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See CNAD AC/326 STANAG distribution

STANAG 4024 JAS (EDITION 3) – AMMONIUM NITRATE (AN) (FOR USE IN EXPLOSIVES), PHYSICAL AND CHEMICAL REQUIREMENTS, SPECIFICATION

References:
a. PFP(AC/326)D(2004)0009 dated 15 March 2004
b. MAS(ARMY)(62)643 dated 25 September 1962 (Edition 2)

1. The enclosed NATO Standardization Agreement, which has been ratified by nations as reflected in the **NATO Standardization Document Database (NSDD)**, is promulgated herewith.

2. The references listed above are to be destroyed in accordance with local document destruction procedures.

ACTION BY NATIONAL STAFFS

3. National staffs are requested to examine **their ratification status of the STANAG** and, if they have not already done so, advise the Defence Investment Division through their national delegation as appropriate of their intention regarding its ratification and implementation.

J. MAJ
Brigadier General, POL(A)
Director, NSA

Enclosure:
STANAG 4024 (Edition 3)

STANAG 4024
(Edition 3)

NORTH ATLANTIC TREATY ORGANIZATION
(NATO)

NATO AGENCY FOR STANDARDIZATION
(NSA)

STANDARDIZATION AGREEMENT
(STANAG)

SUBJECT: AMMONIUM NITRATE (AN) (FOR USE IN EXPLOSIVES), PHYSICAL AND CHEMICAL REQUIREMENTS, SPECIFICATION

Promulgated on 11 July 2006

J. MAJ
Brigadier General, POL(A)
Director, NSA

RECORD OF AMENDMENTS

No.	Reference/date of Amendment	Date Entered	Signature

EXPLANATORY NOTES

AGREEMENT

1. This NATO Standardization Agreement (STANAG) is promulgated by the Director NATO Standardization Agency under the authority vested in him by the NATO Standardization Organisation Charter.

2. No departure may be made from the agreement without informing the tasking authority in the form of a reservation. Nations may propose changes at any time to the tasking authority where they will be processed in the same manner as the original agreement.

3. Ratifying nations have agreed that national orders, manuals and instructions implementing this STANAG will include a reference to the STANAG number for purposes of identification.

RATIFICATION, IMPLEMENTATION AND RESERVATIONS

4. Ratification, implementation and reservation details are available on request or through the NSA websites (internet http://nsa.nato.int; NATO Secure WAN http://nsa.hq.nato.int).

FEEDBACK

5. Any comments concerning this publication should be directed to NATO/NSA – Bvd Leopold III - 1110 Brussels - BE.

STANAG 4024
(Edition 3)

NAVY/ARMY/AIR

NATO STANDARDIZATION AGREEMENT
(STANAG)

AMMONIUM NITRATE (AN) (FOR USE IN EXPLOSIVES), PHYSICAL AND CHEMICAL REQUIREMENTS, SPECIFICATION

ANNEXES:

A. Table 1: Physical and chemical requirements for pure AN
B. Table 2: Physical and chemical requirements for AN containing surface additives
C. Table 3: Physical and chemical requirements for phase stabilized AN
D. Test procedures

RELATED DOCUMENTS

STANAG 4515:	Explosives, thermal characterization by Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA)

AIM

1. The aim of this agreement is to establish a minimum common specification for deliveries of ammonium nitrate (AN) for military purposes from one NATO nation to another.

AGREEMENT

2. The participating countries agree that AN manufactured by NATO countries for delivery to other NATO countries – except when the order is intended for special purposes – must fulfil the minimum conditions of tables 1, 2 or 3 below.

The ammonium nitrate shall either consist of pure AN, of AN containing surface additives or of phase stabilized material. The type of AN must be mentioned, the additive(s) and their content(s) as well.

All three types of AN mentioned above can appear either as crystalline or as prilled (porous spherical particles) material.

DEFINITIONS

3. Definition of lot

A lot shall consist of the total quantity of cross-blended material. For noncross-blended material a lot shall consist of the quantity produced in a single batch or – if produced in a continuous process – of the total quantity offered for acceptance at one time.

GENERAL

4. All information on the proposed manufacturing process must be provided in confidence at the request of the responsible bodies in the purchasing country. Any deviation from this accepted process must be noted and the product thus manufactured must be put aside until the responsible bodies of the purchaser have decided whether to accept or reject it.

DETAILS OF THE AGREEMENT

5. Appearance, granulation and sampling

a) Appearance

The ammonium nitrate shall either be in the form of crystalline AN or of prilled material: If AN contains additives, e.g. anti-caking agents, the purchaser must clearly specify the form and the type of product he requires.

b) Particle size distribution

As the particle size distribution may be a major characteristic of the product, the sizes must be specified by the purchaser.

c) Sampling

A representative sample shall be taken from each lot by a sampling technique which has been agreed to by the purchasing authority. The minimum weight of a sample shall be 200 g.

WARNING

6. This STANAG calls for the use of substances and test procedures that may be injurous to health if adequate precautions are not taken. It refers only to technical suitability and in no way absolves the user from the statutory obligations relating to health and safety at any stage during use.

