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Recommended best practice for the analysis of total nitrogen content in urea ammonium nitrate (UAN) liquid fertilizer

International Fertilizer Industry Association (IFA)

International Fertilizer Industry Association (IFA) - 28, rue Marbeuf - 75008 Paris - France
Tel. +33 1 53 93 05 00 - Fax +33 1 53 93 05 45/47 - ifa@fertilizer.org - www.fertilizer.org

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This recommendation and its background documents are available to the general public on the IFA web site (www.fertilizer.org), or through written request to the IFA Secretariat.

Contents

Annexes

Tables

Executive Summary

The IFA Method Harmonization Working Group's evaluation of analytical methods used globally for the determination of the total nitrogen content in urea ammonium nitrate (UAN) liquid fertilizer indicates that applying these two methods may be considered as best practice in the international trade of fertilizer products:

- EN 15750 – October 2009: Fertilizers – Determination of total nitrogen in fertilizers containing nitrogen only as nitric, ammoniacal and urea nitrogen by two different methods; Method A – Titrimetric method after distillation according to ISO 5315:1984;

- AOAC Official Method 2.4.02 (993.13) Nitrogen (Total) in Fertilizers; Combustion Method.

The following factors were taken into account in developing this recommendation:

- Each method is broadly applied across the global industry and has a global reach, with the use of each one showing a more or less regional pattern;

- The evaluation of statistical data suggests that the methods are statistically sound, thus yielding precise and accurate results. The methods are considered to have a similar level of accuracy;

- Each method is considered to be relatively simple and cost-effective, in that:

    - The EN "wet chemistry" method requires traditional low-cost laboratory equipment that uses reasonably inexpensive and safe reagents, although this method may be somewhat more time-consuming;
    - The AOAC combustion method requires more expensive equipment, which allows good analysis speed and low chemical reagent consumption.

The IFA Method Harmonization Working Group recommends that all laboratories follow the IFA Laboratory Quality Assurance Guidelines[1] to ensure consistent and reliable results.

[1] www.fertilizer.org/ifa/HomePage/LIBRARY/Publication-database.html/Laboratory-Quality-Assurance-Guidelines.html

Recommended best practice for the analysis of total nitrogen content in urea ammonium nitrate (UAN) liquid fertilizer

1. Introduction

As a first step in the IFA Method Harmonization Working Group's process of identifying methods for recommendation as best practice, mapping was carried out of globally-applied methods used to determine total nitrogen content in UAN liquid fertilizer. As an outcome of this exercise, a number of methods were selected and clustered around two basic principles (**Table 1**).

Subsequently, these methods were evaluated against a defined set of selection criteria. Based on previous assessment, method-ranking criteria were developed and two selected methods were subjected to a collaborative study aimed at carrying out an evaluation based on the statistical precision data obtained. A recommended best practice was then determined, based on the Working Group's deliberations, with consideration given to performance criteria as well as to precision data.

2. Evaluation of globally applied methods

2.1 Method selection

Based on an inventory of generally applied methods, a grouping into two categories was made:

- The more "classic" wet chemistry method, comprising reduction (with a reducing agent), hydrolysis and digestion steps. The digestion step is normally applicable only if organic forms of nitrogen are present, or in the case of fertilizers of unknown composition. Whether to apply the hydrolysis or digestion steps will depend upon the nature of the organic nitrogen present. If urea is present as the only organic nitrogen source, the hydrolysis step is not recommended. The final measurement itself is based on (back) titration.
  Within the cluster of these methods, the reducing agent used is one of the major variables. The principle of the methods is generally in line with the procedure of nitrogen determination known as the Kjehldal method (KjN determination). In historical studies there has been a substantial focus on the stability of the reducing agents. Chromium, which has been shown to be more stable than some other reducing agents such as iron oxide, is preferred.

- The second category can be summarized as instrumental methods that are broadly applied in certain regions. These methods are based on nitrogen releases from fertilizer products through high-temperature combustion with oxygen, followed by measurement using thermal conductivity detection.

In each category, the nitrogen is reported as weight/weight percent nitrogen in the test sample.

