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

iTeh STANDARD PREVIEW

Part 3:

Chemical tracers

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

Partie 3: Traceurs chimiques

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.

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, reconcen-

tration techniques can permit the measurement of large discharges (of the order of 1 000 m³/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 millilitres 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;