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Water quality — Determination of nitrogen —

Part 1:
Method using oxidative digestion with peroxodisulfate

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

Partie 1: Méthode par minéralisation oxydante au peroxodisulfate

Reference number
ISO 11905-1:1997(E)

Contents

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Annexes

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 11905-1 was prepared by Technical Committee ISO/TC 147, *Water quality,* Subcommittee SC 2, *Physical, chemical and biochemical methods.*

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 oxidation and combustion to nitrogen dioxide using chemiluminescent detection*

Annexes A to D of this part of ISO 11905 are for information only.

INTRODUCTION

This part of ISO 11905 describes the peroxodisulfate oxidation of nitrogen compounds in water to produce nitrate. Specific details of the determination of a continuous flow method with initial reduction of nitrate to nitrite by copperized cadmium are then reported. The procedures referred to in the normative method is the reference method. Annex C gives examples of alternative techniques suitable for the determination of nitrate in the digest solution. While staying within the scope of this part of ISO 11905, it is permissible to use such alternatives only provided that their performance meets or is better than that given in table A.1, when calculated using procedures described in ISO 5725-2, and when the comparison of precision data between this part of ISO 11905 and any alternative technique is carried out using the procedures described in ISO 2854.

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

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Water quality — Determination of nitrogen —

Part 1:
Method using oxidative digestion with peroxodisulfate

1 Scope

This part of ISO 11905 specifies a method for the determination of nitrogen present in water, in the form of free ammonia, ammonium, nitrite, nitrate and organic nitrogen compounds capable of conversion to nitrate under the oxidative conditions described.

Dissolved nitrogen gas is not determined by this method.

This method is applicable to the analysis of natural fresh water, sea water, drinking water, surface water and treated sewage effluent. It is also applicable to the analysis of sewage and trade wastes in which the amount of organic matter in the test portion can be kept below 40 mg/l, expressed as carbon (C), when measured by Total Organic Carbon (TOC), or 120 mg/l, expressed as oxygen (O_2), when measured by Chemical Oxygen Demand (COD) according to the respective International Standards.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 11905. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 11905 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 current valid International Standards.

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

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results —*
Part 2: Basic methods for the determination of repeatability and reproducibility of a standard measurement method.

3 Range of detection

Using the maximum test portion specified in 9.1, nitrogen (N) can be determined in the range up to 5 mg/l. Much higher concentrations can be determined using smaller test portions.

Using the maximum test portion, the lower limit of detection, expressed as N, is typically 0,02 mg/l. This depends on the method used to measure the nitrate concentration resulting from the oxidation.

4 Sensitivity

Sensitivity will depend upon the method used to measure the nitrate concentration resulting from the oxidation.

The main potential interference effects arise from dissolved or suspended organic matter present in samples, which compete for the oxidation capacity of the peroxodisulfate reagent. To guarantee a sufficient excess of the oxidation reagent, if the COD of the original sample exceeds 120 mg/l, expressed as O_2, or the TOC exceeds 40 mg/l, expressed as C, the sample needs to be diluted.

Not all organic nitrogen compounds are quantitatively converted to nitrate by the oxidation. Poor recoveries can occur with compounds containing double- and triple-bonded nitrogen atoms and also with those substances containing a >C=NH group. Compounds with free amino groups give less than quantitative recovery, but in no case less than 87%; good recoveries of nitrogen are reported for several heterocyclic compounds, see annex B. Overall, the method gives good recovery performance for organic nitrogen compounds and gives results not significantly different from those obtained by instrumental, high temperature oxidation or reduction systems on a wide range of real samples containing significant amounts of organic matter.

5 Principle

Ammonia, nitrite and many organic nitrogen-containing compounds in the test sample are oxidized to nitrate using peroxodisulfate in a buffered alkaline system by boiling at elevated pressure in a closed container.

Subsequent reduction of nitrate to nitrite is carried out by passage of the digest through a mixing coil containing copperized cadmium. The resulting nitrite is reacted with 4-aminobenzene sulfonamide and N-(1-naphthyl)-1,2-diaminoethane dihydrochloride to produce a pink colour. Photometric measurement is carried out at 540 nm.

6 Reagents

During the analysis, use water of purity grade 3 as specified in ISO 3696 and reagents of recognized analytical grade.

