INTERNATIONAL STANDARD 555/II

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Liquid flow measurement in open channels — Dilution methods for measurement of steady flow — Part II : Integration (sudden injection) method

Mesure de débit des liquides dans les canaux découverts — Méthodes de dilution pour le mesurage du débit en régime permanent — Partie II : Méthode par intégration (injection instantanée)

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO Member Bodies). The work of developing International Standards is carried out through ISO Technical Committees. Every Member Body interested in a subject for which a Technical Committee has been set up 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.

Draft International Standards adopted by the Technical Committees are circulated to the Member Bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 555/II (originally ISO/DIS 2638) was drawn up by Technical Committee ISO/TC 113, *Measurement of liquid flow in open channels*, and circulated to the Member Bodies in May 1972.

It has been approved by the Member Bodies of the following countries :

Austria	Ireland	South Africa, Rep. of
Belgium	Japan	Switzerland
Czechoslovakia	Netherlands	Thailand
France	Portugal	U.S.A.
India	Romania	

The Member Body of the following country expressed disapproval of the document on technical grounds :

Sweden

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Liquid flow measurement in open channels — Dilution methods for measurement of steady flow — Part II : Integration (sudden injection) method

1 SCOPE AND FIELD OF APPLICATION

This International Standard deals with the measurement of flow in open channels, under steady flow, by the dilution method using the integration (sudden injection) procedure. This method is applicable to the measurement of the flow in open channels where the degree of turbulence is sufficiently high to ensure efficient mixing of the injected solution throughout the whole flow.

The following clauses describe the principle of the method, the choice of a measuring reach, recommendations relating to the duration of injection and sampling, the operational procedure, the principal tracers used and their analyses, and finally, the calculation of errors inherent in the method.

NOTE — Although this method is mostly used for smaller rivers, in 1970, discharges up to 2 000 m^3/s were measured with confidence using the methods described here and it is anticipated that the measurement of flow rates greater than this will not present insuperable difficulties.

2 REFERENCES

2.1 ISO 555, *Liquid flow measurement in open channels — Dilution methods for measurement of steady flow — [Part I :] Constant rate injection method.*

2.2 ISO 772, *Liquid flow measurement in open channels — Vocabulary and symbols.*

2.3 "A simple method of fitting an asymptotic regression curve." *Biometric Magazine*, Vol. 12, p. 323, September 1956.

3 TERMINOLOGY

For the purposes of this International Standard, the definitions given in ISO 772 apply.

4 UNITS OF MEASUREMENT

The basic units used in this International Standard are : metre, kilogram and second.

5 PRINCIPLE OF THE METHOD

A solution of a suitably selected tracer is injected for a short duration into a cross-section at the entry to the measuring reach of the channel, in which the rate of flow is constant throughout the test period.

At a second cross-section at the downstream end of this reach, far enough from the former for the injected solution to be uniformly diluted throughout this cross-section, samples are taken over a period of time t sufficiently long to ensure that the whole of the tracer has passed the second cross-section.

Since all the tracer injected passes through the sampling cross-section the following equation is obtained :

$$M = Q \int_0^t (C_2 - C_0)\, dt$$

where

M is the mass of the tracer injected;

Q is the volume rate of flow of the stream;

C_2 is the concentration of tracer at the point of sampling during a period of time dt, in kilograms per cubic metre;

C_0 is the concentration of tracer in samples of stream water in its natural state, in kilograms per cubic metre.

This equation implies that the value of the integral

$$\int_0^t (C_2 - C_0)\, dt$$

is the same at each point of the sampling cross-section, and the solution injected can be considered to be well mixed with the stream if this requirement is satisfied.

If V is the volume of solution injected and if C_1 is the concentration of tracer in the solution, then

$$M = C_1 V$$

and

$$C_1 V = Q \int_0^t (C_2 - C_0)\, dt$$

from which

$$Q = V \Big/ \left(\int_0^t \frac{C_2 - C_0}{C_1} \, dt \right) \qquad \ldots (1)$$

The integral of equation (1) can be determined in two different ways :

– either by measuring the concentrations C_0, C_1 and C_2 (see 5.1) independently of each other,

– or by determining the ratio $(C_2 - C_0)/C_1$ by diluting C_1 in known proportions, this being known as the method of comparative dilutions (see 5.2).

5.1 Methods of direct measurement of concentration

5.1.1 *Multiple consecutive samples*

Consecutive samples are taken from a fixed point in the sampling cross-section, the first before the arrival of the tracer and the last after all the injected tracer has passed this point.

The rate of sampling is kept constant during the whole of the sampling period. If m samples are taken during consecutive periods $t_1, t_2, t_3, \ldots, t_r, \ldots, t_m$ and their volumes are respectively $V_1, V_2, V_3, \ldots, V_r, \ldots, V_m$ and their concentrations $C'_1, C'_2, C'_3, \ldots, C'_r, \ldots, C'_m$, it is then possible to determine the mean volume rate of sampling q by the formula :

$$q = \left(\sum_{r=1}^{r=m} V_r \right) \Big/ \left(\sum_{r=1}^{r=m} t_r \right) \qquad \ldots (2)$$

and the dilution ratio N by the formula :

$$N = M \Big/ \left\{ \sum_{r=1}^{r=m} V_r \, (C'_r - C_0) \right\} \qquad \ldots (3)$$

The volume rate of flow Q of the stream is $Q = qN$.

In this method, samples of natural stream water are taken before, during and after the passage of the tracer, upstream of the point of injection.

5.1.2 *Average sample* (single sample)

A single sample is taken at a constant rate q, from a fixed point of the sampling cross-section for a time t, sufficient for the whole of the tracer to have passed this point.