Table 1. List of the methods selected for evaluation[1]

Categorization			Methods selected
Wet chemistry	Principle	Reducing agents	
	Destruction and reduction, hydrolysis and digestion steps, followed by titration of the ammoniacal nitrogen	Raney powder Raney powder Chromium powder Chromium powder Chromium powder Chromium powder Chromium powder Devarda's alloy Iron powder Iron/tin(II) chloride	AOAC 2.063-2.064 Brazilian methods AOAC 2.059-2.060 AOAC 2.061-2.062 AOAC 970.02 EN 15750/Method A ISO 5315 SN/T 0736.5 IST 566739 EN 15750/Method B
Combustion	Principle		AOAC 2.4.02 (993.13)
	High-temperature combustion with oxygen, followed by quantitative measurement using thermal conductivity detector		

1. See Annex 1 for a more complete overview.

Based on the selection criteria, the Working Group decided to submit two methods for a collaborative study:

- EN 15750 – October 2009: Fertilizers – Determination of total nitrogen in fertilizers containing nitrogen only as nitric, ammoniacal and urea nitrogen by two different methods; Method A – Titrimetric method after distillation according to ISO 5315:1984;
- AOAC Official Method 2.4.02 (993.13): Nitrogen (Total) in Fertilizers; Combustion Method First Action 1993-Final Action 1996.

2.2 Statistical evaluation

The inventory of applied methods and available test data revealed that there were no structured and systematic statistical data available comparing the methods under evaluation. Hence, the decision was taken to conduct a collaborative study with the two selected methods, using liquid fertilizer samples of the UAN type. Upon final selection, seven samples were included in the ring test:

- two samples referred to as "pre-qualifying samples"; and
- five blind samples.

A homogeneity check of the pre-qualifying samples was carried out through multiple analysis of the samples. The results were submitted according to the test protocol, which enabled the participating laboratories to verify their test results against data delivered for the pre-qualifying evaluation step. Where there was an unacceptable match, laboratories were requested not to continue testing the other five blind samples. The protocol requested triplicate determinations, including sample preparation in each of the analyte samples.

Following the first ring test, a second ring test was conducted due to the scattered results obtained with the EN method in the first one. A cross check following the first ring test revealed that a number of participating laboratories did not systematically apply this wet chemistry method in their day-to-day operations. To eliminate the bias this could have caused, laboratories that had routine experience with the EN method were requested to participate in the second ring test. In principle, the test protocol was similar to the previous one, with the difference that only one method and two blind UAN samples were tested.

Although 18 laboratories participated in the first ring test, only 9 participated in the second one, which was restricted to the EN method.

Data processing was performed for the first ring test by an external service provider. In the second phase the statistical calculation was carried out based on ISO 5725 (see references 3, 4 and 5).

Summary of the statistical data:

- **Table 2** provides an overview of the statistical data, including the number of laboratories participating;
- The available data and the statistical evaluation of the test results from the collaborative studies reveal that the precision data for the two methods are of the same order of magnitude and reflect an acceptable level compared to similar evaluations of other methods;
- Furthermore, it is a prerequisite that laboratories have a good laboratory proficiency standard and are familiar through laboratory practice with the methods concerned. It was learned in the first IFA ring test exercise that statistical precision data were strongly impacted in a negative way if laboratories were not familiar with the methods to be validated.

Table 2. Overview of the statistical data[1]

Scope	IFA RT AOAC	IFA RT EN/ISO	IFA RT2	IFA RT2
Samples (liquid) description	UAN/ UAN+S	UAN/ UAN+Smake[2]	UAN 30% N	UAN 32% N
Number of samples	2 (familiarization) 5 (blind)	2 (familiarization) 5 (blind)	1 (blind)	1 (blind)
Number of laboratories[3]	17 (18)	8 (9)	9 (9)	9 (9)
Statistical parameters				
Repeatability (s_r) – [%(m/m)]	0.102	0.315	0.04	0.06
Relative repeatability RSD_r	0.341	1.051	0.13	0.19
Reproducibility (s_R) – [%(m/m)]	0.200	0.413	0.21	0.24
Relative reproducibility RSD_R	0.666	1.378	0.71	0.76
Reproducibility limit (R) [%(m/m)]	0.554	1.155	0.60	0.68

1. Also see Annex 2.
2. Fertilizer containing sulphur in the form of water soluble salt.
3. Number of participating laboratories, without exclusion of outliers, shown in brackets.

Remark: Data provided at 95% probability level.

2.3 Evaluation of the correctness of the results obtained

When the methods evaluated are applied, the correctness of the results should be checked regularly. The data obtained through the IFA ring test programme indicate that the test results show a good recovery level of more than 99% for both methods [EN 15750 and AOAC 2.4.02 (993.13)]. Thus, there is no significant difference between the reference value and the results obtained through determination in the ring test.