6.1 Sulfuric acid, $c(H_2SO_4) \approx 4$ mol/l.

Carefully mix (110 ± 0,5) ml of concentrated sulfuric acid (H_2SO_4, ρ = 1,84 g/ml) into about 350 ml of water. Allow to cool to room temperature and dilute with water to (500 ± 10) ml. Store in a glass or plastics container. This reagent is stable indefinitely.

WARNING: This reagent can cause severe burns. Wear gloves and eye protection when handling or preparing the acid.

6.2 Sodium hydroxide solution, $c(NaOH) \approx 0{,}375$ mol/l.

Dissolve (15,0 ± 0,5) g of sodium hydroxide in about 900 ml of water. Allow to cool to room temperature and make up to (1000 ± 10) ml with water. Store in a polyethylene container. This reagent is stable for at least 6 months.

WARNING: This reagent is corrosive. Wear gloves and eye protection when handling or preparing the solution.

6.3 Oxidizing solution.

Dissolve (5,0 ± 0,1) g of analytical reagent grade potassium peroxodisulfate ($K_2S_2O_8$), containing not more than 0,001 % (*m/m*) nitrogen as impurity, and (3,00 ± 0,05) g of boric acid (H_3BO_3) in (100 ± 5) ml of sodium hydroxide solution (6.2). Store the solution in a polyethylene container in the dark at room temperature. This reagent is stable for up to one week.

WARNING: This reagent is corrosive. Wear gloves and eye protection when handling or preparing the solution.

6.4 Hydrochloric acid, $c(HCl) \approx 5$ mol/l.

Cautiously add (450 ± 10) ml of concentrated hydrochloric acid (HCl, ρ = 1,18 g/ml) to (500 ± 10) ml of water with constant stirring. Make up to (1000 ± 10) ml with water. Store in a glass or polyethylene bottle. This solution is stable for at least six months.

WARNING: This reagent can cause severe burns. Wear gloves and eye protection when handling or preparing the acid.

6.5 Hydrochloric acid, $c(HCl) \approx 0{,}1$ mol/l.

Add (10,0 ± 0,5) ml of concentrated hydrochloric acid (HCl, ρ = 1,18 g/ml) to about 900 ml of water. Mix and make up to (1000 ± 10) ml with water. Store in a glass or polyethylene bottle. This reagent is stable indefinitely.

WARNING: This reagent can cause severe burns. Wear gloves and eye protection when handling or preparing the acid.

6.6 Glycine solution, 200 mg/l, expressed as N.

Dissolve (1,072 ± 0,001) g of glycine, H_2NCH_2COOH, in about 800 ml of water and dilute to one litre with water in a calibrated flask. Store in a glass container. If stored in a refrigerator at 0 °C to 5 °C this reagent is stable for at least one month.

6.7 Glycine solution, 2 mg/l, expressed as N.

Pipette (10,00 ± 0,01) ml of glycine solution (6.5) into a one-litre calibrated flask and make up to volume with water. Prepare fresh solution for each batch of analyses.

NOTE — The concentration of this standard glycine solution should be chosen to match the expected range of concentrations of nitrogen to be determined; for example, if lower nitrogen results are expected then the concentration of the standard glycine solution should be reduced. (See also 9.5).

6.8 Reagent blank.

Carry out at least one blank test using the procedure described but replacing the test portion with water.

6.9 Copper sulfate solution.

Dissolve (20 ± 0,2) g of copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5\ H_2O$) in (1000 ± 10) ml of water. Store in a glass or polyethylene bottle. This solution is stable for at least six months.

6.10 Copperized cadmium granules

WARNING: Cadmium is toxic by inhalation, by contact with skin or by ingestion.

Wash (10 ± 0,1) g of cadmium granules (250 µm to 425 µm) in (50 ± 0,5) ml of hydrochloric acid (6.4). Rinse the granules three times in water by decantation. Add (100 ± 1) ml of copper(II) sulfate solution (6.9) and swirl the granules for 5 min or until the blue colour partially fades. Decant off the solution and repeat the procedure with fresh copper(II) sulfate solution (6.9) until a brown colloidal precipitate forms. Finally, wash the copperized cadmium granules with water until all precipitated copper is removed. Carry out a minimum of 10 washes. Store the copperized granules under water until required. Avoid contact with air.