The mass of tracer taken per unit of time is $C_2 q$. The total mass of tracer taken is therefore

$$\int_0^t C_2 q \, dt = q \int_0^t C_2 \, dt \qquad \ldots (4)$$

and if $\overline{C}_2$ is the concentration of the average sample,

$$\overline{C}_2 = \frac{1}{t} \int_0^t C_2 \, dt \qquad \ldots (5)$$

from which

$$\int_0^t (C_2 - C_0) \, dt = (\overline{C}_2 - C_0) \, t \qquad \ldots (6)$$

can be deduced, so that

$$Q = \frac{VC_1}{t \, (\overline{C}_2 - C_0)} \qquad \ldots (7)$$

NOTE – This method may be less suitable than those described in 5.1.1 or even 5.1.3 when the period of passage of the tracer is prolonged.

5.1.3 *Average samples* (successive approximations)

When it is feared that sampling cannot be carried out for a period of time sufficiently long for the solution to pass completely throughout the sampling cross-section, it is advisable to proceed in the following manner :

If t is the estimated period of passage of the tracer throughout the sampling cross-section, n average samples will be taken at a constant rate from one fixed point of the sampling cross-section, all n samples to have the same time-origin prior to the arrival of the tracer. Sampling is terminated at time $t_1, t_2, t_3, \ldots, t_n$.

One alternative, which is the safest but which results in either greater tracer masses or lower concentrations for sampling terminated at time $t_2, t_3, \ldots, t_n$, consists in assuming $t_1 = t$.

In this case, if t has not been under-estimated all samples indicate the true rate of flow.

If t has been under-estimated, the apparent flow rate calculated from the first samples will be too high but some samples such as $t_4, \ldots, t_n$ will give the true value (figure 1). In the most unfavourable case, an asymptotic fit of the curve of Q against t will lead to the correct flow value[1] (figure 2).

Another alternative which is more economical consists in assuming for example that :

$t_3 = t$ with $t_1 < t$ and $t_2 < t$

$t_4 > t, \quad t_5 > t, \quad t_n > t$

– if t has been rightly estimated, the analysis of samples $t_3, t_4, t_5, \ldots, t_n$ will lead to the true value of the flow rate; t_1 and t_2 will lead to values which are too high (figure 1) (t_3 will be at the concentration assumed as optimal for analysis, t_4, t_5 and t_n at smaller concentrations);

1) See 2.3.

— if t has been under-estimated, t_5 and t_6, or the value obtained by the best fit of the curve of Q against t (figure 2), will lead to the true value of the flow rate;

— if t has been over-estimated, all samples will lead to the true value of the flow rate.

For the application of the procedures described in 5.1.2 and 5.1.3, the apparatus shown in figure 3 (A or B) may be used.

5.1.4 *Multiple samples*

Samples are taken at known intervals from a fixed point in the sampling cross-section over a period of time covering the whole of the passage of the tracer. A curve is drawn by plotting the variation of concentration $C_2 - C_0$ against time. The area under the curve is measured in order to evaluate the integral

$$\int_0^t (C_2 - C_0)\,dt$$

and Q is calculated using equation (1), (see figure 4).

Samples may be examined by a chemical, colorimetric or fluorimetric method or by a conductivity measurement. One advantage of the methods based on conductivity or fluorescence measurement consists in allowing measurements to be carried out without a reagent more easily on site than by other methods. Disadvantages are the effect of temperature, the high conductivity of certain streams even before the tracer is added and the instability of fluorescent bodies under light.

5.1.5 *Continuous recording*

During the test, the curve

$$C_2 - C_0 = f(t)$$

is directly recorded by a suitable method, for example by means of a conductivity recorder. The integral is then determined graphically.

5.2 Method of comparative dilutions — Determination of dilution ratio

In this method, known dilutions of the injection solution are prepared using natural water from the stream. A particular property or concentration of a component of the injected tracer present in the prepared dilutions is compared by a physical or chemical method with the corresponding property or concentration in the samples taken at the sampling point. The dilution ratio, N, is thus obtained without measuring any absolute values of concentrations.

When using this method, the equations already given are modified as follows :

5.2.1 *Multiple consecutive samples* (5.1.1)

Calling N_r the dilution ratio corresponding to the rth sample,

$$N = M \Big/ \left\{ \sum_{r=1}^{r=m} V_r\,(C_r' - C_0) \right\}$$

$$= VC_1 \Big/ \left\{ \sum_{r=1}^{r=m} V_r\,(C_r' - C_0) \right\} \qquad \ldots (8)$$

but

$$\frac{C_r' - C_0}{C_1} = \frac{1}{N_r} \qquad \ldots (9)$$

so that

$$N = V \Big/ \left(\sum_{r=1}^{r=m} \frac{V_r}{N_r} \right) \qquad \ldots (10)$$

5.2.2 *Average sample* (5.1.2)

Similarly,

$$\bar{N} = \frac{C_1}{\bar{C}_2 - C_0} \qquad \ldots (11)$$

and

$$Q = \frac{V}{t}\bar{N} \qquad \ldots (12)$$

5.2.3 *Multiple samples* (5.1.4)

The equation is therefore

$$Q = V \Big/ \left(\int_0^t \frac{1}{N_r} dt \right)$$

The values of $1/N_r$ are plotted against time, and the area under the corresponding curve is integrated. This area, divided by the total time, gives the reciprocal of the dilution ratio.

NOTE — When using the method of comparative dilutions, it is sufficient to interpolate the dilution ratio of the samples from a curve drawn by plotting the variation of a given characteristic of the injected tracer against the dilution ratio.

