INTERNATIONAL STANDARD 555

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

Liquid flow measurement in open channels — Dilution methods for measurement of steady flow — Constant-rate injection method

First edition — 1973-09-15

UDC 532.57 : 627.133

Ref. No. ISO 555-1973 (E)

Descriptors : liquid flow, channels (waterways), open channel flow, flow measurement, dilution, injection, colorimetric analysis, volumetric analysis, error estimation.

Price based on 16 pages

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.

Prior to 1972, the results of the work of the Technical Committees were published as ISO Recommendations; these documents are now in the process of being transformed into International Standards. As part of this process, International Standard ISO 555 replaces ISO Recommendation R 555-1966, drawn up by Technical Committee ISO/TC 113, *Measurement of liquid flow in open channels.*

The Member Bodies of the following countries approved the Recommendation :

Belgium	Hungary	Portugal
Chile	India	Romania
Colombia	Israel	Switzerland
Czechoslovakia	Italy	United Kingdom
France	Korea, Rep. of	U.S.A.
Germany	Netherlands	U.S.S.R.
Greece	New Zealand	

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

Japan*

* Subsequently, this Member Body approved the Recommendation.

Printed in Switzerland

CONTENTS

Liquid flow measurement in open channels — Dilution methods for measurement of steady flow — Constant-rate injection method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies methods for the measurement of flow in channels under steady flow conditions by the dilution method using constant-rate injection. The method is applicable to the measurement of the flow in channels where the degree of turbulence is sufficiently high to ensure efficient mixing of the injected solution throughout the whole flow. This is generally the case in hill streams and torrents.

The apparatus and the chemicals to be used, the specifications of the techniques of injection and sampling, and also the methods of analysis, are detailed.

2 REFERENCES

ISO/R 541, *Measurement of fluid flow by means of orifice plates and nozzles.*

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

ISO 2638, *Liquid flow measurement in open channels — Dilution methods for measurement of steady flow — Integration (sudden injection) method.*[1)]

3 TERMINOLOGY

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

4 UNITS OF MEASUREMENT

The units of measurement used in this International Standard are metres (or feet) and seconds.

5 PRINCIPLE OF THE CONSTANT-RATE INJECTION METHOD

A solution of a suitably selected salt is injected at a constant rate, at a cross-section, at entry of the measuring-reach of the channel in which the rate of flow is constant over the period of test.

In a downstream cross-section of this reach, far enough from the first for the injected solution to be uniformly diluted throughout this cross-section, samples are taken at regular intervals of time. Provided that the concentration of the added chemical has attained a steady value, the rate of flow Q in the channel may be calculated from the equation :

$$Q = qN$$

where

q is the rate of injection of the chemical salt solution;

N is the ratio of the concentration of the salt in the injected solution to that at the downstream cross-section of the channel; however, if traces of the chemical salt are already present in the stream prior to the injection, N is defined by the equation given at the end of 5.1.

The ratio N, which is called the dilution ratio, may be determined by one of the following methods.

1) At present at the stage of draft.

5.1 Method of direct measurement of concentration

The concentration of the salt is determined :

a) upstream of the point of injection where the water is in its natural state (concentration C_0). See, however, 8.4 a);

b) in the injected solution (concentration C_1);

c) in samples obtained from the downstream section (where the concentration of the chemical has attained a steady value C_2).

Equating the mass of the salt passing the injection section ($C_0Q + C_1q$) and that passing the sampling section C_2 ($Q + q$) gives :

$$Q = \frac{C_1 - C_2}{C_2 - C_0}\, q$$

and if C_2 is small compared with C_1

$$\frac{Q}{q} = N \approx \frac{C_1}{C_2 - C_0}$$

5.2 Method of comparative dilutions

A set of standard solutions is made by diluting samples from the injected solution with different amounts of water from the natural stream, taken from a point upstream of the injection station. These known dilution ratios N_1, N_2 ... shall be approximately the same as those expected of the samples from the downstream section.

The standard solutions and the samples taken downstream are compared by a similar technique to establish the dilution ratio N of the unknown samples.

6 REQUIRED CHARACTERISTICS OF INJECTED SOLUTIONS

The chemical substance 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 river concerned 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;

b) it shall be stable to light;

c) it shall not be toxic to fish in the dilutions used;

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

e) it shall be used only when the concentration of the chemical in solution in the natural water is relatively low.

The following substances, which may not be suitable for all waters, are given as examples, together with final minimum concentrations at which they can be used after dilution :

- sodium dichromate ($Na_2Cr_2O_7.2H_2O$) : 0,2 mg/l
- sodium chloride (NaCl) : 2 mg/l

Other salts have been used, in particular :

- sodium nitrite ($NaNO_2$) and
- manganese sulphate ($MnSO_4.4H_2O$)

A chemical substance such as fluorescein ($C_{20}H_{12}O_5$) having sufficient colouring power to allow the passage of the cloud in the river to be checked visually is useful, particularly in preliminary tests to check the delay period before sampling (see 7.2.1).

7 CHOICE OF THE MEASURING-REACH

7.1 General considerations for selection of site

There shall be no loss or gain of water in the measuring-reach (for example, for a tributary joining or a distributary leaving the main flow, or overflow from or to the banks of the stream), and its length shall be such that, allowing for the natural mixing action of the stream, the solution injected at its beginning is uniformly diluted throughout the sampling cross-section.

