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Measurement of liquid flow in open channels — Tracer dilution methods for the measurement of steady flow —

Part 3:
Chemical tracers

Mesure de débit des liquides dans les canaux découverts — Méthodes de dilution en régime permanent utilisant des traceurs —

Partie 3: Traceurs chimiques

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Contents

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Foreword

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

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 9555-3 was prepared by Technical Committee ISO/TC 113, *Measurement of liquid flow in open channels*, Sub-Committee SC 4, *Dilution methods*.

ISO 9555 consists of the following parts, under the general title *Measurement of liquid flow in open channels — Tracer dilution methods for the measurement of steady flow*:

— *Part 1: General*

— *Part 2: Radioactive tracers*

— *Part 3: Chemical tracers*

— *Part 4: Fluorescent tracers*

Annex A forms an integral part of this part of ISO 9555.

Introduction

The former standard series ISO 555 was subdivided into parts on the basis of the method of field measurement, i.e. constant-rate injection method and integration (sudden injection) method. Since the choice of the type of tracer to be used in a field measurement will often depend on the expertise and the laboratory facilities available, this new series of standards ISO 9555 is divided into parts based on the type of tracer used. This revision has enabled the unnecessary repetition of text of the various parts to be avoided and will, it is hoped, prove to be a more convenient form of presentation for the user.

ISO 9555 deals with the measurement of steady flow in open channels by dilution methods using tracers. The methods described may also be applied to the measurement of slowly varying flow, but they may only be used when flow conditions ensure adequate mixing of the injected solution throughout the flow.

For the measurement of very large flows, tracer methods can be onerous in terms of tracer costs and measurement times. However, the use of tracers often reduces danger to personnel during flood periods.

ISO 9555-1 presents the general principles of the methods of constant-rate injection and integration (sudden injection). ISO 9555-2, ISO 9555-3 and ISO 9555-4 deal with the specific aspects of the use of radioactive, chemical and fluorescent tracers, respectively, as well as specific analytical procedures.

This approach has been adopted for the following reasons:

— to facilitate subsequent updating, additions or revisions which concern only ISO 9555-2, ISO 9555-3 or ISO 9555-4;

— to provide a more practical document for the user, who is often obliged to choose the tracer best suited to the available analytical equipment.

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Measurement of liquid flow in open channels — Tracer dilution methods for the measurement of steady flow —

Part 3:
Chemical tracers

1 Scope

This part of ISO 9555 deals with the use of chemical tracers in discharge measurements by the dilution method. Apparatus and methods of general application are set out in ISO 9555-1 and are not repeated here, with the exception of those relating specifically to chemical tracers.

Chemical tracers have several advantages as follows.

a) As with fluorescent tracers, the handling of the tracer follows normal chemical laboratory practice, and no special equipment (e.g. radiation shielding) is required. Care is still required, however, when handling concentrated tracer, to avoid contamination of samples and, with some tracers, for reasons of chemical toxicity.

b) In general, chemical tracers are widely available commercially, and may be stored indefinitely.

c) Analysis may be possible using laboratory facilities currently used for water quality determination.

d) In general, chemical tracers are photochemically stable.

The disadvantages of chemical tracers are as follows:

a) Their detection limits are relatively high and therefore a larger quantity of tracer is required for each gauging than in the case of radioactive or fluorescent tracers. For practical reasons this may restrict their application to small discharges. However, for certain tracers, reconcentration techniques can permit the measurement of large discharges (of the order of 1 000 m^3/s) where conditions of mixing and tracer loss are acceptable.

b) With the exception of the conductivity method for sodium choride, the determination ranges of laboratory analysis methods are limited, so dilution of river samples may be necessary before analysis. This limitation means that the constant-rate injection method is preferable for chemical tracers (excepting the conductivity method) since determination of the peak concentrations resulting from a sudden injection would be difficult.

c) Natural background levels, particularly of conductivity (resulting from dissolved solids in natural waters), may be high and variable, and this necessitates the use of a larger amount of tracer than would be apparent from a consideration of detection limits only.

d) It is not possible to use a carrier, as in the case of radioactive tracers, and losses by adsorption may be serious in some cases.

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this part of ISO 9555. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this part of ISO 9555 are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 772:1988, *Liquid flow measurement in open channels — Vocabulary and symbols.*

3 Definitions and symbols

3.1 Definitions

Definitions relating to many aspects of flow measurement, including dilution methods, are given in ISO 772. For the purposes of this part of ISO 9555, the following definitions apply.

