Method evaluation in total Nitrogen in solid fertilizers

International Fertilizer Association (IFA)

Content table

Method evaluation in total Nitrogen in solid fertilizers

1. Introduction

Following an IFA internal membership request, the IFA Method Harmonization Working Group embarked on the process of identifying methods for recommendation as best practice on determination of Nitrogen content for nitrogen containing solid fertilizers.

The mapping was carried out of globally-applied methods used to determine total nitrogen content in solid fertilizers. At the starting point of this exercise, the Working Group realized the complexity of this task due to existence of many globally applied methods with their own restrictions and covering a broad portfolio of products.

Based on the agreed protocol methods have been evaluated based on the set of selection criterial developed as an evaluation matrix for IFA Method Harmonization Working Group's method harmonization activities.

2. Evaluation of globally applied methods

2.1 Method selection

Based on an inventory of generally applied methods one could notice that the generally applied methods are mostly clustering around two frames: classical wet chemistry methods and the more instrumental type of methods each with their own strengths and weaknesses.

Furthermore applicability of the methods was quite often restricted to some N-based compositions rather than having a broad applicability range. Evaluation of their suitability for a broader range would imply doing quote some extra method development coupled to extra ring-testing. The latter not being seen as a task of this Working Group; once the Working group was established and settled there was agreed that the scope of activities would restricted to recommendations of existing by preference globally applied methods a broad window of application.

The outcome of the inventory is summarized in table 1 whereby the methods have been evaluated against a defined set of selection criteria.

2.1.1 Applicability and dynamic range

The literature review carried out during the method inventory phase reveals that today's methods applied seems to be applicable in a broad N-range albeit the scope of several methods was not clearly indicated. Hence clarifying the applicability and the dynamic range of the method would imply substantial testing work. Nevertheless as quite some methods have a regional applicability, there is some evidence in both literature as well as by the statistical data on precision data - albeit restricted availability – that methods are appropriate for determining the N-content in solid N-fertilizers.

2.1.2 Use and general acceptance

The methods mapped seem to have at least on regional level a high acceptability. 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.

2.1.3 Time requirement

Albeit 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.

2.1.4 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.

2.1.5 Environmental impact and safety considerations

Safety is an extremely important aspect of all laboratory activities. Therefore, due consideration should be given to safety during laboratory procedures. Risks 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. The environmental impact of the analysis methods is based on chemical reagents, residues and wastes.

2.2 Statistical consideration

The first step in the statistical evaluation of the methods was checking which statistical data was readily available. Different sources have been consulted:
1. statistical data which is available in the method itself.
2. statistical data on AOAC methods extracted from the Magruder website.
3. check which methods could be considered as being equivalent so that statistical data could be cross-used.

Methods where no statistical data have been found, have been excluded from the evaluation.

There are two levels of statistical data:

Level 1 contains only a few basic available parameters like repeatability (r) and reproducibility (R):

- r (repeatability); variation in measurements taken by a single person or instrument on the same item, under the same conditions
- R (reproducibility); the amount of variation in a measurement system assigned to differences in employees, measurement tools and equipment, techniques, setup or other physical factors)

Level 2 include a few more parameters which allows to calculate more advanced statistical parameters like reproducibility limit (R%) and HorRat:

- R% (reproducibility limit); the value below which the absolute difference between two single test results obtained under reproducibility conditions may be expected to lie within a probability of 95%
- HorRat (is indicating the robustness of the method); (= RSDR/ PRSD); Horwitz has developed a formula that calculates the Predicted Relative Standard Deviation (PRSD). For the evaluation of an analysis method one calculates the quotient of the RSDR that one get for the method in a ring test and the Predicted RSD (PRSD) from Horwitz. This (HorRat) ratio = RSDR/PRSD. If this ratio is in the range 0.5 – 2 the method is statistically acceptable.