The distance between the injection and sampling cross-sections shall be as short as practicable and the dead-water zones shall be as small as possible, to reduce the duration of injection and the quantity of salt injected.

For rivers, this condition is easier to satisfy in relatively narrow channels; mixing is also improved by disturbances such as bends, narrows, shelves, falls, etc. In particular, very wide channels shall be avoided, and reaches in which the stream divides into a number of branches shall not be used.

Great care is required to make a satisfactory choice of a reach suitable for the measurement of discharge by the dilution method using constant-rate injection. This choice is facilitated by carrying out the preliminary tests described in 7.2.

7.2 Preliminary tests

It is essential to the success of the method that the injected material have a constant concentration over the whole of the cross-section at the downstream sampling station during the whole of the sampling period.

Before selecting the measuring-reach, it is advisable to make preliminary tests to ensure that efficient mixing in the river will be achieved, to choose the injection and sampling cross-sections and, once these have been chosen, to determine the duration of the injection period.

7.2.1 *Determination of length of measuring-reach*[1)]

A first test can be made by using a strong dye such as fluorescein. A concentrated solution of this dye can be injected for a relatively short time at a point on a cross-section of the upstream portion of the measuring-reach. Study of the diffusion of the solution will make it possible to determine whether there are any dead zones or similar side-tracking of the chemical and be a rough guide on the minimum distance between the injection point and a suitable sampling cross-section.

7.2.2 *Duration of injection and of the steady-regime condition*

Duration of injection shall be such that a steady regime of the concentration may be achieved for an adequate duration, generally 10 to 15 min, in the sampling-section.

The duration of the injection, which is generally related to the degree of turbulence, will vary directly according to the length of the measuring-reach and the extent of the dead-water zones, and inversely according to the mean velocity of the water.

When the measuring-reach has been selected, preferably where the river bed is stable, the duration of injection may be determined from preliminary tests at different values of the rate of flow. These tests consist of determining the variation, as a function of time, of the concentrations of an injected chemical substance at a number of sampling cross-sections.

An instantaneous injection of fluorescein may also be used for this purpose. For a given flow, observation of the time of appearance and disappearance of coloration in each cross-section allows curves 1 and 2 of Figure 1 to be plotted. If it is desired to obtain, at a selected sampling cross-section, a steady-regime condition of duration Δt, it is only necessary to add the time Δt to the time of disappearance of coloration at this point (Figure 2), and to trace through the point obtained in this way a curve (1′) parallel to the curve (1) of appearance of the coloration. The ordinate at the origin of this curve gives the minimum duration of injection to be made.

The same figure directly gives the time-lag between the beginning of the injection and the beginning of the steady regime (Δt_1).

7.2.3 *Non-absorption of chemical*

It is particularly necessary to check that there is no absorption of the injected chemical in the measuring-reach, either by matter in suspension or by the material of the river-bed. For this purpose, samples shall be taken from the sampling cross-section and at least one other cross-section farther downstream to check that there is no systematic difference in the mean concentration from one sampling section to another.

---

1) The length of the measuring-reach l, between the injection cross-section and a cross-section where mixing may be expected to be within 1 % of complete homogeneity, cannot be predicted with certainty; but, as a guide, an empirical formula has been evolved, though not widely established on experimental data, as follows :

$$l = 0{,}13\, K \frac{b^2}{d} \text{ (in SI units)}$$

where

b is the average width of the water-surface in the measuring-reach (in SI units);

d is the average depth of the water in this same reach (in SI units);

K is the coefficient defined below :

$$K = \frac{C\left(0{,}7\,C + 2\sqrt{g}\right)}{g}$$

where

C is the Chezy coefficient for the measuring-reach, and $15 < C < 50$;

g is the acceleration due to gravity (in SI units).

It is emphasized that the length obtained from the above equation may only be used as a preliminary guide, because the equation may not apply at all in certain instances due to very low turbulence, and the actual length required should be established by practical tests. For example, since the equation was based on injection at a single point in a straight reach, the length will be shortened if multiple injections across the cross-section are used. In addition, some tests seem to show that the equation under-estimates the length for small streams of the order of 5 m in width and over-estimates the length for rivers of the order of 50 m in width.

