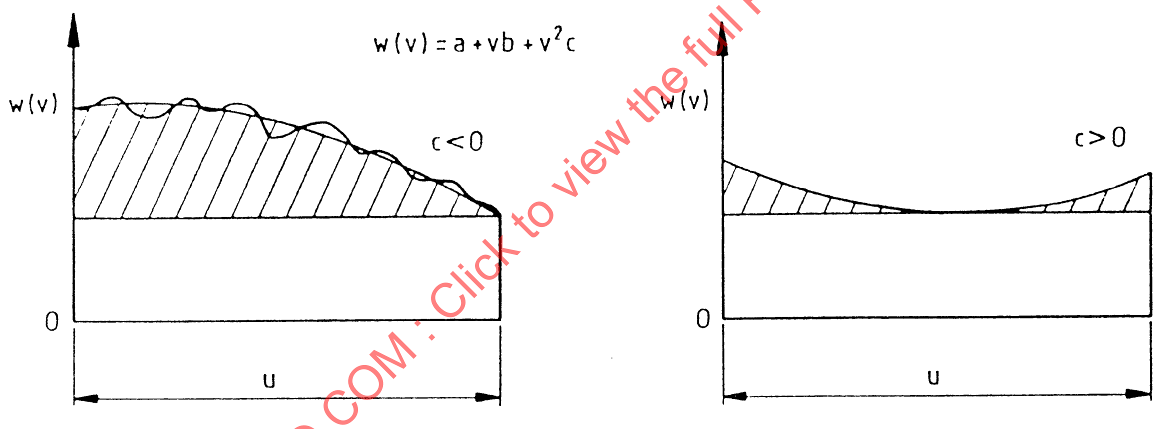
Similarly:

$$E\{(Y(a) - Z(a))^2\} = \frac{1}{W} \int_0^{W-u} \left(\int_a^{a+u} w(v)\,dv - u\,\frac{w(a) + w(a+u)}{2} \right)^2 da$$

$$< \frac{1}{W} \int_0^{W} \left(\frac{u^3}{12} w''(\tau_a) \right)^2 da \approx \frac{u^6}{144.W} \int_0^{W} w''^2 (v)\,dv \qquad (55)$$

where w'' (v) represents the second derivative of w (v).

To calculate w'', the second derivative of the smoothed signal, w(v), has to be taken. In view of the general size of u's with regard to the oscillation of w(v), it can be assumed that the smoothing of w(v) is on the parabolic type segment u.



a) b)

variation = shaded area

Figure 5 - Illustration of variation

$\frac{1}{W} \int_0^{W} w''^2 (v)\,dv$ represents the mean value of w''^2 on {0, W}.

As the mean w" on {0, W} is zero, w''^2 can be replaced by the square of w*, which has a value such that 60 % of the |w"| are less than w* using Gaussian approximation.

It can be assumed that for at least 60 % of the segments:

$$|w''| < \frac{0,2}{u^2} \tag{56}$$

Otherwise, this means that for the remaining segments, the sum of the variations in water content (see figure 5) represent at least 0,33 % (V/V) of the total quantity W of fluid to be transported (without taking into account the white areas in figure 5), which is hard to reconcile with a water content w of the order of 1 % (V/V) to 2 % (V/V).

This therefore gives:

$$E\,\{(Y(a) - Z(a))^2\} \leq \frac{u^2}{0,7.10^4} \tag{57}$$

Take:

$\tau_i = Y(v_i) - Z(v_i)$ with $u = V_i + 1$

This gives:

$$A = \frac{1}{W} \sum_{i=o}^{N-2} \tau_i \tag{58}$$

and:

$$|E(A)| \leq \frac{1}{W} \Sigma |E(\tau_i)| = \frac{1}{W_2} \sum_i E(V^2{}_{i+1}) = \frac{V^2}{W^2} \sum_i \{(1 + c_{1_1})^2 + c_3\}$$

$$= \frac{1}{N^2(1 + \delta_3)^2} \{N(1 + 2\delta_3) + Nc_3\} = \frac{1}{N}(1 + c_3) \tag{59}$$

NOTE - The term in 2 δ 3 disappears. The terms in δ_3 have been disregarded, which presupposes that $|\delta_3|$ is sufficiently small as a function of the quality of the flowmeter (see formulae (67) and (67a)).

N - 1 has been replaced by N, which, in view of the size of N, introduces a negligible error.