3.1.1 ion-selective electrode: Potentiometric probe, the output potential of which, when measured against a suitable reference electrode, is proportional to the activity of the selected ion in the solution under test.

3.1.2 interference: Error in the determination of a chemical ion, caused by the sensitivity of the analytical method to the presence of other ions in solution.

3.1.3 Beer-Lambert law: A physical law stating that the absorption of light energy by an absorbing medium varies exponentially with the light path length through the medium and with the molar concentration of the medium.

3.1.4 colorimetry: Chemical analysis method based on the measurement of the absorption of visible light in a given range of wavelengths by substances in solution according to the Beer-Lambert law.

3.1.5 atomic absorption flame spectrometry: Chemical analysis method based on the measurement of the absorption of visible light in a given range of wavelengths by a sample atomized in a flame according to the Beer-Lambert law.

3.1.6 atomic emission flame spectrometry: Chemical analysis method based on the measurement of light in a given range of wavelengths emitted by a a sample atomized in a flame according to the Beer-Lambert law.

3.1.7 adsorption: Removal of ions from solution by a solid surface.

3.1.8 conductivity method: Technique for determining the concentration of the tracer by means of electrical conductivity.

3.2 Symbols

The symbols used in this part of ISO 9555 are defined where they occur in the text.

3.3 Units of measurement

The units of measurement used in this part of ISO 9555 are SI units.

4 Tracers used

4.1 General

The chemical tracers in common use are as follows:

a) iodide as sodium iodide, solubility 1 800 kg per m^3;

b) lithium as lithium chloride, solubility 600 kg per m^3;

c) chloride as sodium chloride, solubility 350 kg per m^3;

d) chromium as sodium dichromate, solubility 800 kg per m^3.

Bromide and fluoride are satisfactory tracers but are not in common use. Other substances such as manganese sulfate and sodium nitrate have also been used.

The general characteristics of commonly used chemical tracers are given in annex A.

4.2 Iodide

Sodium iodide and potassium iodide are highly soluble, and solutions of both have been used as tracers; sodium iodide is cheaper per unit mass of iodide. The iodide ion may be determined by catalytic spectrophotometry, or by using an ion-selective electrode. In each case the detection limit is approximately 1 µg/l and a practical working range is 10 µg/l to 100 µg/l. Concentrations in natural fresh waters may reach 2 µg/l but are usually much lower. The catalytic spectrophotometric method is preferred for laboratory analysis (see 5.1.1.1) while the ion-selective electrode method may be applied *in situ* (see 5.1.1.2 and 5.2.1).

4.3 Lithium

Lithium is available as a variety of salts and the chloride is generally used for tracer studies. Lithium chloride is the cheapest chemical form for a given weight of lithium; lithium brine, which may contain up to 83 g of lithium per litre, is more convenient to handle than anhydrous lithium chloride which is deliquescent and dissolves exothermically (see 10.2.1).

Lithium is normally determined either by atomic emission flame spectrometry or atomic absorption flame spectrometry, and the detection limits are

typically 0,1 µg/l and 10 mg/l respectively. Concentrations in open-channel flows range from less than 0,1 µg/l in mountain streams to greater than 10 mg/l in mineral processing plant effluents. Sewage effluents, and some rivers receiving these, can contain typically 10 µg/l to 50 µg/l. Destructive analysis uses a few millitres of sample, but techniques such as flameless atomic absorption spectrometry may be used if only very small sample volumes are available.

4.4 Chloride

The conductivity method owes its popularity to the relative simplicity and low cost of conductivity meters that can be used in the field, and to the properties of the tracer (sodium chloride) which is characterized by a high degree of electrolytic dissociation when dissolved in water, easy availability and low price, and a moderate solubility, with little dependence of solubility on temperature. Furthermore, sodium chloride is relatively harmless to animal and plant life in the concentrations used, and shows little adsorption by vegetation and the materials of the streambed.

A disadvantage of the conductivity method is the high background level, typically 25 mS/cm to 500 mS/cm, resulting from naturally occurring dissolved solids. Although the detection limit of sodium chloride approaches 0,5 mg/l with generally available conductivity meters, the conductivity of natural waters is such that large quantities of sodium chloride may be required to give an accurately measurable change in the conductivity of the stream water. The tracer must be diluted with large quantities of water to obtain an injection solution with a specific gravity that is sufficiently low to avoid density segregation.

4.5 Chromium

Chromium is used as a tracer in the form of sodium dichromate; the process of solution is endothermic.

