

NOXy[®]

UREA SOLUTION 32,5 %

WT-2015/ZA-30

1. SUBJECT OF THE SPECIFICATION

The subject of the technical specification is 32.5% aqueous urea solution which is commercially marketed as NOXy[®] (also known as AdBlue[®] ¹). NOXy[®] is a specific urea solution due to its ultra high purity and thus containing no additional compounds.

2. REQUIREMENTS

2.1 GENERAL REQUIREMENTS

Clear or slightly yellow liquid, odorless or having slight scent of ammonia.

2.2 DETAILED REQUIREMENTS

Detailed requirements are shown in Table 1 (below).

Table 1

No.	Requirements	Unit	Limits
1.	Urea content	%	31.8 - 33.2
2.	Density	kg/m ³	1087.0 - 1093.0
3.	Refractive index at 20°C	-	1.3814 - 1.3843
4.	Ammonia content	%	max. 0.2
5.	Biuret content	%	max. 0.3
6.	Aldehyde content	mg/kg	max. 5
7.	Insoluble particles content	mg/kg	max. 20
8.	Phosphate content	mg/kg	max. 0.5
9.	Calcium content	mg/kg	max. 0.5
10.	Iron content	mg/kg	max. 0.5
11.	Copper content	mg/kg	max. 0.2
12.	Zinc content	mg/kg	max. 0.2
13.	Chromium content	mg/kg	max. 0.2
14.	Nickel content	mg/kg	max. 0.2
15.	Aluminum content	mg/kg	max. 0.5
16.	Magnesium content	mg/kg	max. 0.5
17.	Sodium content	mg/kg	max. 0.5
18.	Potassium content	mg/kg	max. 0.5
19.	Identity	Identical to reference	

3. LABELLING

Product label shall be located in conspicuous location and shall be permanently affixed to the packing. Label text and information should be in a size of type large enough to be readily legible.

Labelling includes the following elements:

- The commercial product name: NOXy[®]
- The other product name: AdBlue[®]

¹ AdBlue[®] is a registered trademark of the Verband der Automobilindustrie e.V. (VDA)

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- The name, address, logo and telephone number of the manufacturer
- The nominal quantity of the product
- Information on compliance with ISO 22241 AUS 32 specification
- Usage, storage and transport information
- The batch number
- Shelf life
- Handling symbols: "Keep dry", "This way up", "Keep away from heat" and "Temperature limitations".

4. PACKAGES

32.5% urea solution is filled into the following containers:

- Tank vehicles and tank wagons
- Intermediate bulk containers (IBC type) with capacity 1000 kg

Cisterns and containers for NOXy® should be made of materials approved by standard ISO 22241-1/-2/-3/-4 as suitable for contact with the product.

Materials recommended for use with 32.5% NOXy®: alloy steel, plastic i.e. polyethylene, polypropylene, Vinton

Materials not recommended for use with 32.5% NOXy®: copper, copper alloys, non-alloy steel and galvanized (zinc) steel.

Additional recommendations:

- Before loading, tanks and containers should be rinsed with demineralized water, unless they are foreseen for NOXy® solution only and they were not in contact with other substances being possible source of impurities.
- Avoid contamination of this product

5. STORAGE

The 32.5% urea solution should be stored in non - pressure tanks or containers characterized by proper volume. Store in cool, dry and well – ventilated areas at temperatures between -11.5° and 30°C. Tanks and containers with urea solution should be protected against exposure to direct sunlight. Storage temperature should be kept above -11.5°C to prevent crystallization of urea from solution. Non adherence to the above mentioned precautions may affect product quality.

Prolonged storage above 35°C will generate a self-hydrolysis reaction with the continuous ammonia emission.

6. TRANSPORT

32.5% aqueous urea solution (technical grade) should be shipped in tank vehicles, tank wagons or in a smaller containers (i.e. drums, canisters). To avoid contamination, it is necessary to apply the highest standards during transport. The product is not subject to RID and ADR regulations.

7. ANALYTICAL METHODS

7.1. TESTING SCHEDULE

The testing schedule is given in Table 2

Table 2

No.	Test	Test description as per:
1.	General requirements	7.4.
2.	Urea content	7.5.
3.	Density	7.6.
4.	Refractive index at 20°C	7.5.
5.	Ammonia content	7.7.

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6.	Biuret content	7.8.
7.	Aldehyde content	7.9.
8.	Undissolved particles content	7.10
9.	Phosphate content	7.11
10.	Calcium content	7.12.
11.	Iron content	
12.	Copper content	
13.	Zinc content	
14.	Chromium content	
15.	Nickel content	
16.	Aluminum content	
17.	Magnesium content	
18.	Sodium content	
19.	Potassium content	
20.	Identity	7.13

7.2. BATCH SIZE

Product batches are released for further use by following the relevant procedures and when the results of testing fully conform with the specification of the standard. The meaning of product batch is considered as well defined and possible to determine amount.

Each batch shall contain not more than 300 tons of the urea solution.

7.3. SAMPLING

Bottles for sampling

Use 1000 ml wide-neck bottles. Proper materials for these bottles are: high density polyethylene (HDPE), high density polypropylene (HDPP), polyfluoroethylene (PFE), polyvinylidenedifluoride and tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA) .

In case of dispute, bottles of choice should be made of PFA.

Before first use, the bottles should be washed and rinsed with deionized water and then filled up with 32.5% urea solution.

Labelling of sampling bottles

Each sampling bottle should be provided with a label (dimension approx. 10 x 5 cm) or a tag. These labels must be waterproof and resistant to 32.5% urea solution.

Sampling procedure

Open a sampling wide-neck bottle and place its cap upside down on the clean flat surface. After rinsing the sampling pipe, fill up the bottle completely with the urea solution from the tank. Then, empty the bottle, refill it with the above mentioned solution and cap the bottle tightly. Attach a label/tag to the bottle.

During sampling particular care should be taken to prevent dusts and liquid pollutants from getting into the bottle.

Upon sampling, the sample should be kept in a cooler (0°-15° C) while protected from light (to prevent growth of algae) and delivered to the analytical laboratory as soon as possible.

Volume of sample

The Minimum volume of the sample needed depends on the scheduled analyses. Recommended volume for analytical testing is 1 litre plus at least the same volume which is required for full verification of the 32.5% solution requirements.

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Details on labelling:

Labelling must mention:

- The product name
- The name of company which owns the sample product*
- The address of the place where the sample was taken*
- The manufacturer of the sample product*
- The batch number or lot number
- Designation of container from which the sample was taken*
- Determination of part of the container from which the sample was taken* (sampling point)
- The date and time of sampling
- The shipping date*
- The name, surname and signature of person responsible for sampling*

* Required in dispute only.