IMPLEMENTATION OF THE AGREEMENT

7. This STANAG is implemented when a country has given the necessary orders to enforce it.

Table 1: Physical and chemical requirements for pure AN

Property	Requirement	Test Method see Annex D para
Ether soluble matter	max. 0.1%	2
AN content (Purity)	min. 99%	3 or 4
Water insoluble	max. 0.18%	5
Moisture (at time of packing)	max. 0.15%	6 or 7
Acidity (as nitric acid)	max. 0.02%	8
Alkalinity (as sodium hydroxide)	none	9
Nitrites	specified by purchaser	10 or 11
Sulphates (as ammonium sulphate)	max. 0.02%	10
Chlorides (as ammonium chloride)	max. 0.02%	10 or 12
Particle size distribution	specified by purchaser	13 or 14

Table 2: Physical and chemical requirements for AN containing surface additives

Property	Requirement	Test Method see Annex D para
Ether soluble matter	specified by purchaser	2
AN content (Purity)	specified by purchaser	3 or 4
Water insoluble	specified by purchaser	5
Moisture (at time of packing)	max. 0.15%	6 or 7
Acidity (as nitric acid)	max. 0.02%	8
Alkalinity (as sodium hydroxide)	none	9
Nitrites	specified by purchaser	10 or 11
Sulphates (as ammonium sulphate)	max. 0.02%	10
Chlorides (as ammonium chloride)	max. 0.02%	10 or 12
Particle size distribution	specified by purchaser	13 or 14
Anti-caking agents	specified by purchaser	must be provided by supplier
Other additives	specified by purchaser	must be provided by supplier

Table 3: Physical and chemical requirements for phase stabilized AN

Property	Requirement	Test Method see Annex D para
Ether soluble matter	specified by purchaser	2
AN content (Purity)	specified by purchaser	3 or 4
Water insoluble	specified by purchaser	5
Moisture (at time of packing)	max. 0.25%	6 or 7
Acidity (as nitric acid)	max. 0.02%	8
Alkalinity (as sodium hydroxide)	none	9
Nitrites	specified by purchaser	10 or 11
Sulphates (as ammonium sulphate)	max. 0.02%	10
Chlorides (as ammonium chloride)	max. 0.02%	10 or 12
Particle size distribution	specified by purchaser	13 or 14
Anti-caking agents	specified by purchaser	must be provided by supplier
Other additives	specified by purchaser	must be provided by supplier
Phase stabilizing agents	specified by purchaser	must be provided by supplier
Phase conversions	specified by purchaser	15

Test Procedures

Paragraph 1

INDEX

Paragraph

AN content

Moisture

Nitrites

Sulphates

Chlorides

Particle size distribution

Phase transitions

Test Procedures

Paragraph 2

Ether soluble matter - Gravimetric Method

2.1 Principle

Some AN based technical products may contain organic substances as additives, e.g. nitric acid esters, wax, etc. and organic impurities. These substances may cause problems while determining the AN content by titration and can be removed by extraction with diethyl ether using a Twisselmann or a Soxhlet extractor. The residue is dried and weighed. The loss of weight is calculated.

2.2 Apparatus

Twisselmann or Soxhlet extractor
Steam bath
Analytical balance
Sintered glass crucible (D4) [D4 (new ISO 4793 classification P 16) describes crucibles with pore diameters of the widest pores of 10-16 µm.]
Desiccator
Drying cabinet

2.3 Reagents

Diethyl ether, analytical reagent grade

2.4 Procedure

The crucible should be pretreated by rinsing with diethyl ether, drying for 1 hour at 80°C, and cooling in a desiccator. It should then be weighed to the nearest 0.001 g (w1). Weigh approximately 10 g of the homogenized sample accurately to the nearest 0.001 g into the crucible (w2) and place it in the extractor. Add 150 ml of diethyl ether and extract the soluble components 5 hours at a steam bath temperature of 80 °C.

The residue in the crucible (diethyl ether insoluble matter) is dried for 1 hour in a drying cabinet at 80°C and cooled down to ambient temperature in a desiccator. After determination of weight (w3) the residue can be used for determination of AN content using the titrimetric methods (see paragraphs 3 and 4).

2.5 Reporting

Percent diethyl ether insoluble matter :

Ether insoluble matter [%] = $\frac{(w3 - w1) * 100}{w2}$

Where w1 [g]: the weight of the empty crucible rams.

w2 [g]: the weight of the AN containing sample.

w3 [g]: the weight of the crucible after extraction with diethyl ether.

Ether soluble matter [%] = 100 % - Ether insoluble matter [%]

Test Procedures

Paragraph 3

AN content - Titrimetric Method 1

3.1 Principle

AN and water soluble additives or impurities are dissolved in water. The AN content is determined by titration with an aqueous sodium hydroxide solution to pH 11.

3.2 Apparatus

Analytical balance

Sintered glass crucible (D4) [D4 (new ISO 4793 classification P 16) describes crucibles with pore diameters of the widest pores of 10-16 µm.],
see «Test procedures paragraph 2 Ether soluble matter»

Volumetric flask, 500 ml

pH electrode

Filtering flask with filtering attachment

Pipette, 50 ml

Beaker, 250 ml

Volumetric apparatus

3.3.1 Reagents

Water, reagent grade

Aqueous sodium hydroxide solution 0.5M, analytical reagent grade

Potassium hydrogen phthalate, analytical reagent grade

Nessler´s reagent, analytical reagent grade

pH 7 and 11 standard solutions to standardize the pH meter.