Hexavalent chromium at 0,1 mg/l can be analysed directly by colorimetry using suitable reagents, but it is also possible to perform a preliminary reconcentration by extraction, and thus to improve the sensitivity of the method by a factor of 10, or even 100, to detect 1 µg/l.

Total chromium in similar concentration ranges is analysed by atomic absorption flame spectrometry.

5 Tracer measurement

5.1 Principles

5.1.1 Iodide

5.1.1.1 Catalytic spectrometric method

The iodide ion in weak solution may be determined by its catalytic effect on the rate of the reaction between the ceric ion and arsenious acid. The yellow colour of a ceric solution is measured spectrometrically at a fixed time after the start of the reaction and the reduction in absorbance, caused by a faster reaction in the presence of iodide, is recorded. Close control of the temperature of the reacting solutions is essential. Concentrations of iodide are determined by reference to a calibration curve. Standards for the preparation of the calibration curve are made up using a large "background" sample, taken from the flow upstream of or before the injection, as a diluent.

Background coloration, turbidity or the presence in the water of substances capable of reducing ammonium cerium(IV) sulfate interfere in the procedure. Reaction mixtures derived from coloured or turbid waters have a lower transmission than those derived from distilled water, and this shift in transmission is more pronounced in those reaction mixtures containing higher concentrations of iodide, leading to a lowered gradient of the calibration curve for coloured waters. This behaviour and the curvilinear nature of the calibration curve mean that it is necessary to construct a calibration graph for each gauging exercise, using background water as a diluent. This procedure also has the advantage that any other unknown interfering substances are present at the same concentration in both the samples and the standards.

5.1.1.2 Ion-selective electrode method

The ion-selective electrode (or more precisely the cell consisting of the ion-selective electrode, the sample and a reference electrode) produces a difference in electrical potential which is related, within a certain range, to the activity of the iodide ion in solution. For solutions of concentration less than about 0,000 1 mol/l (12,7 mg/l, or a molar solution of sodium iodide having a concentration of 127 g/l) the following equation holds:

$$E = E_0 - 59{,}12 \lg I \text{ (at 25 °C)}$$

where

E is the potential measured, in millivolts;

E_0 is the standard potential, in millivolts;

I is the concentration of the iodide ion in solution, in moles per litre.

In normal use, both the samples and the standards used to establish the calibration curve are brought to a constant total ionic strength by the addition of an equal volume of 2 mol/l analytical reagent grade potassium nitrate solution. The potential across the cell is measured using a high-impedance meter, and the iodide concentration is determined by reference to a calibration curve.

In dilution gauging, it is necessary to know only the concentration of tracer added to the river water during the gauging, and it is preferable to use stream background water as a diluent when making up calibration standards, as this procedure overcomes problems with interfering substances, i.e. those substances, in addition to iodide, to which the electrode is sensitive. Iodide present in the background water could lead to slight deviations from linearity in the curve of logarithmic concentration versus electrical potential.

5.1.2 Lithium

The flame spectrometric method, normally used in the laboratory, is based on measuring the energy transitions which lithium atoms undergo in a flame. In this method lithium atoms are produced by feeding the sample solution, as fine droplets, into a flame. In atomic emission instruments the processes in the flame excite the lithium atoms above their ground energy state, and the atoms then stabilize by emitting light predominantly at a wavelength of 671 nm. In atomic absorption instruments light of the principal emission wavelength of 671 nm is passed through the flame and its absorption by lithium atoms, as they are excited from their ground energy state, is measured. The emission method is more sensitive than the absorption method but the latter is less subject to interference, for example by calcium.

There is an optimum flame temperature, since ionization increases with flame temperature, reducing the number of atoms available for excitation in the flame. Elements present in the solution which undergo ionization less readily than lithium, e.g. magnesium, will also increase lithium ionization by competing for free electrons in the flame. Conversely, elements which ionize more readily than lithium, e.g. potassium, will increase the production of free lithium atoms. The formation of complex molecular species of lithium, e.g. lithium oxide or hydroxide, in the flame will reduce the number of lithium atoms, and complex molecules of other elements, e.g. calcium, may interfere spectrally. Clearly, sample composition plays an important part in analytical sensitivity and reproducibility. Where possible all samples, including comparative solutions, shall have as similar a composition as possible, except for their lithium content, and shall be processed in as similar a manner as possible. The stability of the concentration of competing ions, as well as of the naturally occurring lithium, shall be checked during a tracer exercise by a full examination of the samples taken, preferably at the sampling site, before and after the tracer injection. Alternatively, regular samples may be taken upstream of the injection point during a tracer injection provided that there is no ingress of water into the stream between the tracer sampling site and the background sampling site.