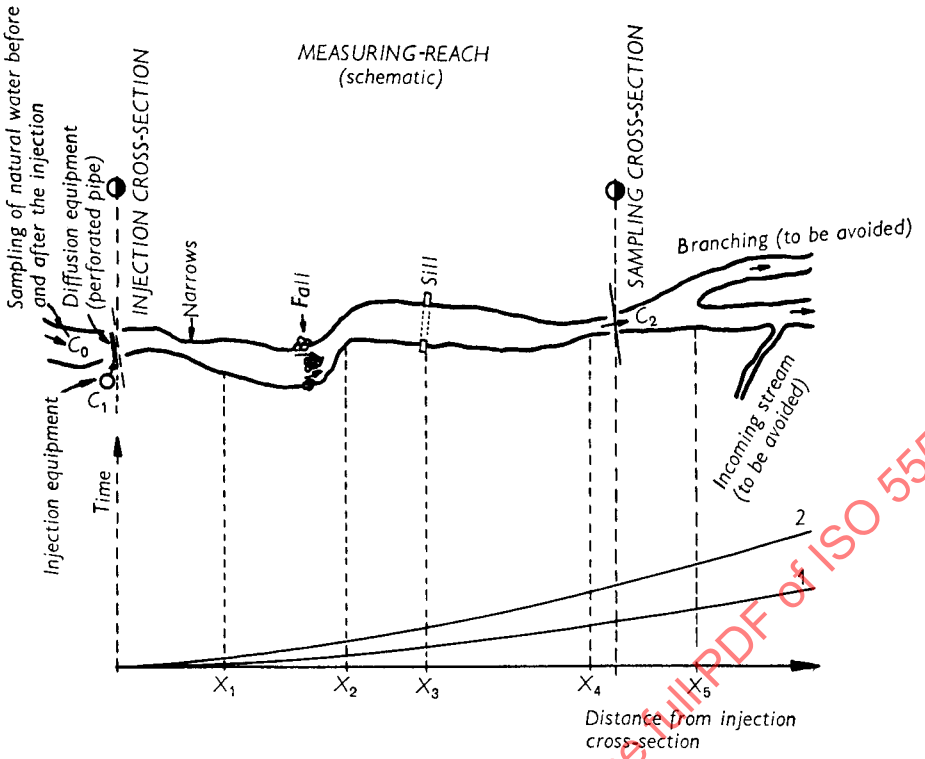

FIGURE 1 — **Curve of times of appearance and disappearance of coloured cloud as a function of distance from point of injection**

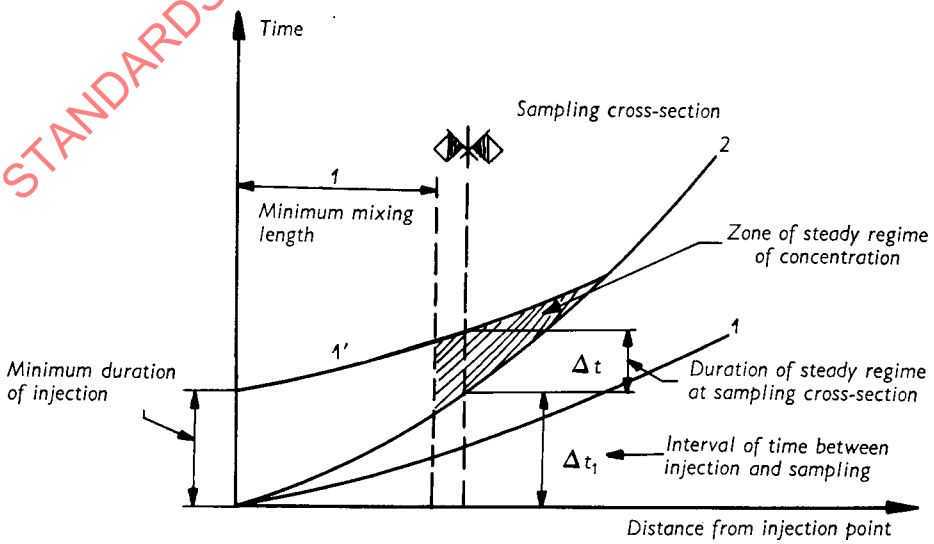

FIGURE 2 — **Determination of duration of injection**

8 PROCEDURE

8.1 Preparation of the concentrated solution

It is essential that the concentration of the injected solution be as homogeneous as possible.

Homogeneity of the solution is achieved by vigorous mixing performed with a mechanical stirrer or with a closed-circuit pump.

It is recommended that the injection solution be prepared in a separate tank from the supply tank (Figure 3). Water taken from the open channel shall be used for preparing the concentrated solution. If, however, the mixing is effected in the supply tank, this tank shall be of sufficient capacity to avoid the need for the addition of water or salt during an injection. The solution shall be drawn from a level above the bottom of the tank and provision shall be made to prevent particles of undissolved salts passing out with the injected solution.

8.2 Injection of the concentrated solution

The concentrated solution shall be introduced into the stream of which the discharge is to be measured at the chosen injection cross-section. The concentrated solution shall be injected at a constant rate of flow which may be controlled by one of the following devices :

a) *A constant-level tank*

This tank (for example as shown in Figure 3) shall be of such dimensions and volume as will permit suitable arrangements to be made internally to disperse effectively the flow emanating from the inlet pipe and to avoid any short-circuiting of flow between the inlet and outlet pipes with the consequent creation of "dead" zones within the tank. The crest of the weir controlling the water-level in the tank shall be sharp, horizontal and of sufficient length to control the head on the outlet pipe within limits of ± 0,25 % of this head regardless of minor fluctuations in the rate of inflow. The back of the weir plate shall be smooth. The weir shall extend completely across one side of the tank to avoid "contractions" and should preferably be situated immediately above the outlet pipe. Arrangements shall be included for the collection of any solution which overflows from the tank during a test. A range of injection flow rates may be obtained by using a set of orifice plates or nozzles of appropriate dimensions.