7.4. GENERAL REQUIREMENTS CHECKING

Testing for compliance with general requirements is performed visually.

7.5. REFRACTIVE INDEX AND UREA CONTENT DETERMINATION BY ANALYSIS OF REFRACTIVE INDEX**7.5.1. Purpose of the method**

This analytical method is suitable for liquids with refractive indexes values between $1.33 \div 1.39$, measured at temperature range of $20^\circ \div 30^\circ\text{C}$. Based on the refractive index measurement it is possible to determine urea content in aqueous solutions within the range of $30\% \div 35\%$ (w/w).

7.5.2. Principle of the method

Measurement of refractive index must be carried out at a constant, specified temperature.

Urea content is specified with the use of the calibration curve.

7.5.3. Apparatus

- a) Refractometer, measuring range of 1.33000 to 1.39000
- b) Analytical laboratory balance with an accuracy of 0.1 mg
- c) Thermostat with temperature control with precision 0.02°C
- d) Drying oven
- e) Laboratory beaker about 150 ml of volume
- f) Common laboratory glass

7.5.4. Reagents and solutions

- a) Demineralized water, conductivity: < 0.5 mS/m
- b) Urea, crystalline, analytical grade (biuret content less than 0.1% (w/w)). Before preparing of calibration curve, urea should be dried for 2 hours at 105°C .
- c) Urea test solution with concentration 32.5% (w/w), prepared precise by weighing urea and water. The desired value and permissible dispersion shall be established through 10 measurements. This solution shall be kept in air-tight, refrigerated container and should be used within 4 weeks maximum.

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7.5.5. Determination procedure

a) General rules

Sample must be thoroughly dissolved in water and free of urea crystals. If needed, heat the sample carefully up to 40°C to obtain homogenous solution.

Various equipment is available on the market to perform the analysis. Due to that, various resources and modes of operations are not an object of this specification. Rather, the test must be performed in accordance with the respective operation manuals delivered with refractometer.

b) Drawing the reference curve and determination of the evaluation factor

Weigh crystalline urea (7.5.4.b) into a glass beaker and add sufficient demineralized water (7.5.4.a) to obtain urea solutions with concentration respectively:

30% (w/w), 31.5% (w/w), 32.5% (w/w), 33.5% (w/w), 35.0% (w/w)

Further, perform refractive index measurements for these urea solutions at temperature 20°C ($\pm 0.02^\circ\text{C}$). Visualization of the refractive index and urea solutions concentration creates significant linear dependence.

Based on urea concentrations and measured refractive indexes calculate evaluation factor F needed for further calculations using the following formula:

$$F = \frac{\sum(w_U)}{\sum(n_U - n_W)}$$

where:

F - evaluation factor, %

$\sum(w_U)$ - sum of all reference urea solutions concentrations, % (w/w)

$\sum(n_U - n_W)$ - sum of subtractions between obtained refractive indexes for reference urea solutions and refractive index for water

Water refractive index is: $n_W = 1.33296$ (when refractometer used for measurement has five decimal places resolution).

c) Checking the equipment function and the reference curve

The instrument performance shall be checked once a week with the use of water or a suitable reference standard. If deviation is greater than 0.00002 of desired value, the instrument should be calibrated as per operation manuals and measurement must be repeated. If deviation occurs again, then abort further measurement and contact the manufacturer's technical support.

Adjust the thermostat to the desired temperature, reading this temperature on the refractometer thermometer on the discharge side. Maintain the flow of water so that the desired temperature shall be reached and maintained within $\pm 0.02^\circ\text{C}$.

Furthermore, the reference curve shall be verified once a week with 32.5% (w/w) urea solution. The refractive index of the test urea solution shall be measured and corresponding urea concentration must be determined with the help of the factor according to item 7.5.6. If the found concentration deviates from desired value by more than 0.1% (w/w), than a fresh test solution shall be used for re-measurement. If the deviation persists, a new reference curve shall be created.

d) Measurement

Refractive index measurements must be performed for original sample without further preparation. These measurements must be carried out at temperature 20°C ($\pm 0.02^\circ\text{C}$). At least two measurements procedures should be performed with different test portions. If the difference between the two measured values exceeds 0.00005, the measurements should be repeated.

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7.5.6. Expression of the result

a) Calculation

Calculate the urea content as weigh percentage (w/w) using the following formula:

$$w_U = (n_p - n_w) \times F - w_{Bi}$$

where:

w_U - is the urea content, % (w/w)

n_p - is the refractive index of the urea sample (with 5 decimals)

n_w - is the refractive index of water (with 5 decimals)

F - is the evaluation factor, %;

w_{Bi} - is the biuret content of the solution, % (w/w)

b) Final result

The final result should be an arithmetic mean of the results of two consecutive tests. Round off result of the refractive index to five decimal places. Round off the result of the urea content calculation to the nearest 0.1% (w/w).

7.5.7. Method precision

a) Repeatability

Refractive index: $r = 0.0001$

Urea content: $r = 0.1\%$ (w/w)

b) Reproducibility

Refractive index: $R = 0.0010$

Urea content: $R = 1.0\%$ (w/w)

7.5.8. Test report

The test report shall include the following data as a minimum requirement:

- a) Type and description of tested product;
- b) References to this Technical Specification;
- c) Sampling method used;
- d) Test result as per item 7.5.6;
- e) Deviations from the specified mode of operation, if any;
- f) Date of analysis.

7.6. DETERMINATION OF DENSITY**7.6.1. Principle of the method**

The method is based on determination of tested solution density.

7.6.2. Analytical equipment

- a) Cylinder – vol. 250 - 500 ml

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b) Hydrometer adequate for density included in the range of 1.0 - 1.1 g/cm³

7.6.3. Determination procedure

Pour the tested urea solution into 250 - 500 ml cylinder. Gently insert the hydrometer (measurement range: 1.0 - 1.1 g/cm³) with volumetric accuracy of +/-0.001.

7.6.4. Expression of the result

Solution density to be read from graduated scale.

7.7. DETERMINATION OF ALKALINITY (calculation on NH₃)**7.7.1. Purpose of the method**

This analytical method allows to determine alkalinity of tested 32.5% urea solution, calculated as ammonia, in the range from 0.1% (w/w) to 0.5% (w/w).

7.7.2. Principle of the method

The measurement is based on potentiometric titration of free ammonia with a standard hydrochloric acid solution to the endpoint at pH = 5.7.

