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Water quality — Determination of nitrogen —

Part 2:
Determination of bound nitrogen, after combustion and oxidation to nitrogen dioxide, using chemiluminescence detection

Qualité de l'eau — Dosage de l'azote —

Partie 2: Dosage de l'azote lié, après combustion et oxydation en dioxyde d'azote, par détection chimiluminescente

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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.

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

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

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

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

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 Technical Reports of type 3 do not necessarily have to be reviewed until the data they provide are considered to be no longer valid or useful.

ISO/TR 11905-2, which is a Technical Report of type 2, was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical, biochemical methods.*

This document is being issued in the Technical Report (type 2) series of publications (according to subclause G.3.2.2 of part 1 of the ISO/IEC Directives, 1995) as a "prospective standard for provisional application" in the field of water quality because there is an urgent need for guidance on how standards in this field should be used to meet an identified need.

This document is not to be regarded as an "International Standard". It is proposed for provisional application so that information and experience of its use in practice may be gathered. Comments on the content of this document should be sent to the ISO Central Secretariat.

A review of the Technical Report (type 2) will be carried out not later than three years after its publication with the options of: extension for another three years; conversion into an International Standard; or withdrawal.

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ISO 11905 consists of the following parts, under the general title *Water quality — Determination of nitrogen*

— *Part 1: Method using oxidative digestion with peroxodisulfate*

— *Part 2: Determination of bound nitrogen, after combustion and oxidation to nitrogen dioxide, using chemiluminiscence detection* (Technical Report)

Annexes A to D of this Technical Report are for information only.

Introduction

It is absolutely essential that the tests described in this Technical Report be carried out by suitably qualified staff.

This Technical Report specifies a method for the determination of bound nitrogen, after oxidation of inorganic and organic nitrogen compounds by combustion to nitric oxide and oxidation (by conversion with ozone) to electronically excited nitrogen dioxide. Quantification is carried out by chemiluminescence detection.

The procedure described is the reference method. Whilst staying within the scope of this Technical Report, it is permissible to use such alternatives as given in annex A, provided that their performance is equal to or better than that given in annex C, when calculated using the procedures given in ISO 5725-2, and when the comparison of performance data between this Technical Report and any alternative technique is carried out using the procedures described in ISO 2854.

All references to mass concentrations of nitrogen are expressed in milligrams of nitrogen per litre of solution (i.e. mg/l).

Water quality — Determination of nitrogen —

Part 2:
Determination of bound nitrogen, after combustion and oxidation to nitrogen dioxide, using chemiluminescence detection

1 Scope

This Technical Report specifies a method for the determination of nitrogen present in water in the form of free ammonia, ammonium, nitrite, nitrate and organic compounds capable of conversion to nitrogen dioxide under the oxidative conditions described. Determination is carried out instrumentally using chemiluminescence detection. Dissolved nitrogen gas is not determined by this method.

This method is applicable to the analysis of natural freshwater, sea water, drinking water, surface water, waste water and treated sewage effluent.

1.1 Range

The concentration range of the method will depend on the injection volume used, which is instrument specific. Nitrogen can be determined in the range up to 200 mg/l. Higher concentrations can, if necessary, be determined by dilution of the sample.

1.2 Limit of detection

The limit of detection will depend on the instrument used. Using a suitable injection volume, the limit of detection is typically 0,5 mg/l.

2 Normative references

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

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

ISO 5667-3:1994, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples.*

3 Principle

Oxidation of the sample containing nitrogen, by combustion in an oxygen atmosphere at 1 000 °C, to nitric oxide. Reaction with ozone to give electronically excited nitrogen dioxide (NO_2^*). Quantification of nitrogen concentration by chemiluminescence detection.

4 Reagents

4.1 General requirements

During the analysis, use Grade 3 purity water as specified in ISO 3696 and only reagents of recognized analytical grade. The content of bound nitrogen in water used for the preparation of calibration solutions shall be negligibly low compared with the lowest concentration to be determined.

4.2 Hydrochloric acid, $\rho = 1,12$ g/ml.

4.3 Nitrogen stock solution, $\rho = 1,000$ g/l.

4.3.1 Dissolve (4,717 ± 0,001) g of ammonium [$(NH_4)_2SO_4$] previously dried at (105 ± 2) °C to constant mass, in a volumetric flask of nominal capacity 1 000 ml, and dilute to volume with water.

4.3.2 Dissolve (7,219 ± 0,001) g of potassium nitrate (KNO_3) previously dried at (105 ± 2) °C to constant mass, in a volumetric flask of nominal capacity 1 000 ml, and dilute to volume with water.

4.3.3 Mix equal volumes of the solutions prepared in 4.3.1 and 4.3.2 to produce a mixed standard solution.

4.4 Nitrogen control stock solution, $\rho = 1,000$ g/l.

Dissolve (5,358 ± 0,001) g of glycine (NH_2-CH_2-COOH) in a volumetric flask, of nominal capacity 1 000 ml, and dilute to volume with water.