3. Outcome of the evaluation of methods for assessing total nitrogen content in solid fertilizers

3.1 Method evaluation

- A broad range of methods are existing with quite often a regional approach. Whereas in Europe and Russia more classical wet chemistry methods are applied, AOAC has more geared towards instrumental (e.g. combustion) methods.
- Especially the more traditional methods are less specific with regard to their dynamic range and frame of applicability.
- As far as the statistical data concern, the more recent developments in Quality Management necessitates from laboratory and their economic operators to demonstrate their proficiency. As a consequence, today's methods applied for process and quality assurance also needs to be assessed on their accuracy. Unfortunately, the lack of precision data hampers a proper evaluation of the many methods applied for determination of the Nitrogen content in solid fertilizers, however an attempt has been made to perform a statistical evaluation based on the available data.
- The full evaluation of the different methods as input for an IFA recommendation would hence imply quite some extra testing work even beyond the scope of comparative ring testing of candidate methods for recommendation.

Based on our learnings, IFA Working Group on Harmonization has decided to issue based on the work done a fact based overview of reported methods that are applied for N-determination of solid fertilizers. It considers that, in order to come up with a proper recommendation, it would necessitate a substantial extra workload beyond what the remits of its WG tasks and activities so far.

As an alternative approach, the Working Group has chosen to issue a resume with the outcome of mapping as a guidance and input document for its membership. Despite that the report has some gaps, the overview summarizing available information on methods could be of interest and help to IFA's membership. As to facilitate a more user-friendly guidance document, the WG has decided to made a qualitative ranking of the methods based on accessible and available information related to the mapped methods. The overview including a qualitative overview by experts is attached as Table 3 in this report. The methods indicated in green blocks are considered to be acceptable.

3.2 Statistical method evaluation

Theoretically, the lower the HorRat ratio is, the better the statistics of the method, however it is not advised to rank the methods based on the different HorRat values between 0,5 en 2 as many methods have been ring tested only once. The below table indicates that the methods do fall within the HorRat limits.

For those methods where the HorRat ratio couldn't be calculated due to lack of statistical data (only level 1 data available), the reproducibility limit R% was calculated as well. The parameter R% is not as strong as HorRat as R% doesn't take the mean value (%N) into consideration, while HorRat is doing. Theoretically, like HorRat, the lower the R% is, the better the method is. The R% value for those methods where the HorRat ratio couldn't be calculated, do fall within the range of the others, which means that also those methods will be statistically satisfactory.

Summarized it can be concluded that the statistical evaluation reveals that all the considered methods are statistically satisfactory, based on their HorRat and/or R% value.

4. Conclusion and recommendation

Based on the statistical evaluation of the methods with at least a minimum set of available precision data it can be concluded that none of the considered methods is statistically failing (see table 2). Making a distinguish between the methods based on statistical data is not advised as the available raw data is limited. By considering this, it is opportune to rate the statistical evaluated methods based on the criteria mentioned in chapter 2.1. Table 3 indicates the full overview of the methods, but the list is drastically reduced if only the acceptable methods (green blocks) are combined with the methods for which statistical information is readily available, which brings down the frame of useable methods to the following (see table 4 as well; listing of methods is not in prioritized order):

- **EN 15476:**
  Determination of nitrate nitrogen and ammoniacal nitrogen, by reduction of nitrate with Devarda alloy, followed by distillation in alkaline solution and titration.

- **EN 15750 Method A or ISO 5315:**
  Determination of total nitrogen. Reduction of nitrates with chromium, digestion of organic nitrogen with sulfuric acid. Distillation in alkaline solution followed by titration.

- **AOAC 978.02 or AgriLasa Alfa 01/1:**
  Determination of total nitrogen, based on reduction with chromium, destruction with sulfuric acid, distillation in alkaline solution followed by titration.

- **AOAC 920.03 or AgriLasa Alfa 02/1:**
  Same as method described above, however the method only determines ammoniacal nitrogen ($N-NH_4$) and no $N-NO_3$ or organic nitrogen like urea hence only distillation in alkaline solution, followed by titration.

- **SN/T 0736.5:**
  Method for total nitrogen, ammoniac nitrogen and nitrate nitrogen. Depending on fertilizer composition, there is a reduction step (Devarda alloy) and/or digestion with sulfuric acid, followed by distillation in alkaline solution and titration.