3.4 Procedure

Put the crucible with the diethyl ether insoluble residue of «Test procedures paragraph 2 Ether soluble matter» on the filtering attachment of the filtering flask and treat it with cold water (approx. 20°C). Collect the water soluble matter of the sample in the volumetric flask. The residue must be free of ammonium ions (test by Nessler‘s reagent).

Fill the volumetric flask with the water soluble matter to the marking. Take an aliquot of 50 ml and transfer it into a 250 ml beaker. Titrate with aqueous sodium hydroxide solution to pH 11. The volume needed is noted (v1).

Run a blank determination using 50 ml of water, titrating to pH 11 as above and note the volume needed (v2).

Determine the factor of the sodium hydroxide solution by weighing 3 g of potassium hydrogen phthalate to the nearest 0.0001 g into a 150 ml beaker (w), dissolve it in 80 ml of water and titrate the solution to pH 7. The volume needed is noted (v3).

Run a blank determination using 80 ml of water, titrating to pH 7 as above and note the volume needed (v4).

3.5 Reporting

Factor of sodium hydroxide solution:

$$\text{Theoretical value [ml]} = \frac{w * 1000}{204.221 * 0.5}$$

Where w: the weight of the potassium hydrogen phthalate in grams.

The number 1000 converts liters into milliliters

The number 0.5 [mole/liter] is the nominal molarity of the sodium hydroxide solution

The number 204.221 [g/mole] is the molecular weight of the potassium hydrogen phthalate.

$$\text{Factor} = \frac{\text{Theoretical value [ml]}}{\text{v3 [ml]} - \text{v4 [ml]}}$$

Where v4: titration volume of NaOH solution needed for titration of water (blank determination).

v3: titration volume of NaOH solution needed for titration of potassium hydrogen phthalate.

$$\text{AN content} = \frac{(v1 - v2) * \text{Factor} * 40.0215 * 10 * 0.5}{w2 * 1000}$$

Where v1 [ml]: titration volume of NaOH solution needed for titration of AN.

v2 [ml]: titration volume of NaOH solution needed in blank determination.

Factor: see above.

w2 [g]: weight of AN containing sample (see « Test procedures paragraph 2 Ether soluble matter »).

The number of 10 accounts for the fact that a 50-ml aliquot was taken out of a sample with a total volume of 500 ml.

The number 0.5 is the nominal molarity of the sodium hydroxide solution.

The number 1000 converts the volume of NaOH from milliliters into liters.

Test Procedures

Paragraph 4

AN content - Titrimetric Method 2

4.1 Principle

AN and water soluble additives or impurities are dissolved in water. After addition of formaldehyde solution nitric acid is set free and can be determined by titration with a aqueous sodium hydroxide solution to the phenolphtalein indicator end-point.

4.2 Apparatus

Analytical balance
Sintered glass crucible (D4) [D4 (new ISO 4793 classification P 16) describes crucibles with pore diameters of the widest pores of 10-16 µm.]
see «Test procedures paragr. 2 Ether soluble matter »
Volumetric flask, 500 ml
Filtering flask with filtering attachment
Pipette, 50 ml
Pipette, 5 ml
Beaker, 250 ml
Volumetric apparatus

4.3 Reagents

Water, analytical reagent grade
Formaldehyde solution 37%, neutralized to phenolphthalein
Aqueous sodium hydroxide solution 0.5M, analytical reagent grade
Ammonium chloride, analytical reagent grade
Phenolphtalein indicator, analytical reagent grade, 0.1 g in 100 ml ethanol

4.4 Procedure

Dissolve and prepare the water soluble matter as stated in paragraph 3.4 page D-3. Instead of titrating with sodium hydroxide solution add 10 ml of formaldehyde solution, stir the mixture and wait 2 minutes. Then add some drops of the indicator and titrate the nitric acid set free by formaldehyde with aqueous sodium hydroxide solution to the end-point of phenolphtalein (light red colour stable for one minute after last addition). The volume needed is noted (v1).

Run a blank determination using 50 ml of water, titrating like stated before and note the volume needed (v2).

Determine the factor of the sodium hydroxide solution by weighing 250 to 300 mg of dried ammonium chloride (2 hours at 100°C) to the nearest 0.0001 g into a 150 ml beaker, dissolving it in 50 ml water, adding 10 ml of formaldehyde solution and treating the mixture like the AN containing solution. The titration volume is noted (v3).

4.5 Reporting

Factor of sodium hydroxide solution :

Factor = mg AN per ml 0.5M sodium hydroxide solution

$$= \frac{w1 * 1.4964}{(v3 - v2)}$$

Where w1 [g]: the weight of dried ammonium chloride.

v3 [ml]: titration volume of NaOH solution needed to reach end-point of phenolphthalein titrating ammonium chloride.

v2 [ml]: titration volume of NaOH solution needed to reach end-point of phenolphthalein titrating water (blank determination).

The number 1.4964 is the weight ratio of ammonium nitrate to ammonium chloride.

$$\text{AN content} = \frac{(v1 - v2) * \text{Factor} * 1000}{w2}$$

Where v1 [ml]: titration volume of NaOH solution needed to reach end-point of phenolphthalein titrating nitric acid, set free from AN.

v2 [ml]: see above.

Factor: see above.

w2 [g]: weight of AN containing sample (see « Test procedures paragraph 2 Ether soluble matter »).

Test Procedures

Paragraph 5

Water insoluble

5.1 Principle

AN and water soluble additives are dissolved in water and filtered using a sintered glass crucible. The water insoluble matter is determined by gravimetry.