6 REQUIRED CHARACTERISTICS OF INJECTED SOLUTIONS

6.1 Requirements

The tracer to be used for the injected solution shall comply with the following requirements :

a) it shall not give any reaction with the natural water of the stream or with any matter (organic matter in particular) which this may contain in solution or suspension, or with the material which forms the river bed and cannot be retained by the said material;

b) it shall be stable to light;

c) it shall not be toxic to the stream flora or fauna (fish or other animals) at the concentration level used;

d) it shall be capable of being accurately determined at the concentration level of the diluted samples;

e) it shall only exist in solution in the natural water of the stream at relatively low concentration;

f) it shall have minimum losses from absorption.

6.2 Examples

The following tracers, which may not be suitable for all waters, are given as examples with their approximate solubility in water and the minimum final concentration level at which they can be used after dilution in water (values generally accepted in 1970) :

sodium dichromate ($Na_2Cr_2O_7.2H_2O$)

a) solubility : 600 kg/m^3;

b) 2×10^{-4} kg/m^3 in direct analysis;
2×10^{-6} kg/m^3 with reconcentration (see 9.1.2.4).

sodium chloride (NaCl)

a) solubility : 350 kg/m^3;

b) 10^{-3} to 10^{-2} kg/m^3 according to original conductivity (see 9.2.1).

rhodamine B ($C_{28}H_{31}ClN_2O_3$)

a) solubility : 10 to 20 kg/m^3;

b) 2×10^{-7} kg/m^3.

lithium chloride (LiCl)

a) solubility : 600 kg/m^3;

b) 5×10^{-3} kg/m^3.

fluorescein ($C_{20}H_{10}O_5Na_2$) (namely salt of fluorescein)

a) solubility : 50 kg/m^3;

b) 5×10^{-6} kg/m^3.

Other tracers have been used, in particular :

sodium nitrite ($NaNO_2$)

manganese sulphate ($MnSO_4.4H_2O$)

Among radio-isotopes used are the following :

bromine (^{82}Br) – half-life 36 h – γ radiation 0,55 and 1,5 MeV (ammonium bromide)

iodine (^{131}I) – half-life 8 d – γ radiation 0,36 MeV (sodium iodide).

sodium (^{24}Na) – half-life 15 h – hard γ radiation (sodium bicarbonate);

gold (^{198}Au) – half-life 2,7 d – γ radiation 0,96 or 0,41 MeV.

generators of radio-elements with caesium-barium and tin-indium couples.

7 CHOICE OF THE MEASURING REACH

7.1 General considerations for site selection

7.1.1 *Essential conditions*

The two essential conditions for the application of the method are the following :

a) the tracer shall be adequately mixed with the river water in the sampling cross-section :

$$\int_0^t C_2 \, dt = \text{constant at all points of the sampling cross-section;}$$

b) the whole of the tracer shall pass through the sampling cross-section.

7.1.2 *Choice of injection and sampling sections*

In addition, it is desirable that the distance between the injection and sampling sections be as short as possible : this allows time gain and economy of tracer. In consequence a reach should be chosen in which the river is as narrow and as turbulent as possible, free of dead-water zones, with numerous transverse currents to promote lateral mixing which is the most difficult to obtain; grassy and vegetation-grown zones as well as separation zones of the river into arms should be avoided.

The length of good mixing may theoretically be reduced by distributing the injection over the whole width of the river, but practical experience shows that to achieve good mixing to an accuracy better than 1 %, noticeable reduction of the mixing length can only be obtained by carefully studying the distribution of injected flow through the various orifices compared with the flow distribution in the river. However, this procedure is difficult to apply in practice.

In all cases it is advisable to make injections in a zone where velocities are high, if possible, in the direction of the opposite bank when injections are made from a bank.

Sampling should preferably be made in a narrow cross-section where there are no back-currents or dead-water zones.

7.1.3 *Inflow into the measuring reach*

Measurement can be made when there is an inflow (affluents or sources) into the river between the injection and sampling cross-sections provided only that good mixing is achieved at the sampling place. It may then be essential, if the inflow water characteristics are different from the river water characteristics, to take natural water samples (see 8.3.1) in the sampling cross-section.

The measured rate of flow then includes intermediate water inflow.

7.1.4 *Abstraction or leakage from the measuring reach*

If there exists a leakage or an abstraction between the injection and sampling cross-sections, the result will be questionable except when the abstraction or leakage location is perfectly well known and situated at a point where good mixing is already achieved; in this case the analysis of samples will lead to the value of the river flow rate upstream from the leakage or abstraction and not to the channel flow rate in the sampling cross-section.

Furthermore, if there are any dead-water zones these may detain part of the tracer and release it only very slowly after the passage of the main cloud so that the measuring time is considerably prolonged. It is necessary to continue sampling until all the tracer collected in the dead-water zones passes through the sampling cross-section. An error of measurement may therefore arise since a considerable amount of tracer may pass through the downstream cross-section at the end of the test when concentrations are too low to be measured.

7.2 Preliminary tests

7.2.1 *Determination of the length of the measuring reach*

It may be shown that the length of the measuring reach necessary to obtain good mixing is the same as for the dilution method with constant rate injection.

The minimum distance for satisfactory mixing may be calculated theoretically in a very approximative way for measurements in a channel or river.

7.2.1.1 MEASUREMENT IN A CHANNEL

In the case where injection is made in an open channel of uniform flow by means of a device distributing the injection flow rate over the whole width of the river in proportion to the flow rate in each elementary vertical section, the minimum length of "good mixing" l is given by the formula :

$$l = 10\,rh \qquad \ldots (13)$$

where

h is the mean depth;

r is the ratio of the mean velocity to the friction velocity.