2.4 Applicability

The literature review carried out during the method inventory phase reveals that both methods are applicable in a broad N-range. The collaborative study focused on UAN liquid fertilizers. Therefore, the test samples in the study were restricted to checking the declared total nitrogen content, which ranged from 28 to 32% N, expressed as total nitrogen in weight/weight percent of the test sample. The outcome of the method validation demonstrates that in this typical “N” window for commercial UAN grades, good precision data and correctness of results are obtained.

2.5 Safety precautions

Safety is an extremely important aspect of all laboratory activities. Therefore, due consideration should be given to safety during laboratory procedures such as wet chemistry, flame atomic absorption, and the use of ICP spectrophotometers. The high and moderate risk conditions identified in the SHE matrix (**Table 3**) can be significantly reduced by having accurate, documented routines in place as well as properly trained laboratory personnel. Modern technology often includes additional built-in safety features.

Sound safety techniques should be applied with respect to all laboratory procedures and equipment. When properly applied, these techniques provide safe means of handling chemicals and residues such as strong acids.

Table 3. SHE matrix

Category	Safety risk[1]	Environmental risk[2]
Wet chemistry	Low, assuming skilled technicians and use of good laboratory practice (GLP)	Low to moderate: chemical reagents handled as waste
Combustion	Moderate: compressed gas High: explosion	Low

1. Safety risk: moderate to high risk requires additional engineering controls and safety procedures.
2. Environmental risk: includes reagents, residue and waste.

2.6 Use and general acceptance

The methods studied are broadly applied and show a high acceptability. Their application has a regional character. While the combustion method is commonly applied in North America, the classic wet chemistry method (including with slight variants) is broadly applied in Europe and Russia. Therefore, both methods are to a major extent used in areas where UAN production and trade is of significant importance.

2.7 Time requirement

It is difficult to judge properly the time requirement per measurement, as it relates to several aspects (e.g. number of combined analyses, degree of automation). Samples may be prepared manually. Hence, a straightforward evaluation of the time requirement cannot be made. Independently of sample preparation, however, it is fair to conclude that the instrumental method may be less time-consuming, generally speaking, than the wet chemistry method, especially if the sequential steps [reduction, hydrolysis, digestion (optional) and titration] in the EN method are considered.

2.8 Complexity and cost

Semi-quantitative statements concerning method complexity and cost can be made in general terms. While the wet chemistry method does not require a high investment cost for glassware and equipment, the instrumental combustion method implies a substantial investment in equipment, combined with a moderate to high maintenance cost.

The wet chemistry method requires more chemical reagents. In the AOAC method, use of high-purity oxygen as carrier gas can be identified as a major cost issue.

In the wet chemistry method, the cost of residual reagents and test samples (often handled as waste disposed through an authorized waste handler) must be considered.

2.9 Dynamic range

Both the literature and ring test results show that the two methods are appropriate for determining nutrient levels in UAN liquid fertilizer at an acceptable level of accuracy.

3. Outcome of the evaluation of methods for assessing total nitrogen content in UAN liquid fertilizer

The evaluation of available methods for assessing the total nitrogen content in UAN liquid fertilizer reveals the following:

1. Based on the methods evaluated, two main categories can be identified:
   - wet chemistry methods, which include reduction, hydrolysis, digestion (not applicable to UAN) and distillation steps, followed by titrimetric determination;
   - combustion methods, with high purity oxygen as carrier gas and determination by thermal conductivity detection.

Use of both methods can be recommended as best practice.

2. Ring test results show that the two methods produce similar precision data. Therefore, each method is appropriate and suitable for assessing total nitrogen content in UAN liquid fertilizer.

3. In view of the selection criteria applied, both methods are characterized by their broad applicability and good historical reference method. The comparability of their statistical evaluation is also well accepted. Regarding SHE criteria, the IFA Method Harmonization Working Group considers that no major problems can be identified compared to other methods based on the same principle of determination. In this respect, it is of the utmost importance that the laboratory is familiar with the methods proposed.

4. Each of these methods is enforced as a standard and is regionally recognized as a reference method:
   - the wet chemistry method as EN 15750, based on ISO 5315;
   - the combustion method as AOAC 2.4.02 (993.13).

5. The IFA Method Harmonization Working Group recommends that all laboratories follow the IFA Laboratory Quality Assurance Guidelines[2] to ensure consistent and reliable results.