5.2 Apparatus

Analytical balance
Sintered glass crucible (D4) [D4 (new ISO 4793 classification P 16) describes crucibles with pore diameters of the widest pores of 10-16 µm.]
Filtering flask with filtering attachment
Desiccator

5.3 Reagents

Reagent grade water
Nessler‘s reagent, analytical reagent grade

5.4 Procedure

The crucible should be pretreated by rinsing with diethyl ether, drying for 1 hour at 80°C, and cooling in a desiccator. It should then be weighed to the nearest 0.001 g (w1). Weigh approximately 10 g of the homogenized sample accurately to the nearest 0.001 g into the crucible (w2) and place it in the filtering attachment. Add 25 ml of water (approx. 20°C), stir and remove the extract by suction. Repeat the extraction until the solution is free of ammonium ions (test by Nessler‘s reagent).

The residue in the crucible (water insoluble matter) is dried for 2 hours in a drying cabinet at 100°C, cooled down in a desiccator to ambient temperature and reweighed (w3).

5.5 Reporting

Water insoluble $[\%] = \frac{(w3 - w1) * 100}{w2}$

Where
w1 [g]: the weight of the empty crucible.
w2 [g]: the weight of the AN containing sample.
w3 [g]: the weight of the crucible after extraction with water.

Test Procedures

Paragraph 6

Moisture - Gravimetric Method

6.1 Principle

Moisture of AN can be determined by calculation of the weight loss while storing the sample at a certain temperature.

Note: It can not be excluded that other volatiles are included in the moisture value.

6.2 Apparatus

Analytical balance
Desiccator
Drying cabinet
Weighing dish with tight-fitting cover, minimum diameter 60 mm, minimum depth 30 mm

6.3 Procedure

Weigh the weighing dish and the tight-fitting cover to the nearest 0.0001 g (w1). Fill the tared weighing dish with a 10 g specimen, weighed to the nearest 0.0001 g (w2). Place the dish with the sample in a drying cabinet and store it for 5 hours at a temperature of 70 °C. Cool the specimen to room temperature in the desiccator. Cover the dish with the tight-fitting cover and reweigh (w3).

6.4 Reporting

$$\% \text{ Moisture} = \frac{w2 - (w3 - w1) * 100}{w2}$$

Where w1 [g]: weight of the empty weighing dish including tight-fitting cover.

w2 [g]: weight of the AN specimen.

w3 [g]: weight of the weighing dish including tight-fitting cover and heated AN specimen.

Test Procedures

Paragraph 7

Moisture - Karl-Fischer-Titration

7.1 Principle

AN is dissolved in dried methanol. Its moisture content is titrated according to Karl ischer (dead stop procedure).

7.2 Apparatus

Karl Fischer titrator (e.g. Metrohm E452 or an automatic titrator)
100 ml beaker
Micro syringe
Analytical balance

7.3 Reagents

Karl-Fischer-solution
Disodiumtartrate dihydrate analytical reagent grade
Methanol analytical reagent grade, dried

7.4 Procedure

Weigh 6 g of AN to the nearest 0.0001 g (w) into a well-dried 100 ml beaker and close it tightly immediately after weighing. Add 50 ml of dried methanol and wait until all AN is dissolved.

The solution is then titrated manually until its colour changes (dead stop principle).

Note the amount of Karl Fischer reagent solution needed (v1).

Run a blank experiment with 50 ml of methanol in parallel to determine the moisture content of the solvent. Note the amount of Karl Fischer reagent solution needed (v2).

Determine the titer of the Karl Fischer solution by titrating a disodiumtartrate dihydrate sample, or alternatively, by directly adding a small amount (50.0 mg) of water through a micro syringe.

If an automatic Karl-Fischer titrator is used, put the sample (6 g of AN) into a well-dried volumetric flask (50 ml) and dilute to the mark with dried methanol. A measured aliquot is then added from the flask to the automatic titrator for titration to a 30 second end point.

Afterwards a blank experiment with 50 ml of methanol has to be run.

7.5 Reporting

The amount of water in the AN sample is calculated by

$$\%water = \frac{T \cdot (v1 - v2)}{10 \cdot w}$$

Where v1 [ml] = amount of Karl Fischer solution for the AN containing solution.

v2 [ml] = amount of Karl Fischer solution needed for the blank solution.

T [mg water/ml reagent] = titer of the Karl Fischer solution (tested by disodiumtartrate dihydrate).

w [g] = weight of the AN specimen.

Test Procedures

Paragraph 8

Acidity (as nitric acid)

8.1 Principle

The acidity of AN is determined by titration of the sample with sodium hydroxide solution to the end-point of an indicator mixture.

8.2 Apparatus

Analytical balance
Beaker, 250 ml
Volumetric apparatus
Measuring cylinder, 250 ml

8.3 Reagents

Distilled water, analytical reagent grade
Aqueous sodium hydroxide solution 0.05M, analytical reagent grade
Methyl red / methylene blue indicator (0.1 g of methyl red and 0.05 g of methylene blue in 100 ml of 95% ethanol)
Potassium hydrogen phthalate, analytical reagent grade (to determine factor)

8.4 Procedure

Weigh a 10 g specimen of AN (w1) to the nearest 0.0001 g in the tared beaker. Add 200 ml of distilled water. Shake by hand from time to time until the ammonium nitrate is completely dissolved. Add 8 to 10 drops of the indicator solution and titrate the AN solution using sodium hydroxide solution until the end-point is reached (the colour of the solution turns from red to green). Note the volume used (v2).