5.1.3 Chloride

The conductivity method is based on the determination of tracer concentration in the stream by an indirect method, i.e. by a change in the electrical conductivity of the water. The application of this principle is facilitated by the fact that in very dilute electrolytes there is a linear relationship between the tracer concentration, c, and the electrical conductivity, S:

$$c = KS$$

where K is a coefficient of proportionality which varies according to the tracer.

NOTE 1 For sodium chloride, for example, the variation in conductivity is 1,86 µS/cm for 1 mg/l of salt at 18 °C, and the linear relation holds up to concentrations of 5,8 g/l.

The water conductivity is measured using an instrument in which the electrical resistance between two electrodes is determined by an alternating current bridge circuit operating at a frequency of the order of 2 kHz. The use of alternating current is necessary to inhibit the production of gas bubbles by electrolysis of the water. It is possible to obtain relatively inexpensive portable instruments, powered by internal batteries, that can be used to make single measurements or to record continuously.

5.1.4 Chromium

5.1.4.1 Colorimetry

Samples are not sufficiently coloured for direct colorimetric analysis; it is necessary to produce a colour by the addition of a reagent. The principal reagent used for colorimetric determination of hexavalent chromium is based on diphenylcarbazide (DPC) $[(C_6H_5)_2CO(NH)_4]$.

The complex formed by the addition of this reagent to aqueous solutions of hexavalent chromium (Cr^{6+}) is rose-violet in colour and obeys the Beer-Lambert law with a peak intensity around 545 nm. The action of the reagent is enhanced in acidic medium.

Several solvents of DPC can be used to prepare the reagent, for example, the preparation 0,125 g of DPC, 2 g of phthalic anhydride and 50 ml of pure ethanol requires vigorous agitation and heating of the solution to about 50 °C to obtain effective solution of the phthalic anhydride, while in the case of the preparation 0,125 g of DPC and 50 ml of highly pure acetone dissolution is almost immediate; however, the flask must be sealed hermetically to avoid evaporation of the acetone.

These two reagent solutions are stable for several days if protected from light.

The colorimetric analysis of sediment-laden water is affected by scattering and diffraction of light by the particles in suspension. Therefore, preliminary clarification of filtration of the solution is necessary in this case (see ISO 9555-1).

5.1.4.2 Atomic absorption flame spectrometry

This physical method for analysing metallic elements uses the property of atoms to absorb quanta of energy at certain wavelengths. The solution to be analysed is vaporized in a flame which atomizes the elements present in the solution. The flame is traversed by a modulated light beam coming from a source consisting of a hollow cathode lamp, whose cathode, composed of the metal to be analysed, emits a spectrum containing the absorption lines peculiar to the element considered. The measurement of the intensity of this light beam before and during vaporization permits the determination of the concentration of the element being analysed.

For chromium the most strongly absorbed spectral line is 357,8 nm and the calibration curve follows the Beer-Lambert law for a range of concentration between 0,5 µg and 100 µg of chromium per litre.

5.2 Field measurement

5.2.1 Iodide

The iodide ion may be determined in the field using the ion-selective electrode in a flow cell. The flow cell offers the advantages of a controlled stirring of the sample, and protection from exposure to light. The temperature of the water flowing through the cell shall be thermostatically controlled, as the standard potential E_0 varies at a rate of $-0,6$ mV/K. For precise measurements it is necessary to carry out a controlled addition of an ionic strength adjuster (see 5.1.1.2).

Even without the sophistication of thermostatic control and the ionic strength adjuster, the ion-selective electrode is a valuable indicator of the passage of the tracer (in the sudden injection method, see ISO 9555-1) or the arrival of the steady state (in the constant-rate injection method).

5.2.2 Lithium

There is no field method for the analysis of lithium. Analysis of samples in a field laboratory is feasible but there is little to gain from such a procedure.

5.2.3 Chloride

The amount of tracer injected may be determined indirectly by measuring the electrical conductivity of the injected solution. The linearity of the relation between concentration and conductivity does not hold for very concentrated solutions, and therefore the solution is usually diluted before measurement to bring its concentration into the optimum measuring range (see 5.1.3). The dilution factor is such that the concentration of the diluted injection solution, used for calibration, is of the same order of magnitude as the mean concentration of river samples taken during the passage of the tracer.