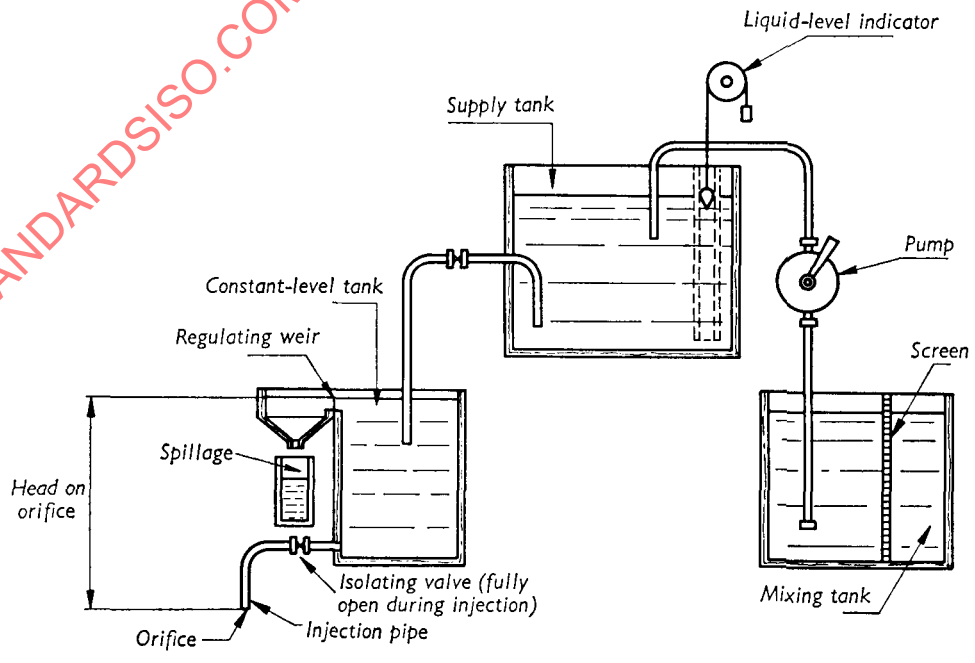

FIGURE 3 – **Arrangement for injecting concentrated solution by means of a constant-level tank with a regulating weir**

b) *A volumetric pump driven by a constant-speed motor*

If a volumetric pump (for example as shown in Figure 4) is used, it shall be of the rotary type and great care shall be taken to ensure that the speed of this pump is constant. The speed can be determined either directly or, if driven by a synchronous electric motor, from a knowledge of the supply frequency.

c) *A Mariotte vessel* (for example as shown in Figure 5).

d) *A floating siphon* (for example as shown in Figure 6).

8.2.1 *General recommendations*

It is generally desirable, even when the injection rate can be calculated from the pump dimensions or from the details of one of the other devices, that a second measurement method be incorporated in the injection apparatus, to serve as a check on the accuracy and repeatability of the methods.

Where the natural turbulence of the stream is not such as to ensure uniform and homogeneous mixing of the two liquids within the predetermined measuring-reach, the distribution of the concentrated solution may be assisted by the use of perforated pipes spanning the injection cross-section. Care shall be taken to ensure that the whole flow of concentrated solution reaches the stream, i.e. that none is deposited on the banks or on rocks above the water-level.

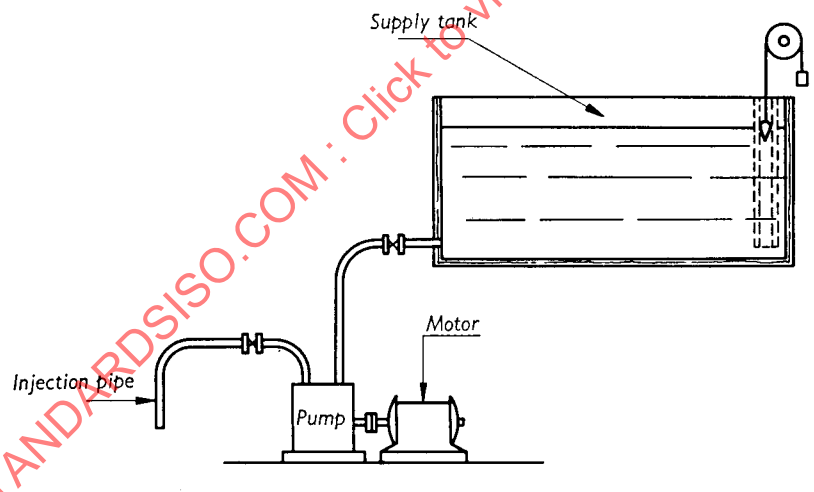

FIGURE 4 — **Arrangement for injecting concentrated solution by rotary volumetric pump**