Carry out a blank test. For this purpose fill 200 ml of distilled water in a beaker, add 8 to 10 drops of the indicator solution and titrate using sodium hydroxide solution until the end-point is reached. Note the volume used (v1).

Determine the factor of the sodium hydroxide solution according to paragraph 3.4, but using a weight (w) of only 0.3 g.

8.5 Reporting

Factor of sodium hydroxide solution:

$$\text{Theoretical value [ml]} = \frac{w * 1000}{204.221 * 0.05}$$

Where w [g]: weight of the potassium hydrogen phthalate.

The number 1000 converts liters into milliliters.

The number 0.05 [mole/liter] is the nominal molarity of the sodium hydroxide solution.

The number 204.221 [g/mole] is the molecular weight of the potassium hydrogen phthalate

$$\text{Factor} = \frac{\text{Theoretical value}}{v3 - v4}$$

Where v4: titration volume of NaOH solution needed for titration of water (blank determination) in ml.

v3: titration volume of NaOH solution needed for titration of potassium hydrogen phthalate in ml.

$$\text{Acidity (as nitric acid) [\%]} = \frac{(v2 - v1) * \text{Factor} * 0.315}{w1}$$

Where v1 [ml]: titration volume of NaOH solution needed to reach end-point titrating distilled water (blank determination).
v2 [ml]: titration volume of NaOH solution needed to reach end-point titrating AN.

factor: correction factor to the nominal molarity of 0.05 M of the sodium hydroxide solution (see paragraph 3.5).

w1 [g]: weight of the specimen.

The number 0.315 is the product of the molecular weight of HNO_3 (63.0), the nominal concentration of the NaOH solution (0.05), the conversion factor from liters to milliliters (0.001), and the conversion to percentage (100).

Test Procedures

Paragraph 9

Alkalinity (as sodium hydroxide)

9.1 Principle

The alkalinity of AN is determined by titration of the sample with sulphuric acid solution until the end-point of an indicator is reached. The alkalinity is only to be determined if no acidity is found and if the solution prepared for acid titration is alkaline towards methyl red.

9.2 Apparatus

Analytical balance
Beaker, 250 ml
Volumetric apparatus
Measuring cylinder, 250 ml

9.3 Reagents

Distilled water, analytical reagent grade
Aqueous sulphuric acid solution 0.05M, analytical reagent grade
Methyl red indicator (0.1 g of methyl red in 60 ml of ethanol)
Potassium hydrogen carbonate, analytical reagent grade (to determine factor)

9.4 Procedure

Weigh a 10 g specimen of AN to the nearest 0.0001 g in the tared beaker (w1). Add 200 ml of distilled water. Shake by hand from time to time until the ammonium nitrate is completely dissolved. Add 8 to 10 drops of the indicator solution and titrate the AN solution using sulphuric acid solution until the end-point is reached (colour change from yellow to reddish orange). Note the volume used (v2).

Carry out a blank test. For this purpose fill 200 ml of distilled water in a beaker, add 8 to 10 drops of the indicator solution and titrate using sulphuric acid solution until the end-point is reached. Note the volume used (v1).

Determine the factor of the sulphuric acid solution by weighing 150 mg of potassium hydrogen carbonate to the nearest 0.0001 g into a 150 ml beaker (w), dissolve it in 80 ml of water and titrate the solution to pH 7. The volume needed is noted (v3).

Run a blank determination using 80 ml of water, titrating to pH 7 as above and note the volume needed (v4).

9.5 Reporting

Factor of the sulphuric acid solution

Theoretical value [ml] $\frac{w * 1000}{100.12 * 0.05 * 2}$

Where w: the weight of the potassium hydrogen carbonate in grams.

The factor of 1000 converts volume from liters to milliliters

The number 100.12 is the molecular weight of the potassium hydrogen carbonate in grams/mole

The number 0.05 is the nominal concentration of sulfuric acid in moles/liter

The number 2 accounts for the fact that 2 moles of potassium hydrogen carbonate react with one mole of H_2SO_4

$$\text{Factor} = \frac{\text{Theoretical value [ml]}}{\text{v3 [ml]} - \text{v4 [ml]}}$$

Where v4: titration volume of H_2SO_4 solution needed for titration of water (blank determination).

v3: titration volume of H_2SO_4 solution needed for titration of potassium hydrogen carbonate.

$$\text{Alkalinity (as sodium hydroxide)[\%]} = \frac{(v2 - v1) * \text{factor} * 0.4000}{w1}$$

Where v1 [ml]: titration volume of sulphuric acid solution needed to reach end-point titrating distilled water (blank determination).

v2 [ml]: titration volume of sulphuric acid solution needed to reach end-point titrating AN.

factor: correction factor of the sulphuric acid solution to convert from nominal molarity to actual molarity.

w1 [g]: weight of the specimen.

The number 0.4000 is the product of the nominal molarity of the sulphuric acid solution (0.05), the molecular weight of NaOH (40.00), the conversion factor to change moles of sulfuric acid to moles of NaOH (2), the conversion factor to change milliliters to liters (0.001), and the conversion to percentage (100).