The value of r will be given by

$$r = \sqrt{\frac{8}{\lambda}} \qquad \ldots (14)$$

where λ is the coefficient of the universal formula giving the head loss per unit length

$$\xi = \frac{\lambda}{4\,R_h} \times \frac{\bar{v}^2}{2\,g} \qquad \ldots (15)$$

where

ξ is the head loss per unit length;

R_h is the hydraulic radius;

$\bar{v}$ is the mean velocity;

g is the acceleration of free fall.

NOTE – r may be expressed as follows :

$$r = \frac{K R_h^{1/6}}{\sqrt{g}} \qquad \ldots (16)$$

where

K is the Strickler coefficient in terms of roughness;

R_h is the hydraulic radius;

g is the acceleration of free fall.

This theoretical formula has been the subject of satisfactory experimental checks.

7.2.1.2 MEASUREMENT IN A RIVER

A formula has been given in the footnote* which can only be used as a first indication and the actual mixing length to be used should be determined by practical tests. For example, as the formula is based on a point injection in a straight reach, the length obtained may be shorter if multiple injections are made in the injection Gross section. Besides, certain tests show that the formula gives too low a length value for small streams about 5 m wide and too high a value for rivers 50 m wide.

7.2.2 *Duration of injection and sampling*

7.2.2.1 DURATION OF INJECTION

The duration of injection shall be so selected that the period of passage of the tracer is sufficient for the required number of samples to be taken.

7.2.2.2 DURATION OF SAMPLING

The duration of the passage of the tracer through the measuring section is usually determined by a preliminary test using fluorescein injection. This visual observation method generally gives good results but in some cases may lead to under-estimating the tracer passage time considerably.

In the case of a coated straight channel of constant cross-section and with uniform flow, theoretical developments show that 99,9 % of the mass of the injected tracer passes through the measuring reach in a time interval t given by the formula :

$$t = 9{,}3\sqrt{\frac{mdx}{r\bar{v}^2}} \quad \ldots (17)$$

where

m is the non-dimensional coefficient of longitudinal dispersion equal to or greater than 7,3;

d is the depth;

x is the distance from the measuring cross-section to the injection cross-section;

$\bar{v}$ is the mean velocity;

r is the ration of the mean velocity to the friction velocity.

8 PROCEDURE

8.1 Measurement of the volume of the injected solution

For the measurement by the comparative dilution method, as well as for the direct measurement of concentrations, it is necessary to determine the volume of the injected solution, by means of a calibrated tank for example, or to determine the mass of this solution. It is practical to transport known volumes of a given mother solution in suitably chosen sealed containers.

8.2 Continuous recording

In the case of the conductivity method, and provided that the variations of temperature and natural conductivity of water during the test are negligible, it is possible to make a continuous recording of the water conductivity during the passage of the tracer; this is equally possible when using fluorescent tracers but their behaviour under the influence of light and temperature should be studied.

8.3 Sampling

8.3.1 *Samples of natural water*

Two methods are possible for natural water sampling :

1) upstream from the injection cross-section at the beginning of, during and at the end of the test : good representation of the variation of the water characteristic in time is thus obtained, but strictly speaking the sample of the river water should be taken in the sampling cross-section since there may be differences of the water characteristics between the injection cross-section and the sampling cross-section.

* In the case of point injection in the axis of flow, the minimum length of good mixing may be evaluated by an empirical formula which has not yet been checked by systematic experiences :

$$l = \frac{0{,}13\, b^2 C\,(0{,}7\, C + 2\sqrt{g})}{gh} \text{ in SI units}$$

where

b is the mean width, in metres, of wet section in the measuring reach;

h is the mean depth, in metres, of water in this reach;

C is the Chezy coefficient ($15 < C < 120$).

The expression of the Chezy coefficient may be assumed as equal to :

$$C = \sqrt{\frac{8g}{\lambda}}$$

2) in the sampling cross-section, before and after the tracer passage : good representation of the water which has effectively diluted the tracer and is present in the collected samples is then achieved. This second process is indispensable for conductivity measurements when there is an affluent between the injection and sampling cross-sections, the waters of which have characteristics different from those of the main stream, in particular when waters are turbid for colorimetric or fluorescent analyses.

A drawback of the latter method is that it does not take account of the water characteristic evolution during the cloud passage. Natural water sample collection should preferably be made both

a) upstream from the injection cross-section, at the beginning of, during and at the end of the injection, and

b) in the sampling cross-section, before and after the tracer passage.

If a simplification of this procedure is desired, that of both methods which results in the minimum error should be selected according as the river water characteristic is thought to vary more with the time or with the site.

8.3.2 *Sampling of injection solution*

A minimum of three samples of the concentrated injection solution shall be taken at the beginning of, during and immediately before the end of the test.

8.3.3 *Measurement of the concentration in the downstream section*

In the sampling cross-section situated at the downstream end of the measuring reach, and chosen in accordance with the indications given in clause 6, measurements of the concentration shall be carried out on samples taken from at least three points suitably distributed in the cross-section in such a way as to check that the condition of satisfactory mixing is complied with, i.e. that the integral :

$$\int_0^t (C_2 - C_0)\, dt$$

has the same value throughout the section.

Measurements of concentration at each of these points shall be carried out by one of the methods given below. Whatever the method used, sampling shall commence before, and shall not end until after, the passage of the tracer.

a) In accordance with 5.1.1, about ten samples shall be taken consecutively and at a constant rate throughout the whole time of the passage of the tracer through the sampling cross-section. The interval of time between samples shall be as short as possible.

b) A single sample shall be taken over the whole time of the passage of the tracer (see 5.1.2).