7.7.3. Apparatus

- a) analytical balance with resolution of 0.1 mg
- b) automatic burette
- c) potentiometer, measurement precision of 0.01 of pH unit, provided with combined pH electrode
- d) magnetic stirrer
- e) beaker, nominal volume of 150 ml, tall shaped
- f) 100 ml volumetric cylinder

7.7.4. Reagents

During the analysis, use only reagents of analytical grade and distilled or deionized water (conductivity lower than 0.5 mS/m).

a) hydrochloric acid, concentration: 0.01 mol/l,

b) buffer solutions:

- standard buffer solution, pH = 4.008
- standard buffer solution, pH = 9.184
- standard buffer solution, pH = 8.00

7.7.5. Determination procedure

- a) Interferences

Ammonia may be formed if the sample of 32.5% urea solution is stored and transported at temperature above 25°C. Ammonia may evaporate from the sample when container with the sample is not tightly closed and if the analysis is delayed due to unexpected circumstances.

- b) Verification of potentiometric system

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Proper functionality of the potentiometric system is checked by use of the standard buffer solutions at pH = 4.008 and pH = 9.180.

The potentiometric system should be checked every day with using buffer solution at pH = 8.00.

c) Preliminary test

Weigh about 1 g of the homogenous sample to the nearest 0.05 g (sample mass m_s) and put it into 150 ml beaker containing about 100 ml of deionized water. Titrate with the hydrochloric acid as per item 7.7.4. a) under stirring to the endpoint at pH = 5.7. Calculate the ammonia content.

Based on the alkalinity content found in the preliminary test, weigh the following sample portions for the determination:

Alkalinity content determined on the basis of the preliminary test, % (w/w):	0.02	0.05	0.1	0.2 to 0.5
Mass of test sample for the determination, (g):	10	5	2	1

d) Test sample preparation and measurement

Weigh the mass of the homogenous sample to the nearest 0.05 g determined by the preliminary test (sample mass m_s) and put it into 150 ml beaker containing about 100 ml of deionized water. Titrate with the hydrochloric acid as per item 7.7.4. a) under stirring to the endpoint at pH = 5.7. From pH = 7.5 to pH = 5.7 titrate the urea solution with reduced speed. Perform two measurements.

7.7.6. Expression of the result

a) Calculation

The alkalinity, expressed as a percentage by mass of ammonia (NH_3), is calculated according to the following formula:

$$w(NH_3) = (V \times 0.017) / m_s$$

where:

$w(NH_3)$ - is the alkalinity, calculated as ammonia [% (w/w)];

V - is volume of the hydrochloric acid used for the titration (ml);

m_s - mass of the test sample (g).

b) Final result

The final result should be an arithmetic mean of the results of two consecutive tests. Round off the result to the nearest 0.01% (w/w).

7.7.7. Precision

a) Repeatability, r

$r = 0.01\%$ (w/w) within the range from 0.01% to 0.5% (w/w)

b) Reproducibility, R

$R = 0.2 \times x\%$ (w/w) in the range from 0.1% to 0.5% (w/w) (x - is average value)

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7.7.8. Test report

The test report must contain at least the following information:

- a) Type and description of tested product;
- b) References to this Technical Specification;
- c) Test result as per item 7.7.6;
- d) Deviations from the specified mode of operation, if any;
- e) Sampling method used;
- f) Date of analysis.

7.8. DETERMINATION OF BIURET CONTENT**7.8.1. Purpose of the method**

This analytical method allows to determine biuret content in 32.5% urea solution by photometric method. This analytical method applies to urea solutions with biuret content (w/w) from 0.1 % to 0.5 %.

7.8.2. Principle of the method

In an alkaline medium in the presence of potassium sodium tartrate, biuret and bivalent copper form a violet-colored cupric compound. The maximum absorbance of this solution is measured at a wavelength of 550 nm. The absorption value at that wavelength indicates the biuret concentration in the sample, which is determined by reference to a calibration curve prepared with using standard biuret solutions.

7.8.3. Apparatus

- a) Laboratory balance, resolution in reading 0.001 g
- b) Vacuum filtration set with a diaphragm filter, pore size 0.45 μm
- c) Spectrophotometer, relevant for measurements at 550 nm wavelength
- d) Cell, $d = 5\text{cm}$
- e) Volumetric flasks: 1000 ml, 250 ml, 100 ml, 50 ml, class A-compatible
- f) Pipettes, class AS-compatible
- g) Rotary evaporator
- h) Constant-temperature bath

7.8.4. Reagents

Unless otherwise stated, during the analysis, use only chemicals of analytical grade and deionized and boiled out water (to remove carbon dioxide).

- a) Potassium carbonate solution (saturated at ambient temperature)
- b) Standard aqueous solution of copper sulphate pentahydrate. Transfer 15 g of copper sulphate pentahydrate ($\text{CuSO}_4 \times 5\text{H}_2\text{O}$) into 1000 ml volumetric flask.
- c) Standard alkaline solution of potassium sodium tartrate. Transfer 40 g of sodium hydroxide into 1000 ml volumetric flask and dissolve in 500 ml of water. After cooling, add 50 g of potassium sodium tartrate ($\text{KNaC}_4\text{H}_4\text{O}_6 \times 4\text{H}_2\text{O}$) and make up to the mark with water. Leave standing for 24 hours before use.
- d) Biuret standard solution of 0.8 mg biuret/ml. Transfer 800 mg of pure biuret into 1000 ml volumetric flask. Dissolve in water and dilute to volume with the same solvent. Prior to that, biuret must be dried for 3 hours at 105°C. If biuret of relevant purity is not available, then the commercial product should be purified prior to making calibration curve.

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Proceed as follows:

- To the beaker containing 500 ml of 25% ammonia water add approx. 50 g of biuret and stir for 15 minutes;
- Then filter off the biuret, wash with ammonia-free water and dry;
- Dissolve in ethanol (1g of biuret/100ml of EtOH), filter and evaporate to ¼ of volume;
- Cool to 5°C and filter;
- Dry the biuret in vacuum oven at 80°C
- Check biuret purity by spectrophotometric measurements as per item 7.8.5 d)

The re-crystallization step from ethanol should be repeated until purity reaches constant level.

7.8.5. Determination procedure

a) Interferences

Use only optically transparent solutions for spectrophotometric measurements. Any materials causing turbidity should be removed with the use of vacuum filtration with a diaphragm filter of pore size 0.45 µm. Free ammonia or ammonium ions create with bivalent copper a colored complex, which absorbs light energy at 550nm. The method is applicable only if the NH₃ or NH₄ content in the sample does not exceed 500 mg/kg.

If ammonia content is higher than above mentioned then remove the excess by the following way: weigh 50 g of sample with precision 0.001 g and transfer into 1000 ml flask of a rotary vacuum evaporator; add 15 ml of potassium carbonate solution prepared as per item 7.8.4 a).