Because of the influence of temperature on the conductivity of electrolytes, it is necessary to carry out all determinations at the same temperature. For a solution of sodium chloride, the relative variation in conductivity is of the order of 2 % to 3 % per kelvin; thus for accurate measurement (better than ±1 %) the temperature should not vary more than about 0,1 K.

The natural conductivity of the river water is taken into account either by direct measurement or by an appropriate correction of the zero of the measuring instrument. The latter method is appropriate only if there is no appreciable variation in background conductivity with time.

In the constant-rate injection method, measurements of conductivity may be started at the moment when the conductivity rises above the background level. This gives a simple and reliable means of checking that the steady state is achieved.

In the integration method also, the field recording of conductivity is a valuable guide to the start and duration of sampling.

5.2.4 Chromium

There is no *in situ* analytical method. However, the simplicity of laboratory apparatus, e.g. pipettes and flasks for dilutions, and the use of a colorimeter powered by a battery, make it possible to perform an immediate analysis at the measuring site.

5.3 Laboratory measurement

The laboratory analysis of gauging samples necessitates a delay between the gauging and the analysis, during which time the samples may undergo changes in tracer concentration. As the prin-

ciple of the analysis is the comparison between samples taken in the river and a range of standard dilutions prepared with the injection solution and river water, it is recommended that, where possible, these standard dilutions be prepared immediately after the gauging. Standard dilutions prepared at the time of the gauging and stored under similar conditions to the gauging samples have the best chance of developing in the same way as the gauging samples. This is particularly important in sediment-laden water where there is a risk of loss of tracer. A filtration procedure, such as that described in ISO 9555-1, should be considered.

5.3.1 Iodide

Calibration standards shall be analysed before and after each batch of gauging samples are analysed (for example at the beginning and the end of a morning or afternoon run of analyses), and the standards shall be stored meanwhile in stoppered bottles. Both samples and standards shall be subjected to repeat determinations, and determinations in triplicate should be considered if there is any cross-contamination between consecutive samples or standards. The effects of cross-contamination are minimized by analysing the samples in the order of expected concentration trends, and not randomly.

5.3.2 Lithium

A series of comparative solutions shall be prepared to cover the expected range of tracer dilutions. If it is suspected that the concentration of interfering elements varies from sample to sample, thus causing an inconsistent instrument response to lithium, then a solution additive should be used to reduce the interference. For example, a salt of potassium or lanthanum acts as an electron release agent to enhance the formation of free lithium atoms (see 5.1.2).

Each sample shall be analysed a sufficent number of times to ensure good reproducibility of the instrument reading. During a batch of analyses, measurements shall be carried out on one or two samples (e.g. standard solutions) at set intervals (e.g. every 15 minutes or every ten samples) to check the variation in instrument response with time. To prevent cross-contamination, samples shall be analysed in the order of expected concentration trends and not randomly.

5.3.3 Chloride

The normal practice is the determination of concentrations in the field, by measurement of the conductivity using a portable instrument.

5.3.4 Chromium

5.3.4.1 Colorimetry

To ensure that the results of analyses of samples are comparable, a standard procedure should be followed during the development and continued evolution of the coloured complex after the introduction of the reagent.

After making up the range of standard dilutions, the analysis is conducted in the following manner:

a) put an identical volume of each sample and standard dilution into separate beakers;

b) introduce into each beaker, at constant intervals of time, given volumes of reagent and acid, and stir. For example, for a sample or standard dilution volume of 20 ml, add 1 ml of reagent and 1 ml of sulfuric acid (98 % sulfuric acid diluted 50 times);

c) adjust the zero of the colorimeter with distilled water;

d) pass the samples through the colorimeter in the order of treatment, so that for every sample the same time interval elapses between the introduction of the reagent and the reading;

e) check the drift of the instrument by reintroducing the sample of distilled water at the end of the measurements of standard dilutions and samples;

f) for the constant-rate injection method, check the homogeneity of the injected solution by diluting in the same manner the samples of the injected solution taken before, during or after the injection and analysing them successively.

5.3.4.2 Reconcentration

It is possible to reduce the mass of tracer used, for large flows, by using a reconcentration procedure for analysis. The coloured complex (sodium dichromate plus DPC reagent) contained in a volume V of the sample to be analysed is collected in a small volume V' of 1-butanol (butyl alcohol). The concentration ratio is approximately V/V'.

1-Butanol is only poorly soluble in water, but it is a very good solvent for the coloured complex and its density, which is much lower than that of water, permits collection by phase separation in decantation vessels. It is necessary, however, first to saturate the samples with sodium chloride so as to reduce the solubility of the 1-butanol in the water and to improve the reconcentration factor.