Test Procedures

Paragraph 10

Nitrites, sulphates and chlorides (ion chromatographic method)

10.1 Principle

A quantitative analysis of nitrites, sulphates and chlorides can be performed simultaneously by ion chromatography using conductivity as method of detection.

Other methods (e.g. ion-pair chromatography, capillary electrophoresis, direct potentiometry or titraton with ion selective electrodes) can be used if they show equivalent precision.

10.2 Apparatus

Analytical balance
Ion chromatograph
Column: IonPac AS10 or comparable column
Suppressor: AMMS-II or comparable
Detector: conductimeter or comparable
Injection loop: 50 µl
Flow: 1 ml/min
Volumetric flask, 1000 ml
Volumetric flask, 100 ml
Pipette, 10 ml
Pipette, 200 µl

10.3 Reagents

Dilution agent: distilled water, analytical reagent grade
Eluant: aqueous sodium hydroxide solution 0.1M, analytical reagent grade
Standard stock solution 1: 1000 mg/l nitrite standard solution (sodium nitrite in water), analytical reagent grade
Standard stock solution 2: 1000 mg/l sulphate standard solution (sodium sulphate in water), analytical reagent grade
Standard stock solution 3: 1000 mg/l chloride standard solution (sodium chloride in water), analytical reagent grade
Sample stock solution: 13 g AN/l distilled water

10.4 Procedure

Dilute each standard stock solution by taking an aliquot of 100 µl, transfer it in a 1000 ml volumetric flask and fill up with water to the marking (dilution 1:10000). Prepare other dilutions (200 µl standard stock solution / l water and 300 µl standard stock solution / l water).

Perform determination of retention time and peak area of each diluted standard. Repeat this procedure twice. Calculate the mean peak area of each diluted standard. Compare each peak area measured with the mean peak area. The deviation should not be higher than 10 %, otherwise the complete examination of this standard solution must be repeated.

Dilute the sample stock solution 1:10. Run analysis of diluted AN sample as stated before. A chromatogram of a nitric acid solution (37 % by weight, diluted 1:100) which contains nitrite, chloride and sulphate can be seen at figure D-10.

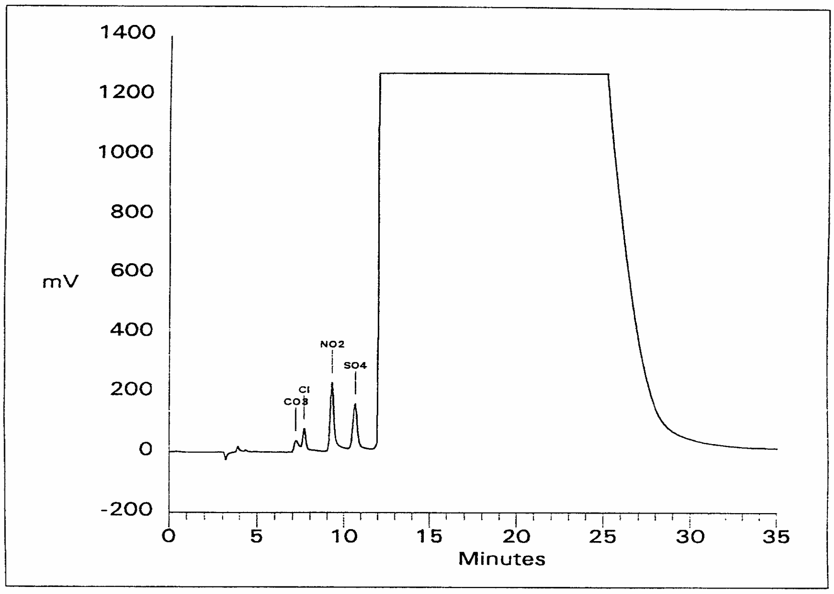

Figure D-10. Chromatogram of diluted nitric acid, containing nitrite, chloride and 0.012% sulphate

10.5 Reporting

The software of the chromatograph compares the mean peak area of the anionic standard with the corresponding peak area of the sample and calculates a content (« % nitrites », « % sulphates » and « % chlorides »).

To report the nitrites, sulphates and chlorides as the corresponding ammonium salts, a correction must be carried out :

$$\text{Content of ammonium nitrite [\%]} = \frac{\text{content of nitrites [\%]} * 64.044}{46.006}$$

Where 64.044: Molar weight of ammonium nitrite.
46.006: Molar weight of the nitrite ion.

$$\text{Content of ammonium sulphate [\%]} = \frac{\text{content of sulphates [\%]} * 132.14}{96.058}$$

Where 132.14: Molar weight of ammonium sulphate.
96.058: Molar weight of the sulphate ion.

$$\text{Content of ammonium chloride [\%]} = \frac{\text{content of chlorides [\%]} * 53.492}{35.453}$$

Where 53.492: Molar weight of ammonium chloride.
35.453: Molar weight of the chloride ion.

Test Procedures

Paragraph 11

Nitrites (colorimetric method)

11.1 Principle

Nitrites react with sulphuric acid and metaphenylenediamine developing a yellowish-brown coloured solution. The intensity of the sample solution is compared with one standard solution of known nitrite amount corresponding to a limited nitrate concentration specified by a purchaser. This comparison can be carried out by visual examination or by using a spectrophotometer.