Further, evaporate ammonia for 1 hour in a warm water bath at 40°C, under a vacuum of 2 kPa to 3kPa with rotating speed of 60r/min. After this operation approximately 20 ml of the solution should remain in the flask. This volume should be poured to a 250 ml volumetric flask and further treatment as specified below should be performed.

b) Preparation of calibration curve

Transfer 2 ml, 5 ml, 10 ml, 15 ml, 20 ml and 25 ml of aliquots of biuret standard solution (prepared as shown in 7.8.4 d)) into a series of six graduated 50-ml flasks. Add water to obtain total mixture volume of about 25 ml. Further, add 10 ml of standard alkaline solution of potassium sodium tartrate prepared according to item 7.8.4 c) and stir it carefully. After obtaining homogeneous solution add 10 ml of copper sulphate solution according to 7.8.4 b) and stir it again. Immerse the flasks in water bath at temperature 30°C and leave them for 15 minutes until color appears. Cool down the flasks to ambient temperature, dilute to volume with water and mix. Measure the absorption using a 5 cm cell at 550 nm wavelength against water as the reference.

Perform a blank test in parallel with the calibration curve determination, by applying the following procedure: add to a 50 ml volumetric flask 10 ml of standard solution of potassium sodium tartrate prepared according to item 7.8.4 c), 10 ml of copper sulphate solution according to 7.8.4 b) and dilute to volume with water. Measure the absorption using a 5 cm cell at 550 nm wavelength against water as the reference.

Subtract the absorbance of the blank test from the absorbance of the measured values and set up the calibration curve. On the basis of the obtained results draw the curve (with water as reference). In the measured range of concentration the curve must be strictly linear.

c) Determination of the calibration factor F

Calculate the calibration factor F using absorption values of the reference solutions specified in item 7.8.5 b) according to the following formula:

$$F = \frac{\sum(m_{Bi})}{\sum(E)} = \frac{61,6}{\sum(E)}$$

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where:

F – is the calibration factor (mg);

m_{Bi} – is the mass of biuret (mg);

E – is the relevant absorbance.

Calibration curve and corresponding calibration factor are determined once a year.

d) Verification of calibration factor

Calibration factor must be tested once a week with using single-point calibration method. Perform measurement as described in item 7.8.5 b) of 10 ml of the biuret standard solution (= 8 mg of biuret) (double marking).

Further, calculate day-factor (F_D) as shown below:

$$F_D = \frac{8}{E_1 - E_2}$$

where:

F_D – is the day-factor;

E_1 – is the absorbance of reference biuret solution (average calculated from two measurements);

E_2 – is the absorbance of the blank test.

The day-factor should differ max. $\pm 5\%$ from the calibration factor specified as per 7.8.5.c). The day-factor should be always used for test sample measurements.

e) Test sample preparation and measurement

Into 250 ml volumetric flask, weigh 100 g of the test sample to the nearest 0.01 g precision. Dissolve in water and dilute to volume with the same solvent.

Pipette 10 ml of such prepared solution and transfer it in 50 ml volumetric flask. Further, add 10 ml of standard alkaline solution of potassium sodium tartrate (7.8.4.c) and stir it carefully. After obtaining homogeneous solution add 10 ml of copper sulphate solution (7.8.4.b) and stir it again. Immerse the flasks in water bath at temperature 30°C and leave them for 15 minutes until color appears. Cool down the flask to ambient temperature, dilute to volume with water and mix. Measure the absorption using a 5 cm cell at 550 nm wavelength against water as the reference.

Perform a reagent blank test in parallel with the test determination, by applying the procedure described in item 7.8.4 b).

Blank value of reagents and the sample should be deducted from the measured value.

7.8.6. Expression of the result

a) Calculations

Calculate the biuret content as percentage by mass (w/w) using the following formula:

$$w_{Bi} = \frac{(E_S - E_B) \times F_D \times 250}{m_s \times 10 \times 1000} \times 100$$

where:

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- w_{Bi} - is the biuret content % (w/w);
- E_S - is the absorbance of the test sample;
- E_B - is the absorbance of the blank test (reagent blank + sample blank);
- m_S - is the mass of the test sample (g);
- F_D - is the day-factor (mg).

b) Final result

Round of the result to the nearest 0.01 % (w/w).

7.8.7. Precision

a) Repeatability, r

$r = 0.01\%$ (w/w)

b) Reproducibility, R

$R = 0.04\%$ (w/w)

7.8.8. Test report

The test report must contain at least the following information;

- Type and description of tested product;
- References to this Technical Specification;
- Sampling method used;
- Test result as per item 7.8.6.;
- Deviations from the specified mode of operation, if any and;
- Date of analysis.

7.9. DETERMINATION OF ALDEHYDE CONTENT**7.9.1. Purpose of the method**

The method specifies the procedure for the determination of the content of bound and free aldehyde, calculated as formaldehyde, in 32.5% urea solution containing aldehyde in the range of 0.5 mg/kg to 10 mg/kg.

7.9.2. Principle of the method

Formaldehyde forms in strong solution of sulphuric acid with chromotropic acid a purple complex with absorption maximum at 565 nm wavelength. This colored complex is read spectrophotometrically at 565 nm and the aldehyde concentration is defined through reference to the calibration curve prepared on the basis of standard formaldehyde solutions.

NOTE: The described method is based on method No. 20062 from *Official Methods of Analysis of Association of Official Analytical Chemists (AOAC) International*.

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7.9.3. Apparatus

- Laboratory balance, resolution in reading 0.001 g
- Spectrophotometer, relevant for measurements at 565 nm wavelength with 10 mm cell
- Volumetric flasks
- Pipettes

7.9.4. Reagents

During the analysis, use only chemicals of analytical grade.

- Sulphuric acid, 96% (w/w);
- Chromotropic acid (4,5-dihydroxynaphthalene-2,7-disulphonic acid sodium salt or 4,5-dihydroxynaphthalene-2,7-disulphonic acid disodium salt dihydrate) in 15% (w/w) sulphuric acid. In order to prepare this solution, add 41 ml of sulphuric acid to 410 ml of water while cooling the mixture and then add 15 g of chromotropic acid and mix well.

NOTE: If the solution is kept in brown glass bottle then it remains usable for at least three months.

- Formaldehyde standard solution. Preparation as follows: place 6.5 to 7 g of 37 % (w/w) formaldehyde solution into 500 ml volumetric flask. Dilute to volume with distilled water and mix well. Formaldehyde content in the solution should be determined accordingly to the procedure specified in ISO 9020. Next, dilute the solution to a ratio of 1:1000. Put label with formaldehyde concentration on the flask (formaldehyde content determined in the previous step divided by 1000).