Appendix 1: Statistical data

Table 1: List of considered methods including availability of statistical data

List of methods

| Basic statistics available (r and R) |
| Advanced statistics available (R% and HorRat) |

List of considered methods:

- EN 15476
- EN 15558
- EN 15559
- EN 15750 A
- ISO 5315
- AOAC 2.061 - 2.062 (edition 13, 1980)
- AOAC 2.063 - 2.064 (edition 13, 1980)
- AOAC 978.02
- AgriLasa Alfa 01/1 (AOAC 978.02)
- AgriLasa Alfa 02/1 (AOAC 920.03)
- SN/T 0736.5

- GB 10511-89
- Japanese method 4.1.3.2
- EN 15750 B
- IST 566739
- Brazil Macro
- Brazil Micro
- AOAC 993.13
- AgriLasa Alfa 02/3
- AgriLasa Alfa 03/1
- AFPC XI 16A (AOAC 993.13)
- AOAC 970.02 1997
- AOAC 2.059 - 2.060 (edition 13, 1980)

Table 2: Overview of Statistical results

Method	HorRat value [b]	Reproducibility limit (R%) value	HorRat and R% combined
EN 15476	0,6	0,6	OK
EN 15750 A = ISO 5315 ≈ AOAC 2.059 - 2.060	1,0	1,6	OK
AOAC 978.02 = AgriLASA Alfa 01/1	6,9 [a]	10,5	OK [a]
AOAC 920.03 (001.10) = AgriLASA Alfa 02/1	1,4	1,1	OK
SN/T 0736.5		0,5 [c]	OK
EN 15750 B	0,9	1,3	OK
AOAC 993.13 (010.60) = AFPC XI 16A	0,8	1,4	OK
AgriLASA Alfa 02/3		1,0 [c]	OK
AgriLASA Alfa 03/1		1,0 [c]	OK

[a] the method has a high average HorRat, however the method actually is good (R% = 0,8, HorRat = 0,7) if the total-N remains below approx 12%

[b] HorRat value between 0,5 and 2,0 means that the method is acceptable, the lower the HorRat, the better the method.

[c] within range of the others

Table 3: Method evaluation

Section 1

Standard/ Source	Prepara tion	Statisti cal Evaluati on	Precision (r & R)	Matrix	Instrumentation Equipment	dosage	Chemistry	Sample Size	Dynamic Range	Remarks	Equip ment costs	Operati onal cost	Time	Environ mental impact	Applica tion range	Global reach
EN 15476 Usable			r=0,12 % (w/w) R=0,77% (w/w)	All fertilizers, including compound fertilizers, in which nitrogen is present in nitrate form or in ammoniacal and nitrate form	Standard laboratory	Preparation Reduction+ Distillation Titration	HCl ethanol Devarda alloy (45 Al,50 Cu,5 Zn) NaOH 30% H2SO4 – NaOH Methylred-methylene blue mix indicator or Methylred indicator	5 - 10 g sample Max. 150 mg N		Single indicator: More difficult endpoint detection	2	2	2	5	2	2
EN 15558 Usable				All fertilizers, including compound fertilizers, in which nitrogen is present in nitrate form or in ammoniacal and nitrate form	Standard laboratory	Preparation Reduction Distillation Titration	Water or HCl H2SO4 30% Powdered iron (Ulsch) NaOH 30% H2SO4 – NaOH Methylred-methylene blue mix indicator or Methylred indicator	5 - 10 g sample Max. 50 mg N		Single indicator: More difficult endpoint detection	2	2	2	5	2	2
EN 15559 Usable				All fertilizers, including compound fertilizers, in which nitrogen is present in nitrate form or in ammoniacal and nitrate form	Standard laboratory	Preparation Reduction+ Distillation Titration	Water or HCl Arnd's alloy (60% Cu+ 40% Mg) MgCl2-solution Pumic stone H2SO4 – NaOH Methylred-methylene blue mix indicator or Methylred indicator	5 - 10 g sample Max. 200 mg N		Single indicator: More difficult endpoint detection	2	2	2	5	2	2