6.11 Buffer solution.

Dissolve (85,0 ± 0,5) g of ammonium chloride (NH_4Cl) in about 800 ml of water. Add (1,0 ± 0,1) g of wetting agent (6.13). Make up to (1000 ± 10) ml with water and store in a glass bottle. This solution is stable for at least one month.

6.12 Colour reagent.
Dissolve (40 ± 0,5) g of 4-aminobenzene sulfonamide ($NH_2C_6H_4SO_2NH_2$) in a mixture of (100 ± 1) ml of orthophosphoric acid (H_3PO_4, ρ = 1,71 g/ml) and (500 ± 50) ml of water in a beaker. Dissolve (2,00 ± 0,2) g of N-(1-naphthyl)-1,2-diaminoethane dihydrochloride ($C_{10}H_7NHCH_2CH_2NH_2 \cdot 2HCl$) in the resulting solution. Transfer to a 1000 ml calibrated flask and dilute to the mark with water. Mix well. Store in an amber glass bottle. The solution is stable for 1 month if stored at 2 °C to 5 °C.

WARNING: N-(1-naphthyl)-1,2-diaminoethane dihydrochloride is toxic by inhalation, by contact with skin or by ingestion.

6.13 Wetting agent.

NOTE — The presence of a wetting agent in a continuous-flow system is desirable in order to promote smooth hydraulic flow.

Use a nonionic surfactant of the polyoxyethylene alcohol type or the alkylphenoxypolyethoxy ethanol type.

6.14 Nitrate solution, containing 1000 mg/l, expressed as N.
Dissolve (7,215 ± 0,001) g of potassium nitrate (KNO_3) (previously dried at 105 °C for at least 2 h) in about 750 ml of water. Quantitatively transfer to a one-litre calibrated flask and make up to volume with water. Store in a glass container. This solution is stable for two months.

6.15 Nitrate solution, containing 100 mg/l, expressed as N.
Pipette (50,00 ± 0,05) ml of nitrate solution (6.14) into a 500 ml calibrated flask and make up to volume with water. Store in a glass container. This solution is stable for one month.

6.16 Nitrite solution, containing 100 mg/l, expressed as N.
Dissolve (0,492 ± 0,002) g of sodium nitrite ($NaNO_2$) (dried at 105 °C for at least 2 h) in about 750 ml of water. Transfer quantitatively to a 1000 ml one-mark volumetric flask and dilute to the mark with water. Store in a stoppered amber glass bottle at 2 °C to 5 °C. This solution is stable for at least one month.

6.17 Nitrite solution, containing 4 mg/l, expressed as N.
Pipette (2,00 ± 0,01) ml of nitrite solution (6.16) into a 50 ml calibrated flask and make up to volume with water. Prepare fresh solution as required.

7 Apparatus

Ordinary laboratory apparatus and:

7.1 Homogenizer.

7.2 Digestion vessels.
Bottles of polytetrafluoroethene (PTFE) or other suitable materials with screw caps, nominal capacity in the range 100 ml to 125 ml, capable of withstanding pressures of up to 200 kPa. See 9.3.

7.3 Autoclave, suitable for pressures up to 200 kPa and operation at 120 °C. See also note in annex C.

7.4 Continuous-flow analysis equipment, comprising:
– sample presentation unit (sampler);
– multichannel peristaltic pump;
– analytical cartridge (manifold) including pump tubes, mixing coils, reduction column (5.5) and dialyser unit;
– spectrometer, incorporating a flow cell and capable of measurement over a wavelength range between 520 nm and 550 nm;
– recorder.

7.5 Reduction column.
Constructed from glass or plastics tubing with an internal diameter identical to that of the mixing coils used elsewhere in the system. Fill the column with copperized cadmium granules (6.10) (HAZARD). The volume, in millilitres, occupied by the granules shall be as close as possible to the total liquid flowrate, in millilitres per minute, passing through the column.

8 Sampling and samples

Collect laboratory samples in plastics or glass bottles. Analyse them as quickly as possible, or store them at between 2 °C and 5 °C for up to 48 h.