7.9.5. Determination procedure

- Preparation of the calibration curve

Into series of seven volumetric flasks, transfer 0 ml, 0.2 ml, 0.5 ml, 1.0 ml, 2.0 ml, 5.0 ml and 10 ml of standard formaldehyde solution and add distilled water to obtain total mixture volume of approx. 10 ml. While stirring add 1 ml of chromotropic acid solution, followed by gradual addition of 20 ml sulphuric acid during the course of 5 minutes. During sulphuric acid addition the temperature rise should exceed 100°C, which is necessary to complete the reaction. Leave these flasks at ambient temperature for 15 minutes without any further cooling. After cooling down to room temperature, dilute the flasks to volume with water and mix well. Measure the absorption using a 10 cm cell at 565 nm wavelength against water as the reference.

Subtract the absorbance of the blank test from the absorbance of the measured values and set up the calibration curve. Within the concentration range the curve should be strictly linear.

- Determination of calibration factor

The calibration factor should be calculated using the following formula:

$$F = \frac{\sum_{i=1}^6 m_{HCHO,i}}{\sum_{i=1}^6 (E_1 - E_2)}$$

where:

F – is the calibration factor (µg);

$m_{HCHO,i}$ – is the mass of the formaldehyde of the i -th sample (µg);

$E_{1,i}$ – is the absorbance of the i -th sample;

E_2 – is the absorbance of blank sample.

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Determination of calibration curve and calibration factor should be repeated once a year and recorded.

c) Check of the method

Every three the months, the method should be controlled as follows:

Into a series of three 50 ml volumetric flasks, transfer 2 ml of standard formaldehyde solution and add distilled water to obtain total mixture volume of approx. 10 ml. Compare the obtained results from spectrophotometric measurements with the content of standard solution. If the deviation is lower or equal to 2 %, then the method is ready for use. If deviation exceeds 2%, then repeat the check procedure. If the deviation is more than 2% again, the method cannot be applied unless a new reference curve is prepared.

d) Test sample preparation and measurements

Weigh, to the nearest 0.01 g precision, 5 g to 10 g of the test sample and transfer into 50 ml volumetric flask. Dissolve and dilute with water to obtain total mixture volume of approximately 10 ml. Add, while stirring, 1 ml of chromotropic acid solution and then add (step-wise) during of 5 minutes, 20 ml of sulphuric acid. During sulphuric acid addition the temperature rise should exceed 100°C, which is necessary to complete the reaction. Leave the flask at ambient temperature for 15 minutes without any further cooling. After cooling down to room temperature, dilute to volume with water and mix well. Measure the absorption using a 10 cm cell at 565 nm wavelength against water as the reference.

Perform a blank test in parallel with test measurement, by applying the same procedure and using the same amounts of all reagents (without addition of test sample) as hereinabove.

7.9.6. Expression of the results

a) Calculations

Calculate the formaldehyde content using the following formula:

$$W_A = \frac{(E_S - E_B) \times F}{m_S}$$

where:

W_A – is the aldehyde content (mg/kg);

E_S – is the sample absorbance;

E_B – is the blank test absorbance;

m_S – is the mass of used sample (g);

F - is the calibration factor (μg).

b) Final result

Round of the result to the nearest 0.1 mg/kg.

7.9.7. Precision

a) Repeatability, r

$r = 0.14$ mg/kg

b) Reproducibility, R

$R = 0.5 \times x$ (x – is average value)

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7.9.8. Test report

The test report must contain at least the following information:

- a) Type and description of tested product;
- b) References to this Technical Specification;
- c) Sampling method used;
- d) Test result according to item 7.9.6;
- e) Deviations from the specified mode of operation, if any and;
- f) Date of analysis.

7.10. DETERMINATION OF INSOLUBLE PARTICLES – GRAVIMETRIC METHOD**7.10.1. Purpose of the method**

Determination of insoluble particles (residue) contained in 32.5% urea solution.

7.10.2. Principle of the method

This method is based on filtration of the test solution sample and the obtained residue is determined by gravimetric analysis.

7.10.3. Apparatus

- a) Filtering equipment for vacuum filtration, suitable for 47 – 50 mm diameter diaphragm filters;
- b) Diaphragm filter, pore size 0.8 µm, mixed cellulose ester;
- c) Diaphragm vacuum pump;
- d) Freeze-dryer/Wolff bottle;
- e) Petri plate with a lid, relevant for diaphragm filter (e.g. 80 mm x 15 mm);
- f) Tweezers with flat tip;
- g) Analytical balance, accuracy 0.01 mg or higher;
- h) Laboratory balance, resolution: 0.01 mg or higher;
- i) Beaker, nom. volume 400 ml (tall, with volume scale);
- j) Drying oven with temperature control 105°C ± 2°C
- k) Desiccator, filled with proper drying agent.

NOTE: Sulphuric acid or calcium chloride are not proper as drying agents.

- l) Typical laboratory glassware.

7.10.4. Reagents

Deionized water having conductivity < 0.1 mS/m.

7.10.5. Determination Procedure

Sample must be completely dissolved and free of urea crystals. If appropriate, heat the sample carefully up to 40°C to obtain homogenous solution.

The filters used for analysis should be previously rinsed with water. For that purpose the filters should be placed in a vacuum filtration and washed with approx. 100 ml of water, which should be sucked through the filter. Dry the filters in the laboratory dryer (to obtain constant mass) and keep them on Petri plates (one filter per one plate) in the desiccator. Prior to the analysis the diaphragm filters should be weighed with 0.01 mg precision.

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NOTE: Filters to be weighed remain on individual Petri plates.

Shake the sample carefully in order to obtain homogenous mixture. After that, immediately pour 100 - 150 ml of the sample (measured with 0.01 g precision) into 400 ml beaker and add 200ml of water. Adding the sample with pipette is forbidden during weighing.

Set up the filtrating equipment and the prepared diaphragm filter together. Moisten the filter with small amount of water (1 to 2 ml) before vacuum application. Put the sample into the filtration vessel and apply vacuum in order to make the sample sucked off properly.

Rinse the beaker with five portions of water, each of approx. 30 to 50 ml. Post-rinsing solution should be also filtered. Before the first rinsing, the sample should have completely passed through the filter (let the filter to dry briefly).

Dismantle the filtration equipment and dry the filter at 105°C to obtain constant mass. Cool down to ambient temperature in a desiccator and weigh with 0.01 g precision.

Indication: Complete washing out of the urea solution from the filter must be ensured. If the filter is found to stick to the Petri plate it will prove insufficient filter washing. Such a filter should be rejected and thus analysis should be repeated.

