International Standard

ISO 6778

Water quality — Determination of ammonium — Potentiometric method

Qualité de l'eau — Dosage de l'ammonium — Méthode potentiométrique

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 6778 was developed by Technical Committee ISO/TC 147, *Water quality*, and was circulated to the member bodies in December 1982.

It has been approved by the member bodies of the following countries:

Austria	Iran	Romania
Belgium	Iraq	South Africa, Rep. of
Brazil	Italy	Spain
Canada	Japan	Sweden
China	Korea, Dem. P. Rep. of	Switzerland
Czechoslovakia	Mexico	Thailand
Egypt, Arab Rep. of	Netherlands	United Kingdom
Germany, F.R.	New Zealand	USSR
Hungary	Norway	
India	Poland	

The member bodies of the following countries expressed disapproval of the document on technical grounds:

Australia
France

Water quality — Determination of ammonium — Potentiometric method

1 Scope

This International Standard specifies a potentiometric method, using an ammonia-sensing membrane probe, for the determination of ammonium in raw and waste water and sewage.

2 Field of application

2.1 Range

The method is applicable, without dilution of the test portion, to the determination of an ammonium nitrogen concentration, ϱ_N, of up to 50 mg/l.

2.2 Limit of detection

The limit of detection is defined as the limit of Nernstian response (see clause 3) under the conditions specified, and has a value corresponding to approximately $\varrho_N = 0,2$ mg/l.

2.3 Sensitivity

The potential of the probe changes by approximately 60 mV per decadic change in ammonium concentration, in accordance with the Nernst equation.

2.4 Interferences

The ammonia-sensing membrane probe does not respond satisfactorily if it is continually used for determinations on waters having ammonium concentrations exceeding $\varrho_N = 50$ mg/l; for such waters, it is recommended that the test portions be diluted to bring the concentration to below this value.

The response of the probe is affected by the transfer of water vapour through the semi-permeable membrane if there is an osmotic pressure difference across it. Thus, it is necessary to ensure that the osmotic pressure of a sample, after treatment with the alkaline buffer solution, is closely similar to that of the normal internal filling solution of the probe. For this purpose, unbuffered samples having total concentration of dissolved species (i.e. the sum of the concentrations of all ionic and other

species in solution, in moles per litre) greater than 0,1 mol/l should be diluted before measurement, provided that this dilution does not reduce the ammonium concentration to less than 0,2 mg of nitrogen per litre.

Amines may give positive interferences; the interferences listed in table 1 have been reported.

Table 1

Interferent	Concentration of interferent	Apparent increase in an ammonium concentration of $\varrho_N = 1$ mg/l
	mg/l	mg/l
Hydrazine	4	0,06
Cyclohexylamine	1	0,03
Morpholine	10	0,03
Octadecylamine	0,4	0,14
Methanolamine	3,4	0,15*
Urea	11	0,01

* Apparent increase in an ammonium concentration of $\varrho_N = 0,5$ mg/l.

Surface-active agents and some organic solvents reduce the life of the membrane of the probe, and hence increase the frequency with which the probe requires servicing. This effect may be severe, leading to rapid probe failure, in samples containing high concentrations of these interferents.

3 Principle

Treatment of the test portion with an alkaline buffer solution containing sodium hydroxide and a complexing agent in order to raise the pH value of the sample to 12 and to sequester metals which could otherwise complex with the ammonia. In the alkaline medium, the ammonium ions are converted to aqueous ammonia. Determination of the ammonia content using an ammonia-sensing membrane probe, the electrode of which senses the partial pressure of ammonia in the solution.

The potential of the probe changes by approximately 60 mV per decadic change of ammonium concentration, in accordance with the Nernst equation

$$E_p = E_o - 2,3 \frac{RT}{F} \log_{10} c(NH_4^+)$$

where

E_p is the probe potential, in millivolts;

E_o is the conditional standard potential, in millivolts, dependent upon the probe and the reference electrode;

R is the gas constant;

T is the thermodynamic temperature, in kelvins;

F is the Faraday constant;

$c(NH_4^+)$ is the ammonium ion concentration, expressed in moles per litre.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and only water prepared as described in 4.1.

4.1 Water, ammonium-free, prepared by one of the following methods.

4.1.1 Ion exchange method

Pass distilled water through a column of strongly acidic cation exchange resin (in the hydrogen form) and collect the eluate in a glass bottle provided with a well-fitting glass stopper. Add about 10 g of the same resin to each litre of collected eluate for storage purposes.

4.1.2 Distillation method

Add 0,10 ± 0,01 ml of sulfuric acid (ϱ = 1,84 g/ml) to 1 000 ± 10 ml of distilled water and redistil in an all glass apparatus. Discard the first 50 ml of distillate, and then collect the distillate in a glass bottle provided with a well-fitting glass stopper. Add about 10 g of strongly acidic cation exchange resin (in the hydrogen form), to each litre of collected distillate.

4.2 Alkaline buffer solution, containing 1 mol of sodium hydroxide and 0,1 mol of disodium ethylenediaminetetraacetate per litre.