Section 2

Standard/ Source	Preparatio n	Statistical Evaluation	Precision (r & R)	Matrix	Instrumentation Equipment	dosage	Chemistry	Sample Size	Dynamic Range	Remarks	Equipme nt costs	Operatio nal costs	Time	Environ mental impact	Applicati on range	Global reach
GB 10511-89 Usable	ISO 5315			Phosphorus nitrate fertilizer ammoniacal and nitrate nitrogen	Standard laboratory	Preparation Reduction Distillation Titration	Water Chromium powder HCl conc. NaOH 450 g/l H2SO4 – NaOH Methylred-methylene blue mix indicator or Methylred indicator	0,5 – 1 g sample		ingle indicator: More difficult endpoint detection	2	2	2	5	0	2
GB 10511-89 Usable	ISO 5315			Phosphorus nitrate fertilizer ammoniacal and nitrate nitrogen	Standard laboratory	Preparation Reduction Distillation Titration	Water Devarda alloy (45 Al,50 Cu,5 Zn) NaOH 450 g/l H2SO4 – NaOH Methylred-methylene blue mix indicator or Methylred indicator	0,5 – 1 g sample		Single indicator: More difficult endpoint detection	2	2	2	5	0	2
Japanese methods 4.1.3.2. Usable				Fertilizers containing nitrate nitrogen ammoniacal and nitrate nitrogen	Standard laboratory	Preparation Reduction Distillation Titration	Water Devarda alloy (45 Al,50 Cu,5 Zn) NaOH H2SO4 – NaOH Methylred-methylene blue mix indicator or Methylred indicator Or Bromothymol Blue	20-100 mg N		Single indicator: More difficult endpoint detection	2	2	2	5	0	2

Section 3

Standard/ Source	Preparation	Statistical Evaluation	Precision (r & R)	Matrix	Instrumentation Equipment	dosage	Chemistry	Sample Size	Dynamic Range	Remarks	Equipme nt costs	Operatio nal cost	Time	Environ mental impact	Applicati on range	Global reach
ISO 5315 First edition 1984-06-01 Usable	ISO 5315		r = 0,30 % (w/w) R = 1,5 % (w/w)	Liquid fertilizers containing nitrogen in all forms. Not useable > 7% organic matter excluding urea	Standard laboratory	Reduction Hydrolysis or Digestion Distillation Titration	Chromium powder HCl conc. H2SO4 conc.+Al2O3 K2SO4-CuSO4.5H2O Al2O3 H2SO4 conc. Anti bumping granules or Anti bumping device NaOH 400g/l H2SO4 – NaOH Methylred-methylene mix indicator	Max. 235 mg total N Max. 60 mg NO3-N	Tot. N in all forms Not useable > 7% organic matter excluding urea	Chromium powder : Sell-by date < 6 months Digestion step : preferable	2	2	1	5	2	2
EN 15750 Method A Usable	Equal to ISO 5315										2	2	1	5	2	2
EN 15750 Method B Usable			r = 0,27 % (w/w) R = 2,2 % (w/w)	Liquid fertilizers Containing ammoniacal, nitric, organic and urea nitrogen	Standard laboratory	Reduction Digestion Distillation Titration	Iron powder SnCl2.2H2O HCl conc. K2SO4 H2SO4 conc. Anti bumping granules NaOH 400g/l H2SO4 – NaOH Methylred-methylene blue mix indicator	Max. 50 mg NO3-N	Total N only present as ammoniacal, nitric, organic and urea nitrogen	Max. total N not mentioned Check SnCl2 is labour intensive Reduction takes more time Heating input level not exactly described	2	1	0	5	2	2

Table 1

Standard/ Source	Preparation	Statistical Evaluation	Precision (r & R)	Matrix	Instrumentation Equipment	dosage	Chemistry	Sample Size	Dynamic Range	Remarks	SWOT analysis					
											Equipment costs	Operatio nal cost	Time	Environ mental impact	Applicati on range	Global reach
AOAC 970.02 1997 AOAC International Usable				All fertilizer samples ammoniacal, nitric, and urea nitrogen	Standard laboratory	Reduction	Chromium powder HCl conc	0,2 – 2 g sample Max. 60 mg NO3-N	Tot. N	Max. total N not mentioned	2	1	1	0	2	2
						Digestion	K2SO4 HgO Few granules alundum H2SO4 diluted			HgO : poisonous environme nt						
						Distillation	Zn-granules NaOH (15 g per 10 ml H2SO4 conc.)			Heating input level not exactly described						
						Titration	H2SO4 – NaOH Methylred indicator			Single indicator : more difficult endpoint detection						
AOAC 2.059 – 2.060 13e edit. 1980 Usable				All fertilizer samples fluid or solid ammoniacal, nitric, and urea nitrogen	Standard laboratory	Reduction	Chromium powder HCl conc	0.35 – 2.2 g sample containing max. 60 mg nitrate nitrogen	Tot. N	Heating input level not exactly described	2	1	1	0	2	2
						Digestion	K2SO4 HgO or metallic Hg Few granules alundum H2SO4 diluted K2S or Na2S2O3.5H2O			HgO / Hg : poisonous environme nt						
						Distillation	Zn-granules NaOH 50%			Single indicator : more difficult endpoint detection						
						Titration	H2SO4 – NaOH Methylred indicator									