NOTE – In both cases a) and b) the total sampling time shall be carefully recorded. In addition, the rate of sampling shall be constant, and for this purpose a rotating or reciprocating displacement pump and a large, fine filter may be used. The rate of flow of the pump shall be checked before and after the test so as to ensure that the sampling flow has remained completely constant throughout the test. Figure 3 represents two constant rate sampling devices.

c) When the duration of the passage of the tracer is at least 10 min, a series of successive samplings distributed over the whole of the passage of the cloud shall be obtained (see 5.1.3).

In order to obtain sufficient accuracy, at least twenty-five samples shall be taken. In addition, each period of sampling shall be at least 15 s, in order to integrate satisfactorily the rapid fluctuations of concentration which occur at any particular point of flow. The rate of sampling shall be defined in relation to the total time of passage of the tracer and the exact time of each sample shall be recorded.

d) The variation of concentration in relation to time is calculated from the continuous recording carried out as indicated in 8.2. (See also 5.1.5.)

9 MAIN TRACERS AND METHODS OF ANALYSIS USED IN 1970

The chemical substances most used are

– for colorimetric analysis : sodium dichromate;

– for fluorescence analysis : rhodamines, fluorescein;

– for conductivity method analysis : sodium chloride;

– for spectrophotometric analysis : lithium chloride, dichromate;

– for chemical volumetric analysis : sodium chloride, dichromate.

The most widely used radio-isotopes were bromine (^{82}Br), iodine (^{131}I), sodium (^{24}Na), gold (^{198}Au) and generators of radio-elements with caesium-barium or tin-indium couples.

The approximate values of solubilities and analysable concentrations have been mentioned in clause 6. For the choice of these products account should also be taken of national regulations concerning permissible amounts for flora, fauna and drinking water.

9.1 Method of colorimetric analysis

9.1.1 *Selection of tracer — Minimum measurable concentration*

As natural waters do not in general contain chromium ions in solution, the recommended tracer for the application of the dilution method by colorimetric analysis is sodium dichromate. Its solubility in the water is proportionately high (in practice concentrations up to 600 kg/m^3 can be used) and it generally meets the conditions of clause 6.

The nature and quantity of suspended materials in natural water may seriously affect analysis accuracy (see 9.1.2.3).

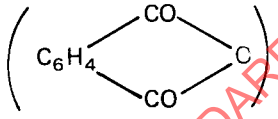
Colorimetric analysis allows measurement of very low concentrations of sodium dichromate. Analysis accuracy depends on the final concentration (generally between 0,2 and 2×10^{-3} kg/m^3) and also on the sensitivity and accuracy of the colorimetric device.

9.1.2 *Analysis method*

The principle of the colorimetric analysis consists in comparing, with a colorimeter, the dilution ratios of sodium dichromate solutions (dilution of samples taken in the channel and dilution of standard solutions) according to the light absorption of the solution to which a reagent has been previously added.

Recommended reagents have the following composition :

first :

- diphenylcarbazide (crystallized) $[(C_6H_5NH.NH)_2CO]$ — $0{,}25 \times 10^{-3}$ kg
- phthalic anhydride (crystallized)  — $4{,}0 \times 10^{-3}$ kg
- ethyl alcohol 95 % (C_2H_5OH) — 100×10^{-6} m^3

second :

- diphenylcarbazide — $0{,}25 \times 10^{-3}$ kg
- high purity acetone — 100×10^{-6} m^3

To 50×10^{-6} kg/m^3 of the sample which is being analysed, 10 drops of concentrated sulphuric acid of a relative density of 1,84 should be added to obtain an acid solution (pH close to 2,2), followed by 2×10^{-6} m^3 of the reagent.

The action of this reagent is sufficiently rapid in an acid medium for the colorimetric measurement to be made about 10 min after the introduction of the reagent into the solution but it is necessary to have the same reaction time for all samples and standard dilutions.

The analysis is carried out in the following manner :

9.1.2.1 Calibration of colorimeter

From one of the samples taken at the injection device outlet a set of standard solutions is made (at least four) with a known dilution close to the dilution in the channel.

To this effect, a sample of the concentrated injection solution is diluted using flasks and pipettes calibrated with water taken in the channel. These samples should then be measured using the colorimeter, the indications of which should be plotted on a curve against the dilution ratio.

It is recommended that a colorimeter be used, the indication of which is proportional to the optical density.

Flask and pipette calibration is one of the main sources of error in this method. With a view to reducing the systematic effect of this error, accurate calibration of the equipment used for preparing standard dilutions must be achieved. Micro-burettes may in particular be used to deliver amounts of the order of 1 mm^3 to within 1 % accuracy.

The homogeneity of the injected solution is to be checked by diluting the various collected samples identically and by analyzing them successively.

9.1.2.2 Measurement of downstream sample dilution

Samples taken downstream are then analyzed with the colorimeter. Previous calibration allows the sample dilution ratio to be determined; its average value and standard deviation may also be calculated.

At this stage it is recommended to proceed to a new calibration of the device with the standard solutions. The deviation between both calibrations due either to colorimeter drift or reagent instability is not to exceed 1 %.

9.1.2.3 Necessary precautions

Taking account of the influence of time on the sodium dichromate diluted solution, it is necessary, when aiming to within ± 1 % accuracy, to make the analysis within the few hours following the test proper.

When a few days' interval is unavoidable between sampling on the one hand and standard dilution preparation and their analysis on the other hand, the following precautions must be taken because of the risk of dichromate solution instability :

- samples are to be kept in the dark;
- at least three standard solutions, with a dilution approximately equal to that of collected samples, are to be prepared on the spot and then kept in exactly the same conditions as all other samples.

Any error due to sample evolution with time may be evaluated by comparing standard solutions of the same concentrated solution prepared at different times. This precaution is recommended in particular when water contains organic materials likely to reduce sodium dichromate.