As $\sum_i \tau_i \approx 0$, it can be assumed that τ_i are negatively correlated, hence

$$\text{var A} \leq \frac{1}{W^2} \sum_i var\tau_i \leq \frac{1}{W^2} \sum_i E(\tau_1^2) \leq \frac{1}{0{,}7\times10^4 W^2} \sum_i E(V_i^2 + 1)$$

$$= \frac{V^2}{W^2\ x\ 0{,}7\times10^4} \sum_i \{(1 + c_{1_i})^2 + c_3\} \approx \frac{1 + c_3}{0{,}7\times10^4 . N} \qquad (60)$$

11 Distortion due to the sampling system

In view of the results obtained in clause 9 and of the independence of variables V_i, a_{2_i}, b_{2_i} and e_i,

$$E\ (B) = \sum_i \frac{w_i}{N} \left(+ \frac{Z_1(N)}{\sqrt{N}}\right) - (+ a_1)(1 + b_1) \sum_i E(w_i E_i)$$

$$\approx \sum_i \frac{w_i}{N} + (1 + a_1)(1 + b_1) \sum_i \frac{w_i}{N} \left(1 + \frac{Z_2(N)}{\sqrt{N}}\right) \approx -w(a_1 + b_1) \qquad (61)$$

where Z_1 (N) and Z_2 (N) are absolute values bounded from above by a fixed number.

Thus:

$$Y = var\ (\sum_i w_i E_i (1 + b_1 + b_{2_i})\ (1 + a_1 + a_{2_i})$$

$$= E\ [(1 + b_1 + b_{2_i})\ 1 + a_1 + a_{2_i})]^2\ var\ (\sum_i w_i E_i)$$

$$+ \sum_i w_i^2\ E\ (E_i^2)\ var\ (1 + b_1 + b_{2i})\ (1 + a_1 + a_{2i}))$$

$$= (1 + b_1)^2 (1 + a_1)^2 \, var \, (\sum_i w_i E_i) + \sum_i w_i^2 E \, (E_i^2) p \tag{62}$$

With:

$$p = a_3 b_3 + (1 + b_1)^2 a_3 + (1 + a_1)^2 b_3 \tag{63}$$

$As \sum_i E_i = 1$, the variables E_i are negatively correlated, hence

$$Y < (1 + b_1)^2 (1 + a_1)^2 \sum_i w_i^2 \, varE_i + (p \sum_i w_i^2)(var \, E_i + E(E_i)^2)$$

$$< \{d_3(p + (1 + a_1)^2 (1 + b_1)^2) + p\} \sum_i \frac{w_i^2}{N^2} = \tau \sum_i \frac{w_i^2}{N^2} \tag{64}$$

With:

$$\tau = d_3 \, (p + (1 + a_1)^2 (1 + b_1)^2) + p \tag{65}$$

From this is deduced:

$$\text{var B} \leq \frac{V_2}{W^2} c_3 \sum \frac{w_i + w_i + 1}{4} + \sum_i \frac{w_i^2}{N^2}$$

$$\leq \sum \frac{w_i^2}{N^2} x \{ \frac{c_3}{(1 + \delta_3)^2} + \tau \} < \frac{W}{N} \{ \frac{c_3}{(1 + \delta_3)^2} + \tau \} \tag{66}$$

12 Calculation of the tolerance D on the estimation of water content T'

Gathering together the above results, the tolerance D can now be expressed as a function of the various parameters considered.

12.1 Input data

The relative systematic uncertainties are generally unknown, the standards and tables generally supplying the relative systematic deviations. Similarly, the relative random uncertainties rather than the variances are referred to.

For example, take:

Size of sample : N

Number of analyses : n

For the flowmeter : proportion of the number of samples at normal rate, ρ_1 and

proportion of the number of samples at slow rate, ρ_2

where

ρ_1 is the proportion of W transported at normal rate

ρ_2 is the proportion of W transported at slow rate

Table 2 - Relative systematic uncertainties and relative random uncertainties

	Relative systematic deviation	Relative random uncertainty
- Degree of non-homogeneity of the water content in the section (S)	a_s	a_r
- Distortion of the water content by the sampling system	b_s	b_r
- Uncertainties on the volume of each sample	d_s	d_r
- Distortion due to storage (R_1) during sampling	h_s	h_r
- Distortion of the water content during transfer into (R_2)	f_s	f_r
- Uncertainties on the determination of the water content due to transfer into laboratory glassware and to the analysis	g_s	g_r
- Flowmeter: normal rate	δ'_1	} c_r
slow rate	δ'_2	

12.2 General formulae

Calculate:

$$a_3 = (\frac{a_r}{2})^2;\ b_3 = (\frac{b_r}{2})^2;\ d_3 = (\frac{d_r}{2})^2;\ c_3 = (\frac{c_r}{2})^2;\ f_3 = (\frac{f_r}{2})^2;$$

$$g_3 = (\frac{g_r}{2})^2;\ h_3 = (\frac{h_r}{2})^2$$

and:

$$\delta'_3 = \rho_1\ \delta'_1 + \rho_2\ \delta'_2$$

With a high or medium performance flowmeter,

$$0'_3 < 5.10^{-2} \qquad (67a)$$

is required.