Reconcentation can be performed easily for ratios V/V' between 10 and 20. However, the solubility of neither the acetone of the reagent in 1-butanol nor the 1-butanol in water, is zero, with the result that volumes of the coloured complex/1-butanol mixture recovered decrease as the sample volume V increases; also it is necessary to increase the volume V' of 1-butanol more than simple theoretical calculations demand. For example, it is necessary to introduce 30 ml of 1-butanol into 1 000 ml of sample to obtain a reconcentration ratio of 100.

This procedure of reconcentration by extraction of the coloured complex by butanol is reproducible; the value of the volume recovered does not enter into the calculation when samples and standard dilutions are treated in exactly the same way.

This procedure results in an improvement in the determination when waters are laden with sediment, as materials in suspension are rarely extracted by 1-butanol and remain at the water/alcohol interface; they can therefore be eliminated at the time of withdrawal from the decantation vessel.

5.3.4.3 Atomic absorption flame spectrometry

After making up the standard dilutions (see ISO 9555-1) the analysis is performed in the following manner;

a) the gas flow to the flame, and the height of the burner, are regulated to obtain maximum absorption;

b) samples and standard dilutions are vaporized in the flame in succession;

c) the drift of the instrument is checked by repeating the measurement of the standard dilutions after that of the samples.

The relatively poor sensitivity (0,1 mg/l) of this method permits the measurement only of low flows by injecting very concentrated solutions of tracer.

It is possible to improve the results by using a reconcentration procedure: the hexavalent chromium contained in a volume V of sample is collected in a smaller volume V' of MIBK (methyl isobutyl ketone or 4-methylpentan-2-ol). The concentration ratio is approximately V/V'.

The transfer of chromium from the aqueous phase to the organic phase is favoured by the presence of acid and by vigorous agitation.

6 Environmental factors affecting tracers

6.1 Chemical factors

6.1.1 Iodide

The iodide ion may be adsorbed by organic matter in the stream water. This is unlikely to be a problem for the short duration of a gauging itself, but prolonged storage (more than a week) of gauging samples between gauging and analysis is to be discouraged. Under certain conditions of sediment type and load, the amount of adsorption may be reduced to acceptable levels by immediate filtration of samples (see ISO 9555-1). If it is possible to obtain samples of the background water, with the appropriate sediment load, well in advance of the gauging, a preliminary experiment can be performed by adding known amounts of tracer to samples of unfiltered background water, storing these standards for a period equivalent to the expected lag between gauging and analysis and then comparing their concentrations with those of similar standards prepared just before the analysis from the same water. Filtration of samples at the river bank will be necessary if adsorption is detected by this experiment. Where significant adsorption by organic sediment has occurred, it has been found that different samples will be affected to varying degrees according to the amount of sediment collected in each sample; so for the constant-rate injection method, a low variance in tracer concentration between samples taken from a given point in the sampling cross-section at various times can be accepted as an indicator of low or zero adsorption.

6.1.2 Lithium

Although the lithium ion is a small positively-charged species which might be expected to undergo some adsorption in water, it is solvated with a sheath of water molecules which decreases the possibility of loss by adsorption. Some adsorption or ion exchange reactions may occur with minerals (e.g. clays) and, to a lesser extent, with organic matter (e.g. sewage solids). If adsorption does occur, the effect is usually reversible and results in an increased tracer time-of-travel and dispersion period rather that an incomplete recovery of tracer at a sampling cross-section. The effect is unlikely to be significant in short-term tracer studies.

Samples shall be filtered at the site of collection or as soon as practicable to reduce any adsorption of lithium by suspended solids (see ISO 9555-1). Hydrochloric acid (approximately 1 µl of 12 mol/l acid per millilitre of sample) is then added to the filtrate to reduce adsorption onto sample containers and also to improve the atomization processes in the flame during analysis. Samples may be acidified before filtration, subject to the type of suspended

solids present, if prolonged storage of unfiltered samples is anticipated. A compromise must be considered between the risk of releasing interfering agents and the benefit of either preventing tracer adsorption or releasing adsorbed tracer. Filter papers shall be chosen to give adequate filtration in a short time and should be tested for their ability to adsorb lithium or to contaminate samples with lithium or interfering elements. Comparative solutions shall be prepared by diluting injection solutions in water collected from the sampling site as a spot sample before the tracer test or as an average sample collected immediately upstream of the injection point during the tracer test (see 5.1.2). The sample of dilution water shall be filtered before use and the comparative solutions acidified as described above.