11.2 Apparatus

Volumetric flask, 100 ml
Pipette, 1 ml
Pipette, 2 ml
Analytical balance
Beaker, 50 ml
Measuring cylinder, 50 ml

11.3 Reagents

Distilled water, analytical reagent grade
Aqueous sulphuric acid solution 10% by weight, analytical reagent grade
Aqueous metaphenylenediamine solution, 0.5 % by weight, analytical reagent grade
Aqueous sodium nitrite solution, analytical reagent grade (concentration according to a specification of a purchaser, a concentration of 0.1360 g/l corresponds to 0.01 % nitrite content)

11.4 Procedure

Prepare a test solution consisting of 1 g of sample dissolved in 20 ml of water, 1 ml of the sulphuric acid and 1 ml of the metaphenylenediamine solution.

Prepare a comparative solution, consisting of 19 ml of water, 1 ml of the sodium nitrite solution, 1 ml of the sulphuric acid solution and 1 ml of the meta-phenylenediamine solution. Compare the colours.

11.5 Reporting

If the colour of the first test solution is less intense than the comparative solution, the content of nitrites is less than the limit specified by a purchaser. If it is more intense, then the nitrite concentration exceeds the given limit.

Test Procedures

Paragraph 12

Chlorides (gravimetric method)

Note: This gravimetric method should only be used, if there is no other method available (ion chromatographic method, ion-selective electrodes). The quantity of a sample needed for this kind of determination is very high – the maximum permitted ammonium chloride content of a 100 g AN specimen is 20 mg!

12.1 Principle

Dissolved chlorides react with silver ions in nitric acid conditions under precipitation of silver chloride which can be determined by gravimetry.

12.2 Apparatus

Analytical balance
Sintered glass crucible (D4) [D4 (new ISO 4793 classification P 16) describes crucibles with pore diameters of the widest pores of 10-16 µm.]
Volumetric flask, 250 ml
Beaker, 400 ml
Pipette, 100 ml
Filtering flask with filtering attachment
Desiccator
Drying cabinet

12.3 Reagents

Distilled water, analytical reagent grade
Aqueous silver nitrate solution (0.1 M), analytical reagent grade
Nitric acid solution, 2M, analytical reagent grade

12.4 Procedure

Perform conditioning of the crucible (storage at 120 °C in the drying cabinet for 1 hour, cooling down to ambient temperature in the desiccator) and weigh it (w2).

Weigh a 100 g specimen of AN to the nearest 0.0001 g (w1) in the tared volumetric flask and dissolve it in distilled water. Fill up with distilled water to the marking. Transfer an aliquot of 100 ml into the beaker. Add some drops of nitric acid until a pH of 2 to 2.5 is reached.

Add – drop by drop – a total amount of 10 ml of the silver nitrate solution. The precipitate (silver chloride) is sensitive to light. Therefore it should be filtered as soon as possible. Dry the crucible with the silver chloride precipitate under the same conditions as the crucible was conditioned. Reweigh the crucible (w3).

12.5 Reporting

$$\text{Ammonium chloride [\%]} = \frac{0.3732 * 100 * (w3 - w2) * 2.5}{w1}$$

Where w1 [g]: Weight of the AN specimen.
w2 [g]: Weight of the empty crucible.
w3 [g]: Weight of the crucible and residue.

The factor of 0.3732 in the equation is the ratio of the molecular weights of ammonium chloride and silver chloride.

Test Procedures

Paragraph 13

Particle size distribution (LALLS method)

13.1 Principle

„LALLS“ means Low angle laser light scattering. Particles in a suspension cause scattering of a focussed laser beam. The angle of scattering depends on the size of the particle.

13.2 Apparatus

LALLS spectrometer (e.g. Malvern MasterSizer) including cell and dispersion unit Spatula

13.3 Reagents

Dispersant (solvent in which AN is insoluble)

13.4 Procedure

Choose optics according to the particle size distribution expected. Place the dispersant in the dispersion unit and let it circulate. Perform alignment and measuring of background. Take the spatula and fill small portions of the specimen into the dispersion unit. The obscuration shall be between 0.1 and 0.3.

Start measurement of the sample.

13.5 Reporting

The software of the spectrometer calculates the particle size distribution from the distribution of the laser light intensity measured. It is possible to determine the number distribution, the length distribution, the surface distribution and the volume distribution. The result should be reported as volume distribution. The type of LALLS spectrometer, the dispersant, the optics and the velocity of the stirrer of the dispersion unit must be mentioned.

Test Procedures

Paragraph 14

Particle size distribution (Sieve analysis)

14.1 Principle

Particles are sorted into categories solely on the basis of their sizes. The sieves are stacked on top of each other, with the sieve containing the coarsest openings on top. This set of sieves is vibrated until the residue on each sieve can pass through the upper sieve and cannot pass through the lower sieve. The residues on each sieve are weighed.

14.2 Apparatus

Sieving machine
Sieves
Spatula
Analytical balance

14.3 Reagents

Carbon black to avoid adhesion and caking. Alternatively tricalcium phosphate may also be used.

14.4 Procedure

Weigh each empty sieve (w1*i*), where *i* = 1,2,…n, for a stack of n sieves, including the pan at the bottom of the stack. Stack the sieves on top of each other, with the sieve containing the coarsest openings on top. Tare this set of sieves and add approx. 30 g of the specimen weighed to the nearest 0.1 g (w2). Put the sieves on the sieving machine, fix them and start the vibration program. Release the sieves when this program is finished and reweigh the sieves (w3*i*).