If the water is not perfectly clear and contains solid materials in suspension, several cases are to be considered:

a) if simple sedimentation is enough to clarify the samples, standard dilutions prepared with the river water and collected samples are placed in identical containers and decanted for equal time intervals until satisfatory clarification is obtained;

b) if sedimentation is not enough to clarify the water, vacuum filtering of samples and standard dilutions can be made using plastic filters with a porosity of 1 μm. It is then necessary to use one filter per sample and one per standard dilution and to saturate each filter with the solution to be filtered. To this effect a certain amount of the sample to be analyzed is filtered then thrown away keeping only for the measurement the liquid subsequently filtered (thus the first 10×10^{-6} m^3 filtered should be thrown away for filters of 0,043 m diameter).

If the water is very loaded with clayey colloidal materials and clogs the filters very rapidly, it is possible to accelerate sedimentation previous to filtration by adding a solution of aluminium sulphate [$Al_2(SO_4)_3.18H_2O$] to the samples in the most simple cases, or a solution of sodium silicate (Na_2SiO_3) then of aluminium sulphate in the most difficult cases. These procedures do not theoretically involve sodium dichromate loss but it is still wiser to deal with samples and standard dilutions strictly in the same way.

9.1.2.4 Reconcentration

It is possible to reduce the mass of the tracer to be used when flow rates are high by using a reconcentration process for the analysis : this consists in collecting in a volume V_1 of *n*-butanol [$CH_3(CH_2)_3OH$] the whole coloured complex (sodium dichromate + diphenylcarbazide reagent) contained in a volume V_2 of the sample to be analyzed. The concentration ratio is close to V_2/V_1.

Butanol is only very slightly soluble in water and constitutes an excellent solvent of the coloured complex; its density, very different from that of water, allows its collection by phase separation in decanting containers. It is, however, necessary first to saturate samples with sodium chloride (NaCl, 300 kg/m^3).

Reconcentrations may easily be made for V_2/V_1 ratios between 10 and 20. For greater reconcentration rates it is necessary to use larger butanol volumes V_1 on account of the solubility of this substance in the water; 25 to 30×10^{-6} m^3 of butanol should thus be put in 1 l of sample to obtain a reconcentration ratio of 100 as only 10×10^{-6} m^3 of butanol containing almost all the coloured complex are recovered in the decanting containers. Standard dilutions and samples should be reconcentrated in the same conditions.

It is therefore possible, by previously reconcentrating 100 times, to successfully analyse samples the original concentrations of which in sodium dichromate are 2×10^{-6} kg/m^3.

9.1.2.5 Reoxidation

There is always a risk of reduction. Reduced ions then take the form Cr^{+3} and must be regenerated to Cr^{+6}.

It is recommended that the following procedure be adopted :

- take 50×10^{-6} m^3 exactly of the sample to be oxidized;
- add a solution of 10 % potassium permanganate ($KMnO_4$) until a persistent pink tint is obtained;
- boil for 3 min;
- add sodium azide (NaN_3) drop by drop until complete discoloration of the solution, without significant excess;
- add 10 drops of phosphoric acid (H_3PO_4);
- let the solution cool;
- make up to 50×10^{-6} m^3 in distilled water;
- add the reagent.

Colorimetric measurement may then be undertaken.

If it is desired to avoid reoxidation, one of the easiest and most efficient processes to prevent the reduction phenomena from leading to exaggerated errors consists in preparing the standard dilution range with the river water during gauging so that standard dilutions and samples have exactly the same evolution.

9.1.3 *Use of rhodamines*

Rhodamine is a very powerful organic colouring substance. It is not very soluble in water (10 to 20 kg/m^3) but is more soluble in acetic acid (CH_3COOH) (300 to 400 kg/m^3).

9.1.3.1 Colorimetric analysis

Direct colorimetric analysis allows the measurement of concentrations up to 2×10^{-5} kg/m^3. Extraction in *iso*amyl alcohol ($C_5H_{11}OH$) in a slightly acid medium is easily achievable and allows measurement of concentrations up to 100 times lower, i.e. 2×10^{-7} kg/m^3. It is useless to add a reagent.

The colorimeter should be set for a maximum extinction coefficient on a wavelength of 553 nm. The optical density is a linear function of concentration.

In the case of the colorimetric analysis, samples may be kept 8 days without alteration.

9.1.3.2 FLUORIMETRIC ANALYSIS

As rhodamine is a fluorescent body its concentration may be measured by fluorimetry. The maximum excitation wavelength is 546 nm and the emission spectrum has a sharp maximum for a wavelength close to 570 nm.

A suitably selected secondary filter considerably increases the sensitivity and fidelity of the apparatus.

The fluorimetry law is linear at the concentrations used.

The fluorimetric analysis is critical as the apparatus may overheat and the results are affected by a variation of 3 % per degree of the emitted light intensity.

In the case of the fluorimetric analysis, it is also advisable to carry out the analysis within a few hours after the test as rhodamine diluted solutions deteriorate after 4 days when in the dark and after 1 or 2 h only when exposed to light.

9.2 Conductivity method

9.2.1 *Choice of tracer — Minimum measurable concentration*

The injected tracer is to meet the requirements stated in clause 6. In particular, its ionizing power must be high so that in low concentration in natural water it nevertheless causes an increase in conductivity that can be measured with sufficient accuracy.

The tracer most frequently used is sodium chloride (NaCl), which has a solubility of 360 kg/m^3 at 15 °C. For concentrations up to 0,05 kg/m^3, the relation of its conductivity to concentration is almost linear. In aqueous solutions, at a temperature of 18 °C, the variation of conductivity is 186 µs/m for 1×10^{-3} kg/m^3. This coefficient is smaller when the water in which the salt is dissolved already contains an appreciable concentration of dissolved salts.