6.1.3 Chloride

There are no significant chemical phenomena affecting sodium chloride used as a tracer.

6.1.4 Chromium

Under the influence of chemical or organic substances the transformation of hexavalent chromium ions (Cr^{6+}) into ions of different valency (Cr^{4+}) prevents accurate determination by colorimetry with DPC reagent. To overcome this disadvantage several procedures are possible.

6.1.4.1 Analysis of total chromium by atomic absorption flame spectrometry

The laboratory analysis procedure remains the same as far as the preparation of standard dilutions, but the comparison of these standard dilutions with the samples is achieved with the use of a flame spectrometer (see 5.1.4.2).

6.1.4.2 Reoxidation

The procedure consists of the regeneration of hexavalent chromium ions using potassium permanganate, phosphoric acid and sodium azide following a well-defined manipulation process. This procedure demands many precautions to ensure reproducibility and shall be carried out if possible by specialists. Certain of the substances to be handled are hazardous.

Reoxidation shall be performed on samples and standard dilutions before the introduction of reagent and acid.

6.1.4.3 *In situ* dilutions

If there is doubt about interaction between the river water and the tracer, it is imperative to prepare the range of standard dilutions in the field immediately after the gauging, so that the reduction phenomenon acts in the same way on the samples and on the standard dilutions. By preparing in the laboratory, at the time of analysis, a new range of standard dilutions, with the same concentrated solution, it is possible to check whether there have been changes in the samples with time.

6.2 Physical factors

6.2.1 Iodide

Concentrated iodide solutions tend to acquire a brown colour on exposure to light. This is caused by the release of iodine, and does not affect the usefulness of the solution as a tracer.

Standard solutions with concentrations as low as 1 mg/l may be kept for long periods in glass bottles, provided that they are not exposed to light and are made up with distilled water. Except for special experimental purposes (see 6.1.1), no attempt should be made to keep standard solutions made up with river water.

6.2.2 Lithium

In addition to the interference effects possible during analysis (see 5.1.2), chemicals in solution may interfere during the tracer study. Lithium may be precipitated as sparingly soluble salts in the presence of certain anions (e.g. carbonate, fluoride, phosphate); this effect may be checked by carrying out tests on a "typical" water sample collected before the dilution gauging exercise. When concentrated tracer solutions (e.g. injection solutions) are prepared and stored for long periods before use, they shall be checked for any insoluble salts which may have formed. Solutions shall be decanted or filtered if necessary.

6.2.3 Chloride

When a conductivity electrode is used *in situ* in flowing water, bubbles of air, leading to erroneous results, may form on the electrode surfaces. In addition, the conductivity of aerated water containing air bubbles, as occurs for instance near a waterfall, is lower than that of still water containing only dissolved gases. Highly turbulent zones in the flow should be avoided: alternatively water can be pumped through a flow cell. Withdrawing the electrode from the water and replacing it will normally remove all bubbles from the electrode surfaces.

6.2.4 Chromium

Sunlight, heat and colloidal materials in suspension are factors which may influence the tracer directly or in the presence of other substances acting as catalysts. In sediment-laden waters adsorption of tracer is to be expected.

To overcome these risks, it is necessary to protect samples from light and all significant sources of heat. In waters laden with colloidal material (glacial or lateritic waters for instance) it is recommended that the range of standard dilutions be prepared in the field immediately after the gauging.

6.3 Biological factors

6.3.1 Iodide

Iodide is likely to be taken up as a micronutrient by micro-organisms in river water, and at the low concentrations normally used in river gauging this uptake may be significant during the storage of samples. The filtration procedure recommended for samples containing organic sediment will help to remove micro-organisms, while refrigeration at 4 °C also retards their activity and would tend to reduce losses of iodide from solution.

6.3.2 Lithium

Losses of lithium as a result of biological activity in a measuring reach are unlikely. There is, however, some evidence of uptake by marine algae, and fish toxicity data (see 10.2.2) suggest biological activity may affect long-term studies.

6.3.3 Chloride

There are no significant biological phenomena affecting sodium chloride used as a tracer.

6.3.4 Chromium

Foams, algae and organic materials are factors likely to affect the concentration of chromium in very dilute solution. It is recommended that sampling devices be fitted with filters to prevent the inclusion of foams or suspended materials in the sample.

7 Techniques for tracer injection

All chemical tracers shall be injected into the stream channel in as dilute a solution as practicable, to minimize density effects (see ISO 9555-1).