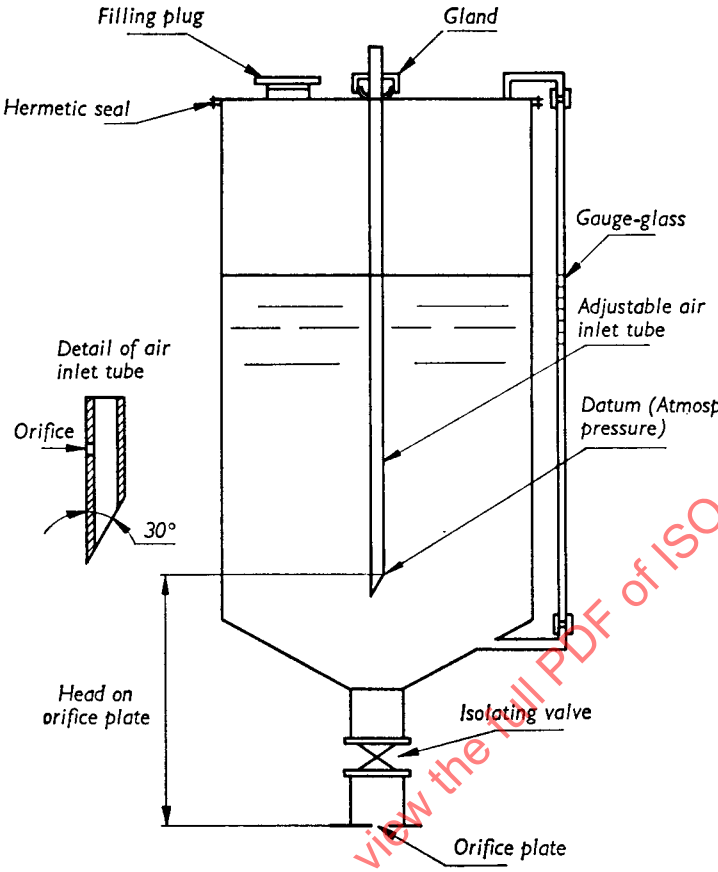

FIGURE 5 – **Mariotte vessel for injecting concentrated solution**

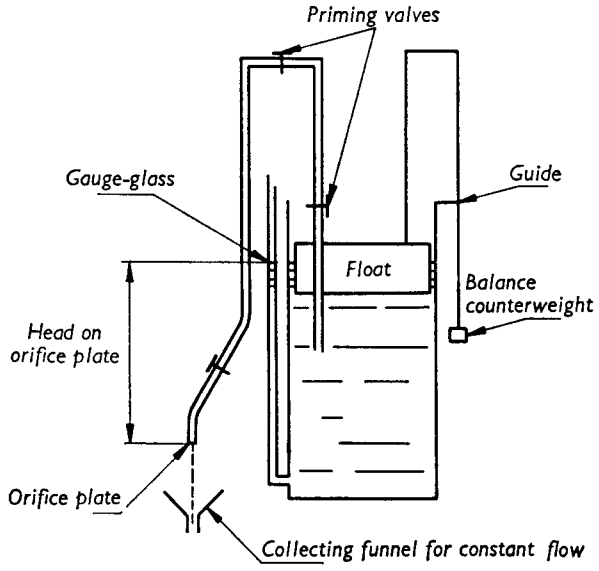

FIGURE 6 – **Floating siphon for injecting concentrated solution**

8.3 Measurement of rate of injection

The rate of injection of the concentrated solution may be measured by direct observation if the regulating device used has been previously calibrated. Where the rate of injection is controlled so that it is constant but is not exactly determined, it may be ascertained indirectly by measuring the total volume of solution discharged over a measured period of time.

The degree of accuracy with which the rate of injection can be measured depends on the particular measuring device used. Suitable devices are described in 8.3.1 and 8.3.2, and the estimates of accuracy associated with the particular device shall be taken into consideration when estimating the overall accuracy of the flow measurement in the channel.

8.3.1 *Direct measurement of rate of injection*

The rate of injection shall be determined from readings, taken during the injection period, of one of the following characteristics, depending on the device used :

a) level of constant-level tank in relation to terminal orifice;

b) speed of pump;

c) level of orifice in relation to the atmospheric pressure datum in the Mariotte vessel;

d) height between solution surface and orifice of floating siphon arrangement;

e) reading of flow-meter.

For procedures a), c) and d) described above, the rate of injection of the concentrated solution can then be determined from the calibration curves for these devices. The devices shall be calibrated both before and after the tests, and if the two calibrations differ by more than 1 %, the tests shall be repeated. If a volumetric pump is used as in procedure b), it is advisable that a calibration check be carried out before and after the tests to check that there is no leakage or, alternatively, to determine the leakage if this exists, that is to calibrate the pump under the same conditions as those experienced during the test. There shall not be a difference of more than 1 % between the two calibrations.

A flow-meter may be installed in the injection apparatus for the specific purpose of measuring the rate of injection. It shall be calibrated before and after the test and these calibrations shall be carried out with the meter installed in the apparatus.

Calibration is not necessary :

a) if the meter has been manufactured and installed in conformity with the specifications laid down in ISO/R 541, in particular if sufficient lengths of straight pipe have been installed on either side of the meter;

b) if it can be shown that an adequate straightening device has been incorporated to ensure that the available meter-calibration data are unaffected by any flow disturbances caused by the injection apparatus.

The flow-meter may conveniently be an orifice plate placed between the flanges of two lengths of straight pipe connecting the injection apparatus to the injection point. Its parts shall not be affected by the chemical solution being used.

The average of the two calibrations of the device or meter, carried out before and after the test, shall be used in the calculation of the rate of injection.