7.10.6. Expression of the result

- a) Calculations

$$W_{ins} = \frac{(m_{FR} - m_{FL}) \times 1000}{m_S}$$

where:

- W_{ins} – is the content of insoluble particles (mg/kg);
 m_{FL} – is the mass of the dried empty filter (mg);
 m_{FR} – is the mass of dried filter with sample residue (mg);
 m_S – is the sample mass (g).

- b) Final result

The final result should be an arithmetic mean of the results of two consecutive tests. If the difference between the results exceeds 25% of the highest value then analysis should be repeated. Round off the result as follows:

<10 mg/kg to the nearest 0.1 mg/kg

≥10 mg/kg to the nearest 1 mg/kg

The method detection level is at 1 mg/kg.

7.10.7. Precision

- a) Repeatability, r

$$r = 0.23 \times \bar{x} \text{ mg/kg} \quad (\bar{x} - \text{is average value})$$

- b) Reproducibility, R

$$R = 0.38 \times \bar{x} \text{ mg/kg} \quad (\bar{x} - \text{is average value})$$

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7.10.8. Test report

The test report must contain at least the following information:

- a) Type and description of tested product;
- b) References to this Technical Specification;
- c) Sampling method used;
- d) Test result according to item 7.10.6;
- e) Deviations from the specified mode of operation, if any and;
- f) Date of analysis.

7.11. DETERMINATION OF PHOSPHATE CONTENT– PHOTOMETRIC METHOD**7.11.1. Purpose of the method**

This method describes the procedure for determination of the total content of phosphorus, calculated as phosphates, in 32.5% urea solution containing phosphates in the range from 0.05 mg/kg to 10 mg/kg. The increase of the measurement range is possible by the sample volume change.

7.11.2. Principle of the method

The sample is evaporated, incinerated with calcium carbonate to mineralize phosphorus compounds.

Then the sample is dissolved in hydrochloric acid solution, which results in transformation of phosphates into orthophosphates.

In acidic medium orthophosphate ions react with molybdate and antimony ions creating an antimony-phospho molybdate complex.

The reduction of this complex with ascorbic acid leads to generation of intensely coloured molybdenum blue. The colour intensity is proportional to orthophosphate ions concentration.

7.11.3. Apparatus

- a) Analytical balance, accuracy 0.01 mg or higher;
- b) Incineration dish (made of platinum or quartz glass)
- c) Heating plate or sand bath;
- d) Muffle furnace (700°C);
- e) Spectrophotometer, relevant for measurements at 800 nm wavelength and 1 cm cuvette
- f) Cell, d = 1cm
- g) Volumetric flasks;
- h) Transfer pipettes.

7.11.4. Reagents

- a) Demineralized water, conductivity < 0.1 mS/m
- b) Calcium carbonate, analytical grade
- c) Hydrochloric acid – concentration of 25% (w/w),
- d) Sulphuric acid – concentration of 96% (w/w),
- e) Ascorbic acid, analytical grade
- f) Ammonium heptamolybdate tetrahydrate, analytical grade
- g) Potassium antimony (III) oxytartrate hemihydrate

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h) ascorbic acid solution – concentration of 100 g/l. Dissolve 10 g of ascorbic acid in 100 ml of water.

NOTE: Durability of this solution is two weeks, if stored in the refrigerator. The solution can be used until it remains transparent;

i) Molybdate solution

Dissolve 13 g of ammonium heptamolybdate tetrahydrate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ in 250 ml of water. While stirring and cooling the main solution, add 150 ml of sulphuric acid. Next, dissolve 0.35 g of potassium antimony (III) oxytartrate hemihydrate $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6\cdot \frac{1}{2}\text{H}_2\text{O}$ in 100 ml of water and mix with molybdate solution in sulphuric acid.

NOTE: Durability of the final solution is two months, if it is stored in a brown glass bottle.

j) potassium dihydrogen phosphate, KH_2PO_4 , analytical grade, dried at 105°C;

k) Basic phosphate solution – concentration of 200mg/l.

Preparation as follows: Weigh 286.6 mg of potassium dihydrogen phosphate and transfer into 1 liter volumetric flask. Dissolve in water and add 2 ml of sulphuric acid. Dilute to volume with water and mix well.

NOTE: The solution remains usable for at least 3 months, if stored in a closed glass bottle.

l) Basic phosphate solution – concentration of 2mg/l.

Preparation as follows: Dilute the phosphate solution having concentration of 200mg/l with water in a ratio of 1:100.

7.11.5. Determination Procedure

a) Preparation of the calibration curve

Into a series of five 50 ml volumetric flask transfer 0 ml, 1 ml, 2 ml, 5 ml and 10 ml of the basic phosphate solution (which corresponds to 0 µg, 2 µg, 4 µg, 10 µg and 20 µg of phosphates). Dilute with water to obtain total mixture volume of approx. 40 ml. Then to each flask add 1 ml of ascorbic acid solution and 2 ml of molybdate solution, dilute to volume with water and mix well. After 10 – 30 minutes measure the absorption of each solution using a 1 cm cell at 800 nm wavelength against the sample containing 0 µg of phosphates as the reference sample. Each concentration should be measured 10 times.

b) Determination of calibration factor

The calibration factor should be calculated using the following formula:

$$C = \frac{\sum_{i=1}^4 m_{\text{phosphate},i}}{\sum_{i=1}^4 (E_{1,i} - E_2)}$$

where:

C – is the calibration factor (µg);

$m_{\text{phosphate}, i}$ – is the mass of phosphate of the i -th sample (ug);

$E_{1,i}$ – is the absorbance of the i -th sample;

E_2 – is the absorbance of the blank test.

c) Check of the method

- Requirements:

It should be checked whether the method provides correct results.

- Rule:

The basic phosphate solution should be analysed as a routine sample. The phosphates content in this solution is the measured value and it should be proved.

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- Procedure:

Transfer 5 ml of the basic phosphate solution into a 50 ml volumetric flask. Dilute with water to obtain total mixture volume of approx. 40 ml. Then add 1 ml of ascorbic acid solution and 2 ml of molybdate solution, dilute to volume with water and mix well.

Repeat the measurement three times.

The method is considered as correct if the measured values differ less than 2% as compared to the specified phosphates content.

- Frequency:

The method should be verified every three the months.

d) Calibration curve checking**- Requirements:**

The slope of the calibration curve should be checked for correctness in constant intervals.

- Rule:

Phosphate basic stock solutions will be analysed and the results will be compared to the calibration curve values.

- Procedure:

At least three concentrations within measuring range of the calibration curve should be determined three times.

The calibration curve is considered as valid if the average value of the calculated values differs less than 2% from a given point of the calibration curve. If the difference is bigger, the procedure should be repeated.

If the difference is more than 2% again, the method for determination of phosphate contents cannot be applied unless a new calibration curve is prepared.