14.5 Reporting

Calculate the total mass of the sample recovered, w4 as follows:

$$w4 = \sum_{i=1}^{n} (w3i - w1i)$$

Where: w1*i* [g]: weight of empty i^{th} sieve.

w3*i* [g]: weight of i^{th} sieve (and residue) after sieving.

For each sieve, the percentage of the sample retained on the sieve will be reported, together with the sieve opening size, as:

$$\%\text{retained on i}^{\text{th}}\text{ sieve }(\text{m}_\text{i}) = \frac{(\text{w3i} - \text{w1i})}{\text{w4}} \times 100\%$$

Where m_i is the size of the openings in the i^{th} sieve in micrometers.

Test Procedures

Paragraph 15

Phase transitions (DTA/DSC method)

15.1 Principle

In Differential Thermal Analysis (DTA) and Heat Flow Differential Scanning Calorimetry (DSC), temperature differences relative to a thermally inert material are measured during heating and cooling of a sample. The DTA/DSC curve records these differences during reactions in the sample, showing thermal effects as deviations from the zero line. Accordingly, whether a chemical reaction or a phase transition requires heat (endothermic reaction) or releases heat (exothermic reaction), the curve slopes towards one side of the zero line or the other.

15.2 Apparatus

Analytical balance
Microspatula
Crucible (aluminium), open or closed with a pierced lid
DTA or DSC apparatus

15.3 Reagents

α-Al_2O_3 as a reference material

15.4 Procedure

Weigh a portion of 10 to 20 mg (for DTA) or 3 to 5 mg (for DSC) of the homogenized sample to the nearest 0.1 mg into the crucible and transfer the crucible into the apparatus. Perform the analysis under following conditions:

Start temperature:	≤ -50°C
Heating rate:	5°C per minute
Atmosphere:	dry air, flow rate 30 to 50 cm^3/min
End temperature:	400°C

If necessary, to achieve a good baseline, use α-Al_2O_3 as a reference material.

DSC curves of AN and PSAN can be seen on one example at page D-23. The phase transition and the melting temperature of pure or phase stabilized AN (PSAN) can be obtained from the DSC (or DTA) curve, see figure D-15.

15.5 Reporting

The phase transitions (PT) and the melting (M) of pure AN or PSAN should be characterized and reported by the „onset temperature“ T_m (see STANAG 4515, pages A-2 and A-3). To determine this temperature, construct the point of intersection between the elongated base line and the inflectional tangent of the peak (see DSC curve on figure D-16). The second phase transition of AN („PT 2“) is sometimes not visible. Absence of PT peaks or PT peaks shifted outside a temperature region to be specified by a purchaser are characteristics of PSAN.

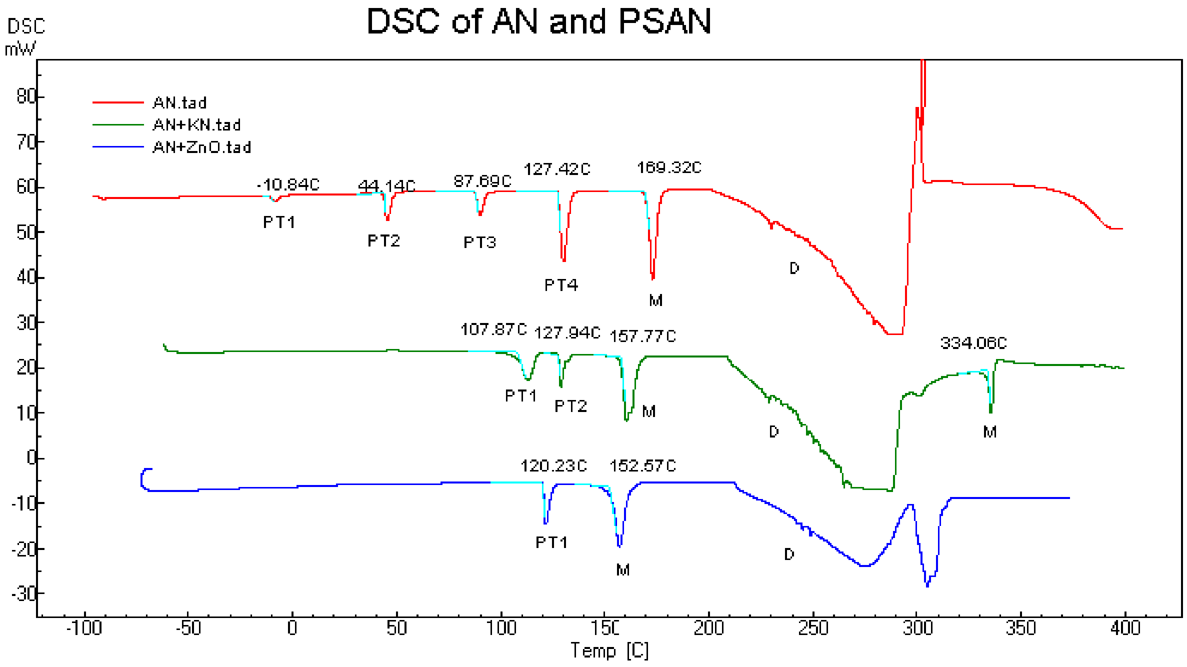

Figure D-15. DSC curves of pure AN (upper curve) and of two different types of PSAN.

Note. The temperatures of PT2 of pure AN depends on the moisture content and may vary between 30°C and 55°C.