8.3.2 *Indirect measurement of rate of injection (volumetric method)*

Indirect measurement of the rate of injection involves the determination of two factors : the duration of the discharge and the total volume of solution delivered :

a) The time which elapses between the commencement of injection and its termination shall be measured to an accuracy of within ± 0,1 % of the period of injection.

b) The volume may be measured by observing the drop in level in a previously calibrated feed-tank or by the use of a positive-displacement meter.

8.3.2.1 CALIBRATION FEED-TANK

Where the volume of concentrated solution is to be measured in a calibrated feed-tank, the tank which has to be calibrated shall be erected so that the vertical axis of the tank is truly vertical. If calibration is made by mensuration of the tank, it shall be ensured that no distortion takes place when the tank is subsequently filled. Horizontal cross-sections shall be measured to an accuracy of 0,1 % at intervals sufficient to enable the height/volume relationship to be determined with an accuracy of ± 0,25 %. Bolt heads or bolt shanks and nuts shall be measured for each type and counted and the appropriate deductions made at the requisite levels. Internal flanges, tie-rods or other structural members shall be measured and the appropriate deductions also made. These measurements shall be carried out immediately before the tank is used.

Alternatively, the height/volume relationship may be determined by the use of a smaller calibrated vessel, the contents of which shall be added to the main tank, and the height measured in successive steps. The smaller vessel shall be calibrated to an accuracy of ± 0,1 % by weighing the contents.

Where the rate of injection is controlled by a constant-head tank, the spillage therefrom shall be collected and measured in a vessel calibrated to an accuracy depending on the ratio of the amount of spillage to the amount injected. If this ratio is a, the spillage shall be measured to an accuracy of

$$\pm \frac{1}{10\,a}\ \%$$

Alternatively, the spillage may be collected and returned to the main tank before the final reading is taken.

8.3.2.2 POSITIVE-DISPLACEMENT METER

Where the volume of concentrated solution is measured by means of a volumetric meter, the meter shall be of a positive-displacement type and shall have been calibrated recently to give an accuracy of ± 1 % or better.

The meter shall be connected in the pipelines between the constant-head tank and the injection point and shall be of such size and so placed, in relation to the constant-head tank, that sufficient operating head is available to sustain flow through the meter to the injection point at the greatest injection rate required.

Precautions shall be taken to remove all suspended impurities from the concentrated solution before it is delivered to the constant-head tank.

The volume of solution delivered shall be ascertained from the difference between the readings on the meter index before and after the injection.

8.4 Sampling

Samples shall be taken as follows :

a) Upstream from the injection cross-section, generally two or three samples before and after the injection.

However, if any variation of the background concentration is anticipated along the measuring-reach, the samples of the natural water shall be taken at the downstream sampling station before and after the passage of the salt solution.

b) At the outlet of the injection apparatus, three to five samples are recommended, either just before and just after the injection period or, alternatively, during the injection period. It should be noted that sampling during the period of injection will affect the total amount of the salt injected and the constancy of the injection rate. However, this source of error is generally negligible.

c) At two or three points in the sampling cross-section, at regular intervals during the steady regime, five to ten samples at each point.

These samples shall be taken by means of immersing bottles or by pumping. With a view to avoiding the influence of more or less rapid chance variations of the concentration in the sampling section, it is recommended that the time taken between successive samples be as short as possible.

9 PRINCIPAL CHEMICAL SUBSTANCES AND METHODS OF ANALYSIS IN PRESENT-DAY USE

9.1 Method of colorimetric analysis

9.1.1 *Choice of chemical substance and minimum concentration that can be measured*

The salt at present favoured for applying the constant-rate injection dilution method with colorimetric analysis is sodium dichromate. Its solubility in water is relatively high (concentrations up to approximately 600 g/l of water may be used in practice) and the salt satisfies most of the requirements of section 6.

Colorimetric analysis permits the measurement of very low concentrations of sodium dichromate. With final concentrations between 0,2 and 2 mg/l, the accuracy of the analysis will depend upon the concentration used and the sensitivity and accuracy of the colorimetric apparatus.

Natural waters do not generally contain chromium ions in solution. The presence of such ions would lead to errors in the measurement. The nature and quantity of any matter in suspension in the natural water can seriously affect the accuracy of analysis.

9.1.2 *Method of analysis*

The principal of colorimetric analysis is to compare, by means of a colorimeter, the dilutions of sodium dichromate (the natural dilution of the samples from the channel and the standard dilutions), by their absorption of light after a reagent has been added to each solution.

The recommended reagent has the following composition :

– Diphenylcarbazide (crystallized)	$[(C_6H_5NH.NH)_2\ CO]$	: 0,25 g
– Phthalic anhydride (crystallized)	$(C_6H_4\langle^{CO}_{CO}\rangle O)$	: 4,0 g
– Ethyl alcohol, 95 % (*V*/*V*)	(C_2H_5OH)	: 100 ml

To 50 ml of the sample which is being analyzed, 10 drops of concentrated sulphuric acid (H_2SO_4) having a relative density of 1,84 should be added to obtain an acid solution, followed by 2 ml of the reagent mentioned.

The action of this reagent is sufficiently rapid in an acid medium for the colorimetric measurement to be made about 2 min after introduction of the reagent into the solution.