- Frequency:

The verification of the calibration curve should be performed once every three years.

e) Sample preparation

Sample must be completely dissolved and free of urea crystals. If required, heat the sample carefully up to 40°C to obtain homogenous solution.

f) Decomposition

Approx. 100 g (record the mass) of the prepared sample should be weighed into the incineration pot and 100 mg of calcium carbonate should be added.

Such prepared sample should be put on a heating plate and dried slowly. Next, incinerate the sample in the muffle furnace at 700°C until the whole sample is totally decomposed. Cool down the sample and add into the pot 1 ml of hydrochloric acid and 20-30 ml of water. Boil until the deposited substances dissolve and CO₂ is removed. Transfer the solution into a 100 ml volumetric flask, dilute to volume with water and stir well.

g) Test sample preparation and measurements

With the use of a bulb pipette transfer into the 50 ml volumetric flask ≤ 40 ml of the solution prepared according to item 7.11.5 f) . If less than 40 ml is used then add water until volume of 40 ml is obtained. Then add 1 ml of ascorbic acid solution and 2 ml of molybdate solution, dilute to volume with water and mix well.

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Carry out a blank test in parallel, following the same procedure but without sample solution.

After 10 – 30 minutes measure the absorption of test sample and the blank test using a 1 cm cell at 800 nm wavelength.

7.11.6. Expression of the result

a) Calculations

$$w_P = \frac{(E_S - E_B) \times C \times V_S \times F_1}{V \times F_2 \times m_S}$$

where:

w_P – is the phosphate content (mg/kg);

E_S – is the sample absorbance;

E_B – is the blank test absorbance;

C – is the calibration factor (μg);

V_S – is the volume of decomposed sample (ml);

F_1 – is the 1000 (conversion factor from kg to g);

V – is the volume of the sample used for photometrical measurement (ml);

F_2 – is the 1000 (conversion factor form mg to μg)

m_S – is the mass of urea solution (g).

b) Final result

The result should be rounded to the closest value of 0.01 mg/kg.

7.11.7. Precision

Phosphate content w_P mg/kg	Repeatability r mg/kg	Reproducibility R mg/kg
0.1 to 1	0.02	0.03

7.11.8. Test report

The test report must contain at least the following information:

- a) Type and description of tested product;
- b) References to this Technical Specification;
- c) Sampling method used;
- d) Test result;
- e) Deviations from the specified mode of operation, if any and;
- f) Date of analysis.

7.12. DETERMINATION OF TRACE ELEMENT CONTENT (Al, Ca, Cr, Cu, Fe, K, Mg, Na, Ni, Zn) by ICO-OES METHOD

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7.12.1. Purpose of the method

The method consist in determination of trace elements like aluminium, calcium, chromium, copper, iron, potassium, magnesium, sodium, nickel and zinc in 32.5% urea solution.

7.12.2. Principle of the method

The content of trace elements is determined with the use of an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). For calibration purposes, a reference curve needs to be established for each element.

Two different analytical methods can be used:

Method A: Drying and incineration of the urea solution (alternatively with use of a microwave muffle furnace). This method requires more time than Method B, but higher sensitivity is obtained.

Method B: Direct determination, dilution 1:5 with water (simple method).

7.12.3. Apparatus

a) Apparatus for method A

- 100 ml volumetric flask.

Class A or B. Plastic or quartz glass flasks can be used. Flasks made of borosilicate glass or Duran glass are not allowed.

- Muffle furnace

Particularly the thermostat should be equipped with programmable ramp temperature controller, and the muffle furnace should be provided with gas outlet. If the gas exhaust is not installed, additional gas burner is required.

- If necessary, Bunsen burner (Note: In the event of too high incineration temperatures alkaline elements like potassium and sodium will volatilize at first);

- Hot plate reaching the surface temperature of 500°C;

- Alternative microwave muffle furnace with suction and a quartz glass plate over the sample;

- Analytical balance, having an accuracy of 0.1 or better;

- Quartz glass bowls,

Nominal volume ≥ 100 ml. Platinum bowls should not be used – their usage leads to understated results.

b) Apparatus for method B

- 100 ml volumetric flask.

Class A or B. Plastic or quartz glass flasks can be used. Flasks made of borosilicate glass or Duran glass are not allowed.

- Calibrated pipettes of fixed volume: 50 μ l, 100 μ l, 200 μ l, 500 μ l, 1000 μ l, 10 ml or variable-volume piston pipettes.

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c) ICP-OES equipment

To supply the sample a spraying system is required, which can change even the large salt loads into aerosol (cross flow, V-slot or similar). It is recommendable to foresee The ICP gas (argon) should be humidified.

If autosamplers are applied, the containers, needles and supply hoses must be made of polymers (HDPE, PP, PTFE etc.). The use of borosilicate glass or Duran glass containers as well as stainless steel needles is not allowed.

7.12.4. Reagents

a) General rules

If not specified otherwise, the chemicals of analytical grade purity and distilled or deionized water (conductivity <0.5mS/cm) should be used.

b) Reagents for method A

- nitric acid (HNO₃) at least 65% (w/w), alternatively hydrochloric acid (HCl) maximum 37% (w/w)
- certified standard ICP solutions of relevant elements at 1 g/l concentration.

c) Reagents for method B

- 32.5% urea solution, manufactured from urea of insignificant metals content, e.g. "for biological purposes"
- nitric acid (HNO₃) at least 65% (w/w), alternatively hydrochloric acid (HCl) maximum 37% (w/w)
- standard ICP solution, m = 1 g/l of each element, standard commercially available ICP solutions can be used,
- multi-element standard solution, m = 10 mg/l of each element.

Preparation as follows: Transfer using pipette 1000 µl from each standard ICP solution into 100 ml volumetric flask. Dilute the flasks to volume with water and shake well. Fresh solution should be prepared everyday.

7.12.5. Determination Procedure

a) Interferences

Understated test results can occur due to sample material splashing while incinerating or when the temperature is too high on pre-incineration with the use of Bunsen burner or in a muffle furnace (particularly for Na and K). Too high results can occur due to introduction of solid mineral particles (e.g. furnace insulation material). Relevant measures must be taken to avoid such mistakes.

Method A: Determination of P element is impossible, due to formation of insoluble polyphosphates during incineration.

Method B (direct determination): Some elements can interfere with crystals containing carbon. The disturbances can also occur due to the applied spraying system. If during direct determination some instrument problems arise then the sample has to be prepared in accordance with item 7.12.5 b).