With technical metering,

$$\delta'_3 < 0,1 \qquad (67b)$$

is required.

If δ'_3 cannot be calculated because the order of magnitude of δ'_1 and δ'_2 is unknown, δ'_3 can be approximated by taking the absolute value of the mean value of the relative systematic uncertainty function (see figure 2) over the range of fluid flow rates used.

Then calculate:

$$A_1 = (1 + f_s)(1 + h_s)$$

$$B_1 = h_3 f_3 + (1 + f_s)^2 h_3 + (1 + h_s)^2 f_3$$

$$A_2 = A_1 \times (1 + g_s)$$

$$B_2 = \frac{g_3}{n} B_1 + (A_1^2) + B_1(+ + g_s)^2$$

$$F_1 = a_3b_3 + (1 + b_s)^2a_3 + (1 + a_s)^2b_3$$

$$F_2 = F_3d_3 + d_3 (1 + a_s)^2 (1 + b_s)^2 + F_1$$

$$A_3 = \frac{1}{N} (1 + c_3)$$

$$B_3 = \frac{1 + c_3}{0{,}7.10^4 N}$$

$$A_4 = w(a_s + b_s)$$

$$B_4 = \frac{W}{N} (F_2 + \frac{c_3}{(1 + \delta_3)^2})$$

$$A_5 = A_2 (A_3 + A_4) + w(A_2 - 1)$$

$$B_5 = (A_2^2 + B_2)(\sqrt{B_3} + \sqrt{B_4})^2 + (w + A_3 + A_4)^2 B_2$$

and $D = A_5 + 2 \sqrt{B_5}$

NOTE - If w is unknown and T has been calculated, w is replaced by T in the above formulae.

12.3 Approximate formulae

Taking into account the orders of magnitude of the systematic uncertainties and repeatabilities,

$$A_5 \simeq \frac{1}{N} + w(a_s + b_s + g_s + f_s + h_s) \tag{68}$$

$$B_s \simeq \frac{1}{N} \{\sqrt{\frac{1}{0{,}7.10^4}} + \sqrt{w} (a_3 + b_3 + c_3 + d_3)\}^2 + w^2 (h_3 + f_3 + \frac{g_3}{n}) \tag{69}$$

and:

$$D = A_5 + 2 \sqrt{B_5}$$

12.4 Numerical test

As an example, the following set of values has been taken:

Mixer	a_s = 1 % (0,01); a_r = 5 % (0,05)
Sampling system	b_s = 1 % (0,01); b_r = 2 % (0,02)
Uncertainties on sampled volume	d_s = 10 % (0,10); d_r = 10 % (0,10)
Storage in (R_1)	h_s = 1 % (0,01); h_r = 1 % (0,01)
Sub-sampling for (R_2)	f_s = 0.5 % (0,005); f_r = 1 % (0,01)
Sub-sampling for analysis and uncertainties on an analysis	g_s = 0.5 % (0,05); g_g = 8 % (0,08)
Flowmeter	c_r = 2 % (0,02)

This gives the tolerance D on water content as detailed in table 3.

Table 3 - Tolerance D on water content

↓ w	↓ n	2 500	5 000	10 000	20 000	← Values of N
0.5 %	1	0,14 %	0,10 %	0,08 %	0,07 %	Values of D
	2	0,13 %	0,09 %	0,07 %	0,06 %	
1 %	1	0,19 %	0,16 %	0,14 %	0,13 %	
	2	0,17 %	0,14 %	0,12 %	0,11 %	
2 %	1	0,30 %	0,27 %	0,26 %	0,25 %	
	2	0,26 %	0,23 %	0,21 %	0,21 %	

Conclusion

The following conclusions may be drawn from the formulae and tables:

a) It should be verified, with the aid of formulae (67) or (67a), that the pumping conditions are compatible with the relative systematic uncertainty function of the flowmeter.

For example:

If at least 80 % (by volume) of the fluid is transported at normal rate with a relative systematic deviation of less than 2 % and if at most 20 % is transported at slow rate with a relative systematic deviation of less than 15 %, then:

$$\delta'_3 = 0,8 \times 0,02 + 0,2 \times 0,15 = 0,046 \text{ (i.e. } 4,6 \text{ \%)}$$

b) In the calculation of D, the part due to the analysis is not insignificant, but this part only decreases proportionally at $1/\sqrt{n}$ which is slow.

For example:

For w = 2 %, N = 20 000 and n = 4,

D = 17,45

against D = 25,0 for n = 1

12.5 Graphs and their uses

12.5.1 The graphs in figures 6 to 11 give the tolerance D with

$$D = D\,(N) = \frac{1}{N} + wS' + 2\{\frac{1}{N}(1,2 \times 10^{-2} + (wR)^{1/2})^2 + w^2 P'\}^{1/2}$$

where

$$S' = a_s + b_s + g_s + f_s + h_s$$