NOTE — Acidification with sulfuric acid (6.1) to pH 2 can also be used as an aid to sample preservation, provided any possible contamination of the acidified sample by absorption of atmospheric ammonia is prevented. In this case, the sample can be stored for up to 8 days.

9 Procedure

9.1 Test portion

The maximum test portion, enabling the determination of nitrogen concentrations in samples of up to 5 mg/l, is 50 ml. Use smaller test portions as appropriate to determine higher nitrogen concentrations. In all cases, the test portion shall be controlled such that its TOC content does not exceed 2 mg as carbon, or such that its COD does not exceed 6 mg as oxygen (see 1.3).

Before taking the test portion, ensure that the laboratory sample is thoroughly mixed. If the sample is inhomogeneous, the homogenizer (7.1) can be used. If laboratory samples are strongly acid (pH < 2) ensure that, after addition of the oxidizing solution (6.3) to the test portion, a pH of 9,7 is attained by carefully adjusting the pH with sodium hydroxide solution (6.2).

9.2 Blank test

Carry out at least one blank test with every batch of digestions, using (50 ± 1) ml of water in place of the test portion.

9.3 Cleaning digestion vessels

Before use in analysis for the first time, add to each new digestion vessel (7.2) about (60 ± 1) ml of oxidizing solution (6.3). Close the vessel and heat it in the autoclave (7.3) for (30 ± 5) min. Remove the vessel, allow it to cool to room temperature and discard the contents. Rinse the vessel thoroughly with water, fill to the brim with hydrochloric acid (6.5), stopper and store until required in the analytical procedure. Immediately before use, empty the vessel and rinse with water.

After cleaning for the first time by the procedure described above, rinse the digestion vessels with water. If significant contamination is known or suspected, clean the digestion flasks again by the procedure described above. Wherever possible, reserve cleaned digestion vessels for the deter-mination of nitrogen.

9.4 Digestion

Pipette a suitable test portion (9.1) of up to 50 ml, (V ml), into a clean digestion vessel (7.2) and if necessary, add water from a burette or measuring cylinder to give a total volume of (50 ± 1) ml. Pipette (10,0 ± 0,1) ml of the oxidizing solution (6.3) into the digestion vessel and immediately close the vessel. Mix thoroughly. Digest for (30 ± 5) min at (120 ± 5) °C. Some digestions require additional time for complete oxidation, for example 60 min.

Remove the digestion vessel from the source of heat and allow to cool to room temperature.

Shake the digestion vessel in order to dissolve any precipitate which may form, and quantitatively transfer the solution to a 100 ml calibrated flask. Make up to volume with water.

NOTE 1 If any particulate matter remains undissolved in the digest, it should be filtered through a prerinsed glass fibre filter paper into the 100 ml calibrated flask. The filter should be rinsed with water to ensure quantitative transfer.

NOTE 2 If necessary, the digest may be kept for up to several weeks in the unopened digestion vessel before completing the analytical procedure. However, avoid contamination from absorption of atmospheric ammonia.

9.5 Verification of recovery of organic nitrogen

With every batch of digestions, include at least one recovery test using (50,00 ± 0,05) ml of glycine solution (6.7) in place of the test portion. If the standard glycine solution specified in 6.7 is used, the nitrogen concentration measured shall not differ from 2,00 mg/l by more than ± 0,20 mg/l. If greater percentage differences for this or other standard solutions are found, the overall method shall be examined and results from the associated batch of samples shall not be reported.

9.6 Starting operation

Connect the system as illustrated in figure 1, but omitting the reduction column. Follow the manufacturers' instructions where appropriate.

With the sample probe at rest in the reagent blank (6.8), place all the reagent lines in their respective reagents and start the pump. When all reagent lines and coils have been filled, stop the pump and insert the reduction column into the system. This procedure avoids air entrapment in the column.