[2] *Laboratory Quality Assurance Guidelines,* IFA, Paris, France (http://www.fertilizer.org/ifa/HomePage/LIBRARY/Publication-database.html/Laboratory-Quality-Assurance-Guidelines.html).

Annex 1. Method evaluation overview

Categorization	Titrimetric Traditional wet chemistry		Combustion Instrumental
Principle	Destruction and reduction, hydrolysis and digestion steps, followed by distillation of ammoniacal nitrogen; determination is based on (back) titration		High-temperature combustion with oxygen, followed by quantitative measurement by thermal conductivity detector
Methods selected for evaluation	AOAC 2.063-2.064 Brazilian methods AOAC 2.059-2.060 AOAC 2.061-2.062 AOAC 2.4.04 (970.02) EN 15750/Method A ISO 5315 SN/T 0736.5 IST 566739 EN 15750/Method B	Raney powder Raney powder Chromium powder Chromium powder Chromium powder Chromium powder Chromium powder Chromium powder Iron powder Iron/tin(II)-chloride	AOAC 2.4.02 (993.13)
Statistical evaluation	Partial back tracing possible to statistical data Precision data found on EN, ISO and AOAC method validation		
Performance	Overall equal performance level (based on known data) Correctness of results: few historical data available		
Scope/applicability	Consultation reveals broad applicability within the range of commercial liquid fertilizers		
Safety/environmental			
• **Safety**	Safety requirements for a laboratory using chemicals (e.g. strong mineral acids and reducing agents) Assumes skilled lab technicians and GLP		Safety requirements for a chemical laboratory using compressed flammable gases; risk of explosion[1]
• **Environmental**	Low to moderate risk, as residues and spent chemicals to be handled as waste		Low risk
Use and general acceptance	Commonly used and well accepted; strongly adhered to in Europe and Russia		Commonly used and well accepted; mainly used in North America
Time	Longer lasting due to different process steps, but not labour-intensive		Less time-consuming
Complexity	Regular method of chemical analysis Necessitates skilled lab technicians, proven competence and skills		Instrumental method Need for skilled lab technicians
Cost and availability	Standard laboratory Low investment Equipment maintenance: costs low Consumables: chemical reagents		Requirement for special equipment High investment Equipment maintenance costs: moderate to high Consumables: carrier gas
Dynamic range	Appropriate, as both methods have a proven track record		
Final evaluation	Considering their broad applicability, global acceptance as a historic reference method and comparable precision data, both EN 15750/Method A and AOAC 2.4.02 (993.13) were selected for the IFA collaborative study.		

1. To control extra risks, additional engineering controls and safety procedures are required.

Annex 2. Comparison of method statistics, including historical data

Statistical parameters	IFA RT AOAC	IFA RT EN/ISO	ISO RT	CEN RT-EU project	IFA RT2	
Samples	UAN/ UAN+S	UAN/ UAN+S	3[1]	UAN +S	UAN 30	UAN 32
Number of laboratories[2]	17 (18)	8 (9)	19	12 (12)	9 (9)	
Repeatability (s_r) – [%(m/m)]	0.102	0.315	0.36	0.10	0.04	0.06
Relative repeatability RSD_r	0.341	1.051	-	0.5	0.13	0.19
Reproducibility (s_R) – [%(m/m)]	0.200	0.413	1.3	0.47	0.21	0.24
Relative reproducibility RSD_R	0.666	1.378	-	2.5	0.71	0.76
Reproducibility limit (R) [%(m/m)]	0.554	1.155	-	1.55	0.60	0.68

1. Three ring tests were carried out, but the exact composition of the samples is not traceable.

2. Number of participating laboratories, without exclusion of outliers, in brackets.

Remark: Data provided at 95% probability level.

References

1. AOAC Official Method 993.13: Nitrogen (Total) in Fertilizers; Combustion Method First Action 1993 – Final action 1996.
2. *Journal of AOAC International,* 77, 829 (1994), revised March 1997. Association of Official Analytical Chemists.
3. EN 15750 – October 2009: Fertilizers containing nitrogen only as nitric, ammoniacal and urea nitrogen by different methods.
4. ISO 5725 – 1: 1994; Accuracy/trueness and precision of measurement methods and results – Part 1: General principles and definitions.
5. ISO 5725 – 2: 1994: Accuracy/trueness and precision of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.
6. Statistical software package applied from service provider; model according to ISO 5725 and AOAC routines.