8 Sampling techniques

No special techniques are necessary for sampling in dilution gauging using chemical tracers (see ISO 9555-1).

9 Analysis and sources of error

Errors are incurred at each of the three stages of a dilution gauging exercise, i.e. during preparation, during field work and during sample analysis. ISO 9555-1 deals at some length with errors associated with the dilution gauging method. In this clause, only errors specifically associated with the use of chemical tracers will be discussed.

Errors during preparation occur mainly in the determination of the quantity of tracer injected and, where possible, mass of tracer solution should be determined in preference to volume to minimize errors. The stability of the injection solution during storage should also be checked (see 6.2).

Errors during field work arise principally because of the non-conservative behaviour of tracers. Furthermore, the mass balance of injected and sampled tracer may be affected by any of the processes already outlined (see clause 6), or by factors of a general nature which affect all tracer methods (see ISO 9555-1).

Errors during the analytical procedures may arise from contamination from, or adsorption onto, sample bottles and filter papers by tracers and interfering elements. For iodide samples, glass bottles have been found to be satisfactory, while for lithium, polyethylene sample bottles should be selected in preference to glass, particularly if samples are to be stored. New bottles shall be rinsed in tap water before use to remove any salts from the bottle manufacture and also to decrease the sorptive capacity of the bottle surface.

Comparative solutions shall be prepared gravimetrically rather than volumetrically for greater accuracy, and mixed adequately, particularly when prepared from dense injection solutions. Where weight-to-volume conversions are necessary, e.g. for volume flow-rate determinations, corrections will have to be made for the density of concentrated solutions. Random and systematic errors which may arise during sample analysis shall be minimized by careful attention to the procedures given (see clause 5). Any errors due to variable background concentrations will be indicated by the analysis of background water samples. Errors due to the deterioration of samples during storage may be minimized by filtration and by reducing the storage time, or by refrigeration or protection from light. They can be estimated by preparing comparative solutions as soon as possible after the gauging and treating and storing them in a similar way to the samples.

10 Special requirements

10.1 Iodide

No objections, on the grounds of toxicity, have been encountered in the use of iodide at the concentrations recommended in this part of ISO 9555. It is present in sea water at comparable concentrations and has at times been added to table salt to prevent disorders of the thyroid. The lowest dose (LD 10) of

sodium iodide reported to give any toxic effect in humans is 500 mg per kilogram of body weight.

10.2 Lithium

10.2.1 Safety of the user

The dissolution of lithium chloride in water is exothermic and concentrated solutions are acidic. Special precautions shall be taken in handling lithium chloride, and cooled solutions shall be checked for any recrystallization of dissolved salts.

Lithium salts are psychotropic, and are used to treat manic-depressive disorders at doses in the range 50 mg to 275 mg lithium ion per day.

10.2.2 Public acceptability

In fish toxicity tests, a 35 day LD 50 of 1,4 mg/l has been found for yearling trout in hard water. This and the hazard to infants has led one national authority to suggest that, for dilution gauging in water mains, the mean concentration of lithium at the next offtake downstream of the injection point should be no more than 0,1 mg/l.

10.3 Chloride

The World Health Organization's Guidelines for Drinking Water Quality regard excessive concentrations of chloride in potable waters as unacceptable on the grounds of taste:

"High concentration of chloride give an undesirable taste to water and beverages. Taste thresholds for chloride (as sodium, potassium or calcium chloride) are in the range of chloride ion concentrations of 200-300 mg per litre."

Chloride can also have effects on freshwater organisms: Benthic fauna affected by saline runoff have been observed to drift at chloride concentrations of around 800 mg/l. While it is unlikely that concentrations of this magnitude will persist in the stream during dilution gauging, high concentrations can occur close to the injection point during the injection.

10.4 Chromium

10.4.1 Precautions for the user

Sodium dichromate, whether in crystal form or as a concentrated solution, is a dangerous substance which attacks human tissues. The handling of this substance shall be attended with suitable precautions; avoid inhaling the dust when transferring dichromate in solid form, and avoid splashes when mixing concentrated solutions.

10.4.2 Legislation

The World Health Organization's Guidelines for Drinking Water Quality set a guideline limit for total chromium at 50 µg/l based on an assumed per capita average daily intake of 2 litres of water. This guideline concentration was set in such a way that the intake from drinking water was less than half of the total intake from water, air and food.

For gaugings performed in non-potable waters, higher concentrations may be permissible (see ISO 9555-1).