Dissolve 40 ± 0,2 g of sodium hydroxide and 37,2 ± 0,2 g of disodium ethylenediaminetetraacetate (EDTA, disodium salt) in about 800 ml of water and dilute to 1 litre.

Store the solution in a polyethylene bottle.

For the determination of low ammonium concentrations (ϱ_N < 0,5 mg/l), this buffer solution should be boiled for about 20 min and then cooled before diluting.

4.3 Ammonium chloride, approximately 0,1 mol/l solution.

Dissolve 5,4 ± 0,1 g of ammonium chloride in about 800 ml of water and dilute to 1 litre.

4.4 Ammonium nitrogen, standard solution, ϱ_N = 1 000 mg/l.

Dissolve 3,819 ± 0,004 g of ammonium chloride (dried at 105 °C for at least 2 h) in about 800 ml of water, and dilute to 1 000 ml in a one-mark volumetric flask.

1 ml of this solution corresponds to 1 mg of N.

Store the solution in a stoppered glass bottle. It is stable for at least 1 month.

4.5 Ammonium nitrogen, standard solution, ϱ_N = 100 mg/l.

Transfer, by means of a pipette, 100 ml of the ammonium nitrogen standard solution (4.4) into a 1 000 ml one-mark volumetric flask and dilute to the mark with water.

1 ml of this solution corresponds to 0,1 mg of N.

Store the solution in a stoppered glass bottle. It is stable for 1 week.

5 Apparatus

Ordinary laboratory apparatus, and

5.1 Ammonia-sensing membrane probe.

5.2 pH/millivoltmeter, accurate to 0,2 mV.

5.3 Magnetic stirrer, with polytetrafluoroethylene (PTFE) or polypropylene coated stirring bars.

5.4 Conical flasks, of capacity 100 ml.

6 Sampling and samples

Laboratory samples should be collected in polyethylene or glass bottles. They should be analysed as quickly as possible, or else stored at between 2 and 5 °C until analysed. Acidification with sulfuric acid (ϱ = 1,84 g/ml) to pH < 2 may also be used as an aid to preservation, provided that possible contamination of the acidified sample by absorption of any atmospheric ammonia is avoided.

However, do not add so much acid that the correct pH value is not attained when the buffer solution (4.2) is added.

7 Procedure

7.1 Preparation of calibration graph

7.1.1 Prepare at least three ammonium calibration solutions having concentrations encompassing the expected concentration range of the samples.

If the expected concentration range of the samples is large, prepare three calibration solutions corresponding to 50; 5; and 0,5 mg of N per litre by diluting, respectively, 500; 50; and 5 ml of the ammonium nitrogen standard solution (4.5) to the mark in 1 000 ml one-mark volumetric flasks. If the range is small, however, it is preferable to prepare calibration solutions of concentrations which bracket the range as closely as possible, by appropriate dilution of the ammonium nitrogen standard solution (4.5); it may then be necessary to prepare calibration solutions of intermediate concentrations.

7.1.2 Transfer 50 ml of the weakest calibration solution, by means of a pipette, into a dry 100 ml conical flask (5.4). (See note 1.)

Stir gently by means of the magnetic stirrer (5.3). (A frequency of rotation of 300 ± 50 min^{-1} is suitable.) To avoid heating the test portion by the stirrer motor, place a thin sheet of insulating material between the flask and stirrer. Immerse the probe tip in the solution, taking care not to trap bubbles on the end, and add, by means of a pipette, 5 ml of the alkaline buffer solution (4.2).

Measure and record the potential, in millivolts, of the probe when this has become constant to within 0,1 mV in 30 s. Remove the probe from the solution and rinse with water.

Repeat this procedure, using the stronger calibration solutions in order of increasing concentration.

NOTES

1   A 100 ml beaker may be used, but a conical flask with an aperture just large enough to accept the probe is preferred, as the loss of ammonia is thereby reduced.

2   Calibration solutions which have been rendered alkaline should be discarded after use, as they will lose sufficient ammonia after 5 to 10 min to make them inaccurate. Fresh portions of the calibration solutions should be used for subsequent calibrations.

3   Check the calibration of the probe using one, or preferably two, calibration solutions every 3 h. The temperature of the calibration solutions should be within 1 °C of that of the test portions.

7.1.3 Plot a calibration graph of the potentials of the probe, in millivolts, against the logarithms, to base 10, of the ammonium concentrations, expressed in milligrams of N per litre, of the calibration solutions.

NOTE — The slope of the linear part of the calibration graph should be $58,5 \pm 2$ mV per decadic change of ammonium concentration at normal laboratory temperatures. If this is not the case, refer to the instruction manual for the probe.

7.2   Setting meter for direct concentration readings

NOTE — This method should not be used if the ammonium concentrations, expressed as nitrogen, of either the calibration solutions or the samples is less than 0,2 mg/l, because the relationship deviates from linearity at such concentrations.

Prepare appropriate calibration solutions as described in 7.1. Calibrate the pH meter as described in its instruction manual, proceeding as described in 7.1 and taking the readings only after they have become constant.

7.3   Determination

Allow laboratory samples to attain room temperature before determination. The temperature of the test portions should be within 1 °C of that of the calibration solutions.