The analytical procedure shall be carried out in the following manner :

9.1.2.1 CALIBRATION OF THE COLORIMETER

From one of the samples taken at the outlet of the injection device, a number of standard solutions (with a minimum of four) shall be made, having a known dilution approximating to the dilution occurring in the channel.

For this purpose, a sample of the concentrated injection solution is diluted by means of calibrated flasks and pipettes with water from the channel, taken from a point upstream of the injection section. These samples can then be measured in the colorimeter and the readings, which are a function of the dilution ratio, plotted on a curve.

It is recommended that a colorimeter be used which gives a linear relationship between colour intensity and meter reading.

The calibration in the flasks and pipettes is one of the major sources of error in this method. With commercial grade equipment, this error may reach ± 1 % for a dilution ratio of 50 000. To reduce the systematic influence of this error, a precise calibration of the apparatus used for carrying out these standard dilutions shall be made.

The concentration of the injected solution shall be checked for uniformity by analyzing identical dilutions of the samples taken (see 8.4 b)).

9.1.2.2 Measurement of dilution of the samples from the downstream section

The samples taken downstream are then analyzed in the colorimeter. The calibration which has already been made makes it possible for the dilution ratio to be obtained, and the average value of the dilution ratio for the samples as well as their standard deviation can be computed.

It is recommended that a further calibration of the apparatus, with the help of standard solutions, be effected at this stage. Variation between the two calibrations, which may occur because of drift in the colorimeter or instability of the reagent, shall not be greater than 1 %.

9.1.2.3 Recommended precautions

Because of the influence of the passage of time on the diluted solution of sodium dichromate, it is necessary, where an accuracy of the order of ± 1 % is required, to make the analysis within a few hours of the actual test.

If, however, some days must elapse between the sampling and the making-up of standard dilutions and their analysis, it is recommended that the following precautions be taken against the risk of changes in the dichromate solutions:

- the samples should be kept in the dark;
- at least three standard dilutions, approximately equal to the dilution in the actual sample, should be made on the spot and kept under exactly the same conditions as all the other samples.

Any error caused by changes in the samples with time can be estimated by comparing standard dilutions of the same concentrated solution prepared at different times. This latter precaution is particularly recommended when the water contains organic matter which would reduce the sodium dichromate.

If, as happens frequently, the water is not perfectly clear and contains solid matter in suspension, the samples shall be left to settle before the colorimetric analysis. In addition, any difference of turbidity between the samples taken at the sampling section and the standard dilutions shall be taken into account. To do this, a correction curve can be obtained of the reading of the colorimeter after the introduction of the reagent into the solution as a function of the reading obtained before the addition of the reagent. This last reading characterizes the turbidity. This technique may lead to errors if the degree of turbidity is very high, or in certain cases where the particles are extremely small. It is recommended that, in such cases, a much stronger concentration than usual be used in the injection solution and that samples taken downstream be diluted with equal amounts of clear water after stirring.

An alternative procedure for silted waters is to filter the dilute samples before the addition of the reagent and also to filter the standard dilutions made up from the concentrated solution and water taken from the cross-section upstream from the injection point. For the standard solutions, filtering is again carried out before addition of the reagent. It is necessary to check that any absorption of sodium dichromate by the silt is negligible before this procedure is adopted.

9.2 Conductivity method

9.2.1 *Choice of chemical substance and minimum concentration that can be measured*

The substance to be injected shall satisfy the requirements stated in section 6, and, in particular, its ionizing power has to be very high in order that when present in small concentrations in natural water, the resulting increase in conductivity can be measured with sufficient accuracy.

The chemical salt most frequently used is sodium chloride (NaCl) which has a solubility of 360 g/l at 15 °C. For concentrations up to 50 mg/l, the relation of its conductivity to concentration is almost linear. In aqueous solutions, at a temperature of 18 °C, the variation of conductivity is 1,86 µS/cm for 1 mg/l. 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 limiting 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 error of the order of ± 1 % by the conductivimetric method are shown in the following table as a function of the conductivity of natural water.

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

Conductivity of natural water (µS/cm)	1 000	200	100	20
Minimum concentration of NaCl, measurable with ± 1 % accuracy (mg/l)	10	2	1	1
Corresponding relative variation of conductivity of water as a percentage	2	2	2	10

9.2.2 *Methods of analysis*

9.2.2.1 Comparison of the variations of conductivity

By continuous recording of the conductivity of the water during the test, the mean value of the variation of

conductivity during the steady-regime condition produced by the injection of salt can be determined. The procedure used is either interpolation in time from the conductivity measurements made before and after the passage of the saline solution, or measurement during the test of the conductivity of the water at a section upstream from the injection section. This latter procedure is the only one possible if the variations of conductivity with the passage of time are relatively large, but allowance must then be made for the time during which the water passes from the upstream measurement section to the sampling 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 to a sample of natural water taken upstream of the injection cross-section a measured quantity of the concentrated solution 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.

Because of the great influence of temperature on the specific conductivity of electrolytes, it is necessary to carry out the calibration at the same temperature as that measured during the test. For a solution of common salt, the relative variation of conductivity is of the order of 2 to 3 % per degree Celsius so that, for accurate measurement (± 1 %), the temperature difference between that in the test and that in the calibration shall not be more than ± 0,1 °C. In addition, the fluctuations of temperature during the test and during the calibration shall be checked to within ± 0,01 °C. Such accuracies can be obtained with instruments such as thermistors. The same instrument shall be used for both the field and laboratory measurements. The temperature shall 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.