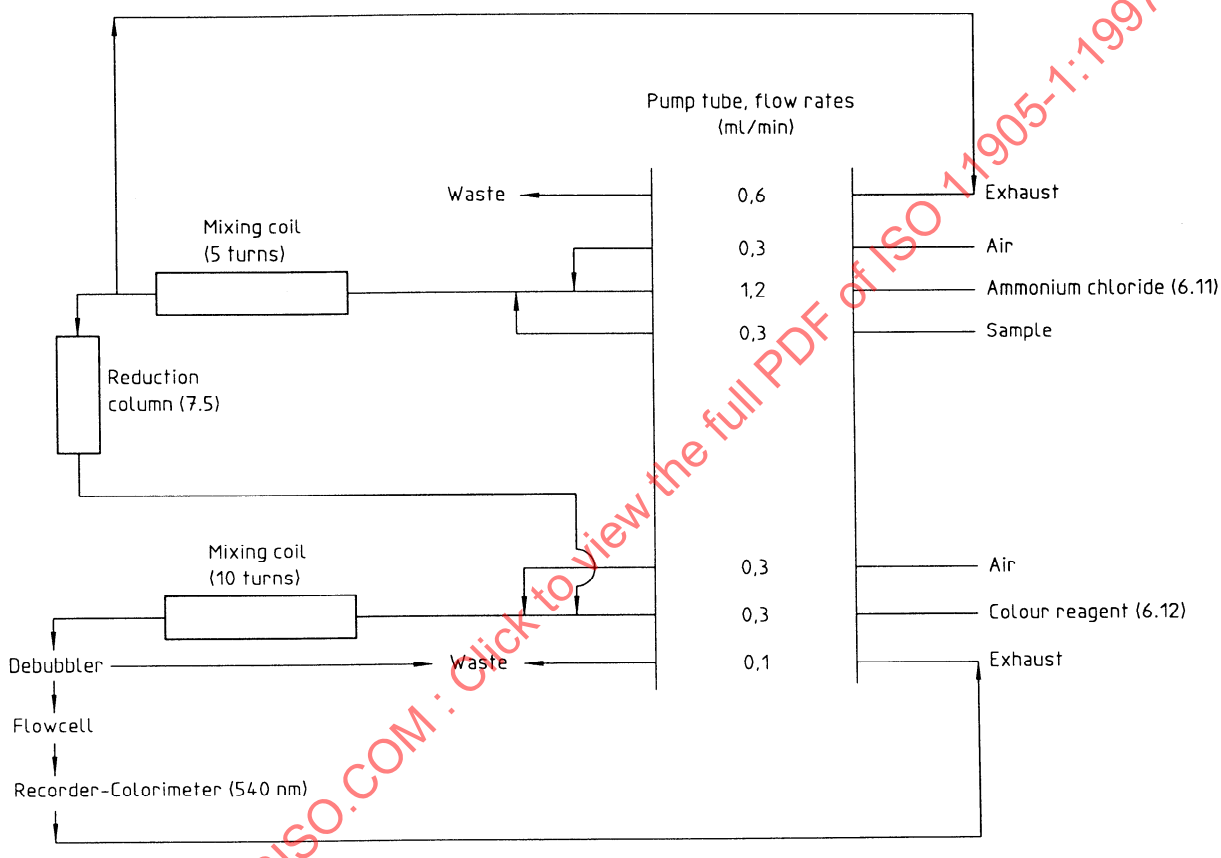

Figure 1

Allow the system to equilibrate and during this period, check that the bubble pattern and hydraulic behaviour of the system are operating to the manufacturer's instructions. If not, eliminate difficulties before proceeding to 9.7.

9.7 Initial sensitivity setting

When a baseline response given at the recorder is stable, adjust to about 5% of the full-scale deflection; transfer the sample probe into the 4,0 mg/l standard nitrate solution (9.8). When there is a positive stable response at the recorder due to the colour produced from this 4,0 mg/l standard nitrate solution (9.8), adjust this response to read about 95% of full-scale deflection.

NOTE 1 The sample probe need remain in the standard solution only for sufficient time to give a steady reading.

Return the sample probe to rest in the wash position, first removing traces of standard solution from the outside of the probe by rinsing with water and cleaning with a clean tissue.

NOTE 2 Periodically, the response from the 4,0 mg/l standard nitrate solution (9.8) and the 4,0 mg/l standard nitrite solution (6.17) should be compared to check efficiency of reduction. The response from the nitrate solution should be at least 90% of that from the nitrite solution. Lower reduction efficiencies should be investigated and attention to the reduction system will usually be required.