4.5 Oxygen, 99,7 % (*V/V*).

5 Apparatus

5.1 Apparatus for the determination of bound nitrogen by oxidation, with, for example: reaction vessel, automatic sample injection device, sample homogenizing equipment, chemiluminescence detector and computing system. A manual injection system may also be used. Equipment should be checked using controlled samples according to the manufacturer's instructions.

5.2 Homogenizer.

5.3 Filtration apparatus.

5.4 Syringes.

6 Sampling and sample preparation

6.1 When sampling, ensure that a representative sample is obtained (this is particularly important for samples containing any undissolved matter), and that the sample is not contaminated. In addition, see ISO 5667-3.

6.2 Withdraw the samples in suitable containers made of glass or suitable plastics and appropriately sealed.

6.2.1 Analyse the samples as soon as possible.

NOTE 1 Delay may result in the reporting of low values (especially in the case of biologically active samples).

6.2.2 Samples may be stabilized by the addition of hydrochloric acid (4.2) to achieve a pH-value of less than 2, and stored in a refrigerator at (4 ± 2) °C for a period of up to 8 d.

6.2.3 If necessary, homogenize the sample using a homogenizer (5.2) so that a representative aliquot of it is obtained for the determination (see clause 7). If this is impracticable, filter through a filter of nominal pore size 0,45 µm.

7 Interferences

Depending on the instrument used, interferences may arise from memory effects. These may occur either in samples or standard solutions with high contents of bound nitrogen. Replicate measurements are therefore necessary and the first value should be rejected.

NOTE 2 Potential problems may arise with samples containing significant total organic carbon (TOC) concentrations. The analysis of samples containing large amounts of TOC will lead to the reporting of lower results for nitrogen. Suspected problems may be identified by determining nitrogen before and after suitable dilution, or by using standard addition techniques.

Not all organic nitrogen compounds are quantitatively converted to nitrogen oxide by the oxidation procedure described, and consequently to nitrogen dioxide by the reaction with ozone.

Poor recoveries can occur with compounds containing either double or triple bonded nitrogen atoms. See the performance data in annexes B and C.

If a homogenized sample containing suspended material produces results (obtained from replicate measurements) which deviate by more than 10 %, the sample needs to be filtered through a 0,45 µm filter, free of compounds containing nitrogen. In this case, only the dissolved portions of the bound nitrogen will be determined and reported.

8 Procedure

8.1 Follow the instructions of the instrument manufacturer.

8.2 Prior to the determination of bound nitrogen, ensure that instrumental operational tests and the verification of the responses to blank and standard solutions are carried out within the intervals specified by the manufacturer.

8.3 Adjust the instrument according to the manufacturer's instructions for each series of measurements.

8.4 If an instrument is fitted with an automatic injection device (see 5.1), ensure that the sample is unlikely to cause any interference with the injection procedure by, for example, homogenizing the sample. (See also clause 7).

8.5 Inject identical volumes of blank solutions and samples into the instrument, according to the manufacturer's instructions, and measure the responses obtained for each solution at least three times.

8.6 Use the mean response from at least three injections, taking into account any memory effects that are likely to occur (see clause 7). Use the calibration graph (see clause 9) to determine the concentration of bound nitrogen in the sample.

9 Establishment of the calibration curve

9.1 Use the mixed standard stock solution (see 4.3.3) to prepare calibration solutions in accordance with the range of concentrations of bound nitrogen expected in the samples to be determined.

9.2 The calibration solutions shall be used on the day of preparation only. For the concentration range of 10 mg/l to 100 mg/l, proceed, for example, as follows.

Into seven separate volumetric flasks of nominal capacity 100 ml, pipette 0 ml (blank); 1,0 ml; 2,0 ml; 3,0 ml; 6,0 ml; 8,0 ml or 10,0 ml of the mixed standard solution (see 4.3.3) and dilute to volume with water. These quantities correspond to mass concentrations of nitrogen of 0 mg/l; 10,0 mg/l; 20,0 mg/l; 40,0 mg/l; 60,0 mg/l; 80,0 mg/l or 100,0 mg/l, respectively.

9.3 The injection volume used for the measurement of each of these solutions shall be identical to the injection volume used for the blank and sample measurements.

9.4 Use a coordinate system to plot the mass concentration of nitrogen in the calibration solutions (see 9.2) on the abscissa, and the response values on the ordinate, respectively. Alternatively, a handling system for laboratory data may be used.

9.5 Establish the linear regression function for the series of measurement so obtained.

9.6 The slope, *b*, of the calibration graph is a measure of the sensitivity, expressed in instrument-related units · litres per milligram.

9.7 Frequently check the slope of the calibration graph, particularly when new batches of reagents are used. Assess the slope of the linear calibration graph from the response values of at least two calibration solutions (see 9.2) covering approximately 20 % and 80 % of the working range of the calibration graph. The slope shall not differ from the slope established in 9.1 to 9.6 by more than 10 %. If the slope differs by more than 10 %, take remedial action and construct a new calibration graph.