The conductivity of the natural water also affects the minimum value of concentration of salt at which the method can be used with confidence.

The minimum concentrations of sodium chloride which may be measured with an accuracy of the order of ± 1 % by the conductivimetric method are shown in the following table against the conductivity of natural water.

A very sensitive conductivity meter must be used, capable of detecting variations of conductivity of about 1/10 000 of that of the natural water. It is necessary that the instrument be capable of balancing any capacity component while the conductivity measurement is being made.

Conductivity of natural water (µS/m × 10^{-3})	100	20	10	2
Minimum concentration of NaCl, measurable with ± 1 % accuracy (kg/m^3 × 10^{-3})	10	2	1	1

When the natural water has a low conductivity the minimum concentrations may be reduced to 1/10th of those indicated in the above table provided that special precautions are taken in making the dilutions and that special equipment is used.

9.2.2 *Methods of analysis*

9.2.2.1 COMPARISON OF THE VARIATIONS OF CONDUCTIVITY

The conductivity of the water at the sampling cross-section is recorded continuously, or is measured at frequent regular intervals, during a period which includes the whole of the time taken for the injected solution to pass this cross-section.

As a result of any variations in the conductivity of the natural water during the period of measurement there will be similar fluctuations of the conductivities measured.

The additional conductivity due to the presence of the injected tracer is determined by subtracting the mean of the conductivities of the natural water, measured immediately before and after the passage of the tracer, from the conductivity values measured during the period of test.

If the variations of conductivity of the natural water are known to be relatively large, the conductivity of the natural stream should be measured continuously at a position upstream from the injection cross-section.

These measurements are to be made simultaneously with those in the sampling cross-section but the time required for the water to pass from this cross-section to the downstream measuring cross-section must then be taken into account. This time-shift being considered, the conductivity in the upstream cross-section is subtracted from the conductivity measured in the downstream cross-section.

A calibration of the conductivity meter is then made in the laboratory. This operation consists of determining the variation in the conductivity produced by adding a measured quantity of the concentrated solution to a sample of natural water taken upstream from the injection section, so as to obtain a known dilution ratio approximating to that obtained in the test.

The conductivity of this sample is measured immediately before and after the addition of the concentrated solution, all other conditions of measurement being identical.

The influence of temperature of the conductivity of electrolytes makes it necessary to carry out the calibration at the same temperature as that measured during the test. For a solution of sodium chloride, and for accurate measurement (± 1 %), the temperature difference between that in the test and that in the calibration should not be more than ± 0,1 °C. Also the temperature should not vary by more than 0,01 °C during the period of calibration and in particular over the period of introduction of the concentrated solution. The fluctuations of temperature during the test and during the period of calibration should be checked within ± 0,01 °C. Such accuracies can be obtained with an instrument embodying a thermistor provided that the same instrument is used for both the field and laboratory measurement.

In the range of concentrations which are usually used, the variation of conductivity of the solutions of sodium chloride is nearly proportional to the concentration, i.e. the inverse of the dilution ratio; it is recommended therefore that the variation of conductivity be plotted as a function of the reciprocal of the dilution ratio.

9.2.2.2 Comparison of conductivities

The quickest method would consist in comparing the conductivity of the water in the channel at the passage of the tracer with the conductivities of a series of standard solutions obtained by diluting in known proportions the concentrated solution with water taken upstream from the injection cross-section.

This method is generally not very accurate due to significant differences of natural conductivities among the various samples.

It is observed that natural conductivity may vary noticeably during the period of test and it is besides difficult to avoid all conductivity variation of the samples between sampling time and analysis time.

9.3 Method of volumetric chemical analysis

9.3.1 *Choice of tracer — Minimum measurable concentration*

As an example, the volumetric method of chemical analysis of the dilution ratio is described in detail in the case of utilisation of sodium dichromate. Sodium chloride may also be used and detected by titration against silver nitrate ($AgNO_3$) using an indicator determining titration end-point. In this case the results may involve serious errors if the natural water contains an appreciable amount of any colouring agent, as in fact this process normally requires sample evaporation so that colour change of the indicator is hardly detectable. When respecting these conditions, electrical apparatus may be used to detect the end-point of titration.

Volumetric analysis of sodium dichromate can be carried out with better than ± 1 % accuracy on final sample concentrations as low as 3×10^{-3} kg/m^3.

As stated in 9.1.1, the use of sodium dichromate is advantageous as natural waters do not generally contain chromium ions. It should be noted, however, that this salt is easily affected by reducing agents in the water and initial tests should then be carried out to ensure that there will be no serious effect on the samples between the time of sampling and of analysis. The samples may be reoxidized by boiling with permanganate but the time of analysis is considerably lengthened if this procedure has to be adopted.

9.3.2 *Method of analysis*

The principle of the method is that the total amount of the dichromate present in the sample reacts with the ferrous ammonium sulphate solution used for the titration, the end-point of the reaction being determined by colour change in the indicator, *N*-phenylanthranilic acid, which has been added to the sample. The amount of ferrous ammonium sulphate used in the titration is directly related to the amount of dichromate present in the sample.

The recommended reagents are as follows :

a) ammonium iron(II) sulphate

A stock N/10 solution of this salt should be prepared by dissolving 0,039 22 kg of pure ammonium iron(II) sulphate [$FeSO_4(NH_4)_2SO_4.6H_2O$] in $0{,}5 \times 10^{-3}$ m^3 of distilled water containing 10×10^{-6} m^3 of concentrated sulphuric acid. The resulting solution is then to be made up to 1×10^{-3} m^3.