9.8 Calibration

Choose the calibration range to match the expected range of concentrations to be determined. (See also 9.5). For example, to a series of five 50 ml calibrated flasks, add, by means of a microburette or calibrated micropipettes, 1,0; 0,8; 0,6; 0,4 and 0,2 ml of nitrate solution (6.15). Make up to volume with water. These flasks now respectively contain the equivalent of 4,0, 3,2; 2,4; 1,6 and 0,8 mg/l, expressed as N, in the original test portion of 50 ml (9.1). These concentrations are in turn equivalent to 0,2; 0,16; 0,12; 0,08 and 0,04 mg of N in the test portion itself.

Run the five calibration standards as indicated in 9.9.

At the end of the determination, measure the system response to the calibration standards from the recorder trace, taking the baseline trace obtained during initial sensitivity setting (9.7) as the blank response value.

Plot a graph of response against concentration of nitrogen in milligrams per litre. The graph shall be linear and pass through the origin. If not, check procedures to ensure that the graph is linear.

9.9 Determination

Rinse and fill each sample container used in the instrument with a portion of the test solution, calibration standard or blank as appropriate. Load the turntable with the filled containers in accordance with the manufacturer's instructions.

NOTE — If cross-contamination occurs between two samples (visible on the recorder trace as incomplete separation of consecutive sample responses), both samples should be reanalysed, separated by a blank solution.

When a stable baseline is obtained on the recorder, re-adjust, if necessary, to about 5% of full-scale deflection and start the sampling unit. When all the system responses due to the processed solutions have appeared on the recorder and a final baseline has been obtained, remove the reduction column from the system, and switch off the recorder and spectrometer. Transfer all reagent lines to water and pump for at least 15 min or a time recommended in the manufacturer's instructions.

10 Expression of results

10.1 Method of calculation

Measure the system response to the samples or standards as appropriate from the recorder trace, taking the baseline trace obtained during initial sensitivity setting (9.7) as the blank response value. Read off the corresponding nitrogen concentration, in milligrams per litre, from the calibration graph. These concentrations correspond to nitrogen in the original sample when the full 50-ml test portion (9.1) has been used in the digestion. Multiply the concentrations by $50/V$ when smaller test portions, of volume V ml, have been taken. Data-handling facilities may also be used.

10.2 Precision data

Precision data obtained in various international laboratories are presented in table A.1 in annex A. Data were calculated using procedures described in ISO 5725-2.

11 Test report

The test report shall include the following information:

a) a reference to this part of ISO 11905;
b) all information necessary for complete identification of the sample;
c) the results and the method of expression used;
d) a statement of the comparison of data obtained using this part of ISO 11905 and the performance data obtained using any alternative technique;
e) the chemical oxygen demand and/or the total organic carbon concentration in the sample;
f) the volume of test portion used;
g) details of any operations not included in this part of ISO 11905, together with any circumstances that may have affected the results.

Annex A

(informative)

Precision data

Table A.1 — Precision data of the results of the total nitrogen international collaborative trial

Sample	LAB	No.	NAP	Mean	s_R	CV_R %	s_r	CV_r %	Mean recovery of spike %
L	17	34	2	1,989	0,071	3,558	0,047	2,364	100
O	17	34	1	99,263	5,692	5,734	2,776	2,796	99
M	17	34	0	7,401	0,535	7,226	0,166	2,241	
R	17	34	1	15,002	0,586	3,904	0,318	2,119	96
N	17	34	0	7,179	0,463	6,447	0,141	1,960	
S	17	34	0	16,941	0,900	5,313	0,202	1,195	98
P	17	34	2	7,222	0,291	4,031	0,171	2,373	
Q	17	34	0	22,247	1,138	5,117	0,501	2,252	99

LAB = Number of laboratories
L = Standard 2 mg/l
O = Standard 100 mg/l
M = Settled sewage
R = Settled sewage spiked with 8 mg/l
N = Final effluent
S = Final effluent spiked with 10 mg/l
P = Estuary
Q = Estuary spiked with 15 mg/l
No = Number of results
NAP = Number of outlier laboratories
s_R = Standard deviation of reproducibility
CV_R = Reproducibility coefficient of variation
s_r = Standard deviation of repeatability
CV_r = Repeatability coefficient of variation