The Inside of plastic containers (sample bottles, volumetric flasks etc.) may contain some traces of elements to be determined, therefore they must be obligatorily cleaned with acid (HCl, HNO₃) before use .

b) Test Sample preparation

Preparation of sample for Method A:

Weigh and put into the quartz bowl 100 g of the sample (with an accuracy of 0.1 g). Carefully evaporate the solution until dryness on a hot plate. If the sample is dried enough to avoid splashing it should undergo total

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incineration in the muffle furnace, starting from the temperature of 350°C and increasing it up to 700°C within two hours. The final temperature of 700°C should be maintained for at least 30 minutes.

NOTE: If a programmable ramp temperature controller muffle furnace with and gases suction is not available, then the sample should be evaporated on the flame (using gas burner under the fume hood) and after that incinerated in the muffle furnace at 700°C.

In the even of sample preparation with use of a microwave muffle furnace the following temperature program is applied:

1. Start in ambient temperature;
2. Increase to 200°C within 30 minutes,
3. Keep temperature of 200°C for 10 minutes,
4. Increase up to 700°C within 120 minutes;
5. Keep the temperature of 700°C for at least 30 minutes.

After cooling to room temperature the deposits should be dissolved while heating in 5 ml of nitric acid (or hydrochloric acid) and 20 ml of water. The solution should be transferred in portions into 100 ml volumetric flask. Cool the volumetric flask to ambient temperature, dilute to volume with water and shake well.

Preparation of sample for Method B:

With the use of a relevant spray system and spectrometer with sufficiently low sensitivity for the individual elements, the samples should be prepared as follows:

Weigh 20 g of the sample with accuracy of 0.01 g and transfer it into the 100 ml measuring flask. Add: approx. 50 ml of water and 5 ml of nitric acid (or hydrochloric acid), dilute to volume with water and mix well.

c) Preparation of calibration curve

The frequency of establishing of the reference curve is due to the spectrometer used (as per instrument manufacturer recommendations and guidelines). Verification and correction of the reference curve drift should be performed on a daily basis by measuring the lowest and standard. The recommended concentrations for elements are given in table 3 and 4.

Reference curve is used to convert the intensities of the individual elements into content (with the use of ICP computer program).

Table 3 is valid for method A

Table 3

Solution	Measured concentration of element mg/l	Acid addition ml/l
0	0	50
1	0.010	
2	0.030	
3	0.100	
4	0.300	
5	1.000	
6	5.000	

Table 4 – valid for method B

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Table 4

Solution	Measured concentration of element mg/l	Acid addition ml/l	32.5% urea solution ml/l
0	0	50	200
1	0.005		
2	0.010		
3	0.020		
4	0.050		
5	0.100		
6	0.200		
7	0.500		

d) Test Sample measurement

Double measurement is carried out.

For emission measurements, use the wavelengths given in Table 5:

Table 5

Element	Wavelength Nm
Calcium Ca	396.85 or 317.93 or 393.37
Chromium Cr	205.56 or 267.72
Iron Fe	259.94 or 239.56
Potassium K	766.49
Copper Cu	324.75 or 327.39
Magnesium Mg	279.55 or 285.21
Sodium Na	588.99 589.59
Nickel Ni	352.45 or 231.60 or 227.07 or 221.65
Zinc Zn	213.85 or 206.20 or 202.55

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Aluminium	Al	396.15 or 394.40 or 167.08
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Each prepared solution should be measured at least three times, making sure that after each sample change a sufficient rinsing time is applied. It is advisable to use 3% nitric acid (or hydrochloric acid) for intermediate measurement rinsing.

7.12.6. Expression of the result
a) Calculations

The values measured in mg/l should be finally recalculated into mg/kg.

b) Result visualization

As the result per element the arithmetic average of two measurements should be given. The results should be provided with precision to two decimal places.

7.12.7. Precision

The accuracies, specified in table 6 are valid for both sample preparation methods.

Table 6

Element	Repeatability	Reproducibility
	r mg/kg	R mg/kg
Ca	0.02	0.1 x x
Fe	0.01	0.3 x x
Cu	0.01	0.2 x x
Zn	0.01	0.3 x x
Cr	0.01	0.3 x x
Ni	0.01	0.3 x x
Mg	0.02	0.3 x x
Na	0.03	0.5 x x
K	0.03	0.5 x x
Al	0.02	0.3 x x
x – is average value		

7.12.8. Test report

The test report must contain at least the following information:

- a) Type and description of tested product;
- b) References to this Technical Specification;
- c) Sampling method used;
- d) Test result according to item 7.12.6;
- e) Deviations from the specified mode of operation, if any and;
- f) Date of analysis.

7.13. DETERMINATION OF IDENTITY WITH THE USE OF FTIR SPECTROMETRY**7.13.1. Purpose of the method**

The method determines the identity of samples from 32.5% urea solution. All aqueous urea solutions with concentration >10% (w/w) will produce IR spectra of the same characteristics.

With the use of this method, the sample from 32.5% urea solution is compared to a known sample and described as "identical" or "non-identical". This method is not suitable to determine concentrations difference or presence of impurities.

7.13.2. Principle of the method

When light passes through the thin layer of urea solution, infrared rays are absorbed in a specific way, and the observed spectrum enables identification of the urea. Alternatively a relevant ATR technique can be applied (reduced total reflection).

7.13.3. Apparatus

- a) FTIR spectrometer or any other relevant spectrometer able to record the spectrum in the range from 600cm^{-1} to 4000cm^{-1} , the selected resolution should be at least 4cm^{-1} or be better;
- b) Cell that are proper for aqueous solutions, e.g. KRS5 (TlBr/TlJ), ZnSe etc. The layer thickness is approx. $100\mu\text{m}$. Alternatively the ATR technique relevant for liquid samples can be applied.

NOTE: Special care must be taken when dealing with very toxic KRS5 material.

7.13.4. Determination procedure

Fill an optical cell with the sample to be tested, taking care that no air bubbles are present. Install the cell inside the FTIR spectrometer, to allow absorption of IR light and recording the spectrum. Alternatively, the sample can be placed on the ATR crystal.

The obtained infrared spectrum should be compared to the reference spectrum of the known 32.5% urea solution and evaluated visually.

7.13.5. Expression of the result

The test result is given in the following form:

YES, i.e. "identical to the reference pattern"

NO, i.e. "non identical to the reference pattern"

7.14. RESULTS EVALUATION AND TEST CERTIFICATE

A batch of NOXy[®] shall be considered to meet the requirements of this Technical Specification if test results conform with the requirements indicated in Table 1.

8. REFERENCES

- ISO 22241-1/2/3/4:2006(E) – Diesel engines – NO_x reduction agent AUS 32
- Analytical procedures according to Fertilizer Research Institute

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WT-2015/ZA-30 supersedes WT-2014/ZA-30