For titrating against the samples, an N/200 solution should be made up by taking $0{,}1 \times 10^{-3}$ m^3 of the stock solution and diluting to 2×10^{-3} m^3 with distilled water.

b) *N*-phenylanthranilic acid (indicator)

$1{,}07 \times 10^{-3}$ kg of *N*-phenylanthranilic acid ($C_6H_5NHC_6H_4COOH$) should be dissolved in 20×10^{-6} m^3 of a 5 % sodium carbonate (Na_2CO_3) solution and made up to 1×10^{-3} m^3; $0{,}5 \times 10^{-6}$ m^3 of this solution should be used for each titration.

To $0{,}5 \times 10^{-3}$ m^3 of the sample which is being analysed, 10×10^{-6} m^3 of concentrated sulphuric acid should first be added and the sample stirred continuously throughout the titration.

The general precautions recommended in 9.1.2.3 should be followed and in particular the standard solutions should be prepared as described in that sub-clause. It is important that a standardized procedure be used in the analysis of all the samples. This applies particularly to the amount of acid and indicator added and to the rate at which the ammonium iron(II) sulphate is added during the titration.

The results of the titrations of the standard solutions can be plotted and the best straight line drawn through the points to compensate for their dispersion with the condition that it passes through a point close to the origin. The position of this line with respect to the origin depends upon the amount of indicator used in the

titration but, if the recommended procedure is followed the intersection point of this line on the ammonium iron(II) sulphate axis should be about $+ 0{,}5 \times 10^{-6}$ m³.

The samples taken at the sampling cross-section are analysed in the same manner by titration against ammonium iron(II) sulphate and the dilution ratio can be determined from the graph by determining the average of the titration values of all samples. The standard deviation of the samples may be computed from the individual results.

In general for unskilled operators, analysis methods by dilution comparison will lead to more accurate results (zero method) than the processes of direct chemical analysis for the low concentrations used.

10 ERRORS IN FLOW MEASUREMENT

No measurement of a physical quantity can be free of uncertainties which may be associated with either systematic deviations caused by errors in the calibrating equipment or a random scatter caused by a lack of repeatability of measuring equipment. The former is unaffected by repeated measurements and can only be reduced if more accurate equipment is used for the measurements. Repetition does, however, reduce the error caused by random scatter. The likely error of the average of m repeated measurements is $\sqrt{m}$ times smaller than that of any of the individual measurements.

When considering the possible error of any measurement of the discharge in an open channel, it is not possible to predict this error exactly, but an analysis of the individual measurements which were required to obtain the discharge can be made on a statistical estimate made of the limit-error. The limit-error at the 95 % probability level on a measurement may be defined statistically as the band width around the calculated value, which, on an average of 95 times out of 100, can be expected to include the true value.

The limit-error can be taken to equal twice the square root of the sum of the squares of the deviations provided that the individual deviations on the various measurements are small and independent.

If the different independent quantities which have been measured are $x_1, x_2, x_3, \ldots$ and the standard deviations on these measurements are $\delta x_1, \delta x_2, \delta x_3 \ldots$, then the limit-error on the measurement of flow is

$$2\frac{\delta Q}{Q} = 2\sqrt{\left(\frac{\partial Q}{\partial x_1} \cdot \frac{\delta x_1}{Q}\right)^2 + \left(\frac{\partial Q}{\partial x_2} \cdot \frac{\delta x_2}{Q}\right)^2 + \ldots}$$

where $\frac{\partial Q}{\partial x_1}, \frac{\partial Q}{\partial x_2} \ldots$ are partial derivatives, the values of which depend on the manner in which Q is a function of x_1, x_2.

If an independent quantity y has been obtained by m repeated measurements, as for example when the average dilution ratio of a large number of samples has been determined, and if the results of these measurements are $y_1, y_2, \ldots, y_m$, then the standard deviation of the average y_0 of the m measurements may be defined by

$$\delta y_0 = \sqrt{\left(\sum_{i=1}^{i=m} (y_i - y_0)^2\right) \Big/ m(m-1)}$$

If the value of an independent quantity (x_1 or x_2 or . . .) is based on a single measurement, then the standard deviation cannot be calculated statistically. For the purposes of this International Standard, however, the standard deviation of such a flow measurement may be taken as half the estimated maximum possible error.

From the preceding considerations it follows that the overall limit-error at the 95 % probability level, for a flow measurement by the integration (sudden injection) method, is given by the following equation :

$$2\frac{\delta Q}{Q} = \pm 2\sqrt{\left(\frac{\delta V}{V}\right)^2 + \left(\frac{\delta t}{t}\right)^2 + \left(\frac{\delta N}{N}\right)^2}$$

NOTE – This equation differs from that given in ISO 555/I since it is not essential in the integration (sudden injection) method to measure the absolute values of the injection or sampling rates, the important quantities being the volume injected into the channel, the time which the cloud takes to pass the measurement cross-section and the dilution ratio.

The standard deviations on the quantities V, t and N, which themselves may have been determined by any of the different methods contained in this International Standard, should be calculated by assessing all the possible sources of both systematic and random errors in each of the measurements used in the computation of these quantities and combining the squares of these, with the appropriate partial derivatives, to obtain the total squared standard deviations, i.e.

$$\left(\frac{\delta V}{V}\right)^2, \left(\frac{\delta t}{t}\right)^2 \text{ and } \left(\frac{\delta N}{N}\right)^2$$

It should be noted that in the constant rate injection method the values of q and N can be established generally from repeated measurements and hence assessment of the reliability of these is more straightforward; in the integration (sudden injection) method the values of V, t and N are inherently single measurements. However, sampling at different points in the measuring cross-section can demonstrate the effectiveness of mixing and hence the reliability of each of these individual measurements.

A numerical example of the estimation of the overall limit-error on flow measurement is given in the annex.