Take, by means of a pipette, 50 ml of the laboratory sample as the test portion, transfer it to a dry 100 ml conical flask (5.4) and proceed as described in 7.1.2.

7.4   Storage of the probe

Store the probe, between determinations, in one of the calibration solutions which has been treated with the alkaline buffer solution.

For storage over longer periods (for example overnight), store the probe with the tip immersed in the ammonium chloride solution (4.3). Rinse the tip of the probe thoroughly before use.

8   Expression of results

8.1   Method of calculation

Determine from the calibration graph the ammonium concentration, expressed in milligrams of N per litre, corresponding to the measured potential of the probe.

The result may be expressed as the mass concentration of nitrogen, ϱ_N; ammonia, ϱ_{NH_3}; or ammonium ion, $\varrho_{NH_4^+}$; in milligrams per litre, or as the amount of substance concentration of ammonium ion, $c(NH_4^+)$, in micromoles per litre. The appropriate conversion factors are given in table 2.

Table 2

	ϱ_N	ϱ_{NH_3}	$\varrho_{NH_4^+}$	$c(NH_4^+)$
	mg/l	mg/l	mg/l	µmol/l
$\varrho_N = 1$ mg/l	1	1,216	1,288	71,4
$\varrho_{NH_3} = 1$ mg/l	0,823	1	1,059	58,7
$\varrho_{NH_4^+} = 1$ mg/l	0,777	0,944	1	55,4
$c(NH_4^+) = 1$ µmol/l	0,014	0,017	0,018	1

Example:

An ammonium ion concentration, $\varrho_{NH_4^+}$, of 1 mg/l corresponds to a nitrogen concentration of 0,777 mg/l.

8.2 Precision

Repeatability and reproducibility standard deviations have been determined as indicated in table 3.

9 Special cases

9.1 Introduction

The analysis of samples of certain waste waters by the procedure specified in clause 7 may be complicated by matrix effects in the sample. To minimize such effects, and to check questionable results, the addition technique described in this clause may be used. Where such effects are severe, as for example in samples containing the interfering substances mentioned in 2.4, prior distillation of the sample should be employed.

9.2 Principle

After measurement of the probe potential in the test portion, addition of ammonium nitrogen standard solution to the test portion and measurement of the new probe potential.

Calculation of the ammonium concentration of the sample from the change in potential and the slope of the calibration graph.

9.3 Procedure

Proceed as described in 7.3, but, after measurement of the potential, leave the probe tip immersed in the test portion.

Add a volume of the ammonium nitrogen standard solution (4.4 or 4.5) to the test portion such that the anticipated ammonium concentration of the test portion is increased by between 50 % and 100 %. Record the new potential, and note the volume of the ammonium nitrogen standard solution added. Thoroughly rinse the probe with water before analysing the next sample.

NOTES

1 If the ammonium concentration of the sample cannot be anticipated, the volume of ammonium nitrogen standard solution added should be sufficient to cause a change in potential of at least 20 mV.

2 The volume of ammonium nitrogen standard solution added should be as small as possible to minimize dilution of the test portion.

3 This procedure is only applicable in the linear range of the probe response.

9.4 Expression of results

The ammonium concentration, $\varrho_{N\,1}$, expressed in milligrams per litre, is given by the equation

$$\varrho_{N\,1} = \frac{k\,\varrho_{N\,2}}{\text{antilog}\,[(E_1 - E_2)/S]\,(k + 1) - 1}$$

where

$\varrho_{N\,2}$ is the ammonium nitrogen concentration, expressed in milligrams per litre, of the ammonium nitrogen standard solution used for the addition;

E_1 is the initial potential, in millivolts, of the probe;

E_2 is the final potential, in millivolts, of the probe;

S is the slope, in millivolts per decadic change of ammonium nitrogen concentration (see clause 3), of the calibration graph (see 7.1);

$$k = \frac{V_1}{V_0}$$

in which

V_0 is the volume, in millilitres, of the test portion;

V_1 is the volume, in millilitres, of the standard solution used for the addition.

10 Test report

The test report shall include the following information:

a) reference to this International Standard;

b) all details required for the complete identification of the sample;

c) details concerning the storage and preservation of the laboratory sample before analysis;

d) a statement of the repeatability achieved by the laboratory when using this method;

e) the results and the method of expression used;

f) any details of deviation from the procedure specified in this International Standard or any other circumstance that may have influenced the result.

Table 3*

Sample	Ammonium concentration, ϱ_N mg/l	Standard deviation** (mg/l)	
		Repeatability	Reproducibility
Standard solution	0,5	0,010	0,012
Standard solution	2	0,030	0,050
Standard solution	25	0,06 to 0,52 ***	0,24 to 1,29 ***
River water	3	0,016 to 0,217***	0,048 to 0,391***
Sewage effluent	3	0,036 to 0,205***	0,045 to 0,476***
Sewage effluent	8	0,035 to 0,310***	0,085 to 0,562***

*   Data obtained in the United Kingdom.

**   All estimates have 9 degrees of freedom.

*** The lowest and highest values obtained in an interlaboratory trial involving three participants.