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, that is to the reciprocal of the dilution ratio; it is recommended therefore that the variation of the conductivity curve be plotted as a function of the reciprocal of the dilution ratio.

9.2.2.2 Comparison of conductivities

The quickest method would be to compare the conductivity of the water of the river at the moment of passage of the salt cloud with that of a series of standard solutions obtained by diluting, in known proportions, the concentrated solution with water taken upstream from the injection section.

This method is not generally of high accuracy, because of the great differences of natural resistivity between different samples.

It is found that the natural conductivity can vary appreciably during the period of time of a test and, furthermore, it is difficult to avoid completely all variations of resistivity in the samples between the time of sampling and the time of analysis.

9.3 Method of volumetric chemical analysis

9.3.1 *Choice of chemical substance and minimum concentration that can be measured*

As an example of the volumetric method of chemical analysis to determine the dilution ratio, that used for the detection of sodium dichromate is given in detail. Sodium chloride may also be used and detected by titration against silver nitrate ($AgNO_3$) using an indicator to determine the end-point of the titration, but the results are liable to serious error if there is any appreciable colouring matter in the natural water as the technique normally requires evaporation of the sample, and the colour change of the indicator is then difficult to detect. Electrical means of detecting the end-point may be used under these conditions.

Volumetric analysis of sodium dichromate can be carried out with better than ± 1 % accuracy on final sample concentrations as low as 3 mg/l.

As stated in 9.1, the use of sodium dichromate is advantageous as natural waters do not generally contain chromium ions. It should be noted, however, that this chemical is easily affected by reducing agents in the water and initial tests shall be carried out to ensure that there will be no serious effect on the samples between the time of sampling and the time of analysis. The samples can be re-oxidized by boiling with persulphate but the time of analysis is considerably lengthened if this procedure is adopted.

9.3.2 *Method of analysis*

The principle of the method is that the total amount of the salt present in the sample should react 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) Ferrous ammonium sulphate

A stock N/10 solution of this salt should be prepared by weighing out 39,22 g of pure ferrous ammonium sulphate [$FeSO_4(NH_4)_2SO_4.6H_2O$] and dissolving it in 500 ml of distilled water containing 10 ml of concentrated sulphuric acid (H_2SO_4) having a relative density of 1,84. The resulting solution is then made up to 1 l.

For titrating against the samples, an N/200 solution should be made up by taking 100 ml of the stock solution and diluting to 2 l with distilled water.

b) *N*-phenylanthranilic acid indicator

1,07 g of *N*-phenylanthranilic acid ($C_6H_5.NHC_6H_4COOH$) should be dissolved in 20 ml of a 5 % sodium carbonate (Na_2CO_3) solution and made up to 1 l.

0,5 ml of this solution should be used for each titration.

To 500 ml of the sample which is being analyzed, 10 ml of concentrated sulphuric acid shall first be added and the sample stirred continuously throughout the titration.

The general precautions recommended in 9.1.2 should be followed and the standard solutions should be prepared as described therein. The results of the titrations of the standard solutions can be plotted and the best straight line drawn through the points with the condition that it passes through a point close to the origin of the axes of the graph. The position of this point depends upon the amount of indicator used in the titration but, if the recommended procedure is followed, the point should be about + 0,5 ml on the ferrous ammonium sulphate axis.

It is important that a standardized procedure be used in the analysis of all the samples. This applies particularly to the amounts of the acid and indicator added and to the rate at which the ferrous ammonium sulphate is added during the titration.

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

10 ERRORS IN FLOW MEASUREMENTS

No measurement of a physical quantity can be free of uncertainties which may be associated with either systematic deviations caused by errors in the standardizing equipment or a random scatter caused by a lack of repeatability of the 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 n repeated measurements is $\sqrt{n}$ 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 and a statistical estimate made of the likely "tolerance". The tolerance with 95 % confidence limits on a measurement may be defined statistically as the bandwidth around the calculated value, which, on an average of 19 times out of 20, can be expected to include the true value. The tolerance with 95 % confidence limits 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 tolerance 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 $x_1, x_2, \ldots$

If an independent quantity y has been obtained by n 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 $y_1, y_2, \ldots, y_n$, then the standard deviation of the average y_0 of the n measurements may be defined by :

$$\delta y_0 = \sqrt{\frac{\sum_{i=1}^{i=n}(y_i - y_0)^2}{n(n-1)}}$$

If the value of an independant 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 tolerance, with 95 % confidence limits, for a flow measurement by the constant-rate injection method, is given by :

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

the partial derivatives being unity here. The standard deviations on the quantities q and N, which themselves may have been determined by any of the different methods contained in this International Standard, shall 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.

$$\left(\frac{\delta q}{q}\right)^2 \text{ and } \left(\frac{\delta N}{N}\right)^2$$

Numerical examples of the estimation of the overall tolerance on a flow measurement are given in Annexes A and B. The examples are only illustrations of the procedure and individual figures should be estimated by the user for each particular test.