10 Quality control determinations

Carry out quality control determinations using dilute solutions of the control stock solution (4.4) in the appropriate range to show any deviations of the response values obtained during the oxidation stage. Deviations of up to ± 5 % of the theoretical value may be tolerated.

11 Evaluation

Provided the calibration graph is linear, calculate the mass concentration of nitrogen in the water sample using the following equation:

$$\rho_N = \frac{(N_1 - N_0) \times f}{b}$$

where

ρ_N is the mass concentration, in milligrams per litre, of bound nitrogen in the sample;

N_1 is the response value of the sample, in instrument-related units;

N_0 is the response value of the blank, in instrument-related units;

b is the slope of the calibration graph, in instrument-related units · litres per milligram;

f is the dilution factor, if applicable.

This equation can only be used where identical injection volumes of the samples and the calibration solutions are employed in the determinations.

12 Expression of results

For a given mass concentration of bound nitrogen in a sample, report the results as follows:

- less than or equal to 10 mg/l to the nearest 0,1 mg/l;
- 10 mg/l to 100 mg/l to the nearest 1 mg/l; or
- greater than or equal to 100 mg/l to a maximum of two significant figures.

13 Test report

The report shall contain the following information:

a) a reference to this Technical Report;

b) identity of the water sample;

c) expression of the results according to clause 12;

d) sample pretreatment, if applicable, and whether the results represent total or dissolved portions;

e) any deviation from this method and information on all circumstances which may have influenced the results.

14 Precision data

See the data given in annex C. Examples of the type of performance that can be obtained are shown in annexes B and C.

Annex A

(informative)

Determination of bound nitrogen using other techniques

A.1 General

There are other techniques, outlined in A.2 to A.4, that are available for the determination of bound nitrogen in water. All these techniques are widely used for the analysis of waters but are not based on oxidation and chemiluminescence detection as described in this Technical Report.

A.2 Oxidation and determination by infrared spectroscopy

Nitrogen compounds present in a sample are oxidized to oxides of nitrogen (NO_x) in an oxygen atmosphere. Quantification is carried out by infrared spectroscopic measurement.

A.3 Reduction and microcoulometric titration

Nitrogen compounds present in a sample are reduced in a hydrogen atmosphere to form ammonia. Quantification is carried out by microcoulometric titration after absorption in an acidic medium.

A.4 Reduction and photometric determination

Nitrogen compounds present in a sample are reduced in a hydrogen atmosphere to form ammonia. Quantification is carried out photometrically.

Annex B
(informative)
Recovery rates of single compounds

Test substance	Recovery rate %	Nitrogen concentration range of the test mg/l
Ammonium sulfate	95 to 100	1 to 100
Potassium nitrate	97 to 105	10 to 50
Sodium nitrate	101	
Caffeine	98	
Glycine	95 to 99	10
Urea	92 to 99	10
Nicotinic acid	98 to 102	
Glutamic acid	97	
Thiocyanates	98	
Acetanilide	99	
1,6-Hexanediamine	96 to 101	10 to 50
Nitrophenols	93 to 102	10 to 50
Nitroanilines	91 to 100	10 to 50
Arginine	94 to 106	10 to 50
Sodium azide	54	
Benzonitrile	94 to 102	20
Potassium hexacyanoferrate(III)	99	10
Potassium hexacyanoferrate(II)	92 to 96	10
Purine	95 to 101	20
Calcium nitrate	99 to 102	10

Annex C
(informative)
Performance characteristics of an interlaboratory trial carried out in Germany in 1990 for comparison of different methods

Sample	l	n	n_a %	$\bar{x}$ mg/l	s_r mg/l	VC_r %	s_R mg/l	VC_R %
A	9	34	10,5	10,3	0,25	2,4	0,82	7,9
B	10	38	0,0	23,7	0,52	2,2	2,15	9,1
C	10	37	2,6	124	1,5	1,2	7,0	5,6
D	9	34	0,0	213	4,5	2,1	10,6	5,0
E	10	37	2,6	64,2	1,00	1,6	3,95	6,2
F	10	38	0,0	65,5	1,25	1,9	2,64	4,0

Description of samples

A	Surface water (river)
B	Municipal sewage effluent
C	Synthetic mixture (NO_3^-, NH_4^+, urea, pyridine and nicotinic acid in the ratio 1:1:1:1:1, concentration = 125 mg/l N)
D	Industrial sewage effluent
E	Industrial waste water (diluted)
F	Mixture of samples B and C

l	Number of laboratories
n	Total number of determinations
n_a	Percentage of outliers
$\bar{x}$	Total mean
s_r	Repeatability standard deviation
VC_r	Repeatability coefficient of variation
s_R	Reproducibility standard deviation
VC_R	Reproducibility coefficient of variation