Table 2

Standard/ Source	Preparation	Statistical Evaluation	Precision (r & R)	Matrix	Instrumentation Equipment	dosage	Chemistry	Sample Size	Dynamic Range	Remarks	SWOT analysis					
											Equipment costs	Operatio nal cost	Time	Environ mental impact	Applicati on range	Global reach
AOAC 2.061 – 2.062 13e edit. 1980 Usable				All fertilizer samples fluid or solid ammoniacal, nitric, and urea nitrogen	Standard laboratory	Reduction	Chromium powder HCl conc	0.2 – 1.6 g sample containing max. 60 mg nitrate nitrogen		Heating input level not exactly described	2	2	1	5	2	2
						Digestion	K2SO4 CuSO4 or CuSO4.5H2O Few granules alundum H2SO4 diluted			Single indicator : more difficult endpoint detection						
						Distillation	NaOH 50%									
						Titration	H2SO4 – NaOH Methylred indicator									
AOAC 2.063 – 2.064 13e edit. 1980 Usable				All fertilizer samples ammoniacal, nitric, and urea nitrogen	Standard laboratory	Reduction+ Digestion	Raney powder (50% Al +50% Ni) K2SO4 H2SO4 diluted Tributylcitraat	0.2 – 2.0 g sample containing max. 50 mg nitrate nitrogen			2	2	1	5	2	2
						Distillation	Zn-granules or alundum NaOH 50%									
						Titration	H2SO4 – NaOH Methylred-methylene blue mix indicator									
IST 566739 (Achema, Lithuania) method 6.7 Usable				Total N present as ammoniacal, nitric and urea nitrogen	Standard laboratory	Reduction	Iron powder H2SO4 30%		Total N present as ammoniacal, nitric and urea nitrogen	Iron powder : stability ?	2	2	0	5	2	2
						Digestion	CuSO4.5H2O CuO H2SO4 conc.			Reduction takes a lot of time						
						Distillation	NaOH 30%			Heating input level not exactly described						
						Titration	H2SO4 – NaOH Methylred indicator			Single indicator : more difficult endpoint detection						

Table 3

Standard/ Source	Preparation	Statistical Evaluation	Precision (r & R)	Matrix	Instrumentation Equipment	dosage	Chemistry	Sample Size	Dynamic Range	Remarks	SWOT analysis					
											Equipment costs	Operatio nal cost	Time	Environ mental impact	Applicati on range	Global reach
SN/T 0736.5 only a) usable	No comprehensive method for determination total nitrogen in UAN containing ammoniacal, nitric and urea nitrogen			NH4NO3 KNO3 NaNO3 Composite fertilizers containing nitrate nitrogen ammoniacal, and nitric nitrogen	Standard laboratory	Distillation	Devarda alloy NaOH 40%	1 g sample (max. 0.5 g NH4NO3)			2	2	2	5	0	2
						Titration	H2SO4 – NaOH Methylred indicator									
Brazil Macro Usable Ref?				Fertilizers containing ammoniacal nitrogen and all forms non-ammoniacal nitrogen	Standard laboratory	Reduction	Raney powder (50% Al +50% Ni) H2SO4-K2SO4 solution	0.2 – 2.0 g sample containing max. 42 mg nitrate nitrogen			2	2	1	5	2	1
						Digestion	CuSO4-K2SO4 K2S or Na2S2O3.5H2O			Why K2S or Na2S2O3. 5H2O ?						
						Distillation	Zn-granules NaOH 450 g/l									
						Titration	H3BO3 H2SO4 Methylred bromocresolgreen mix indicator									
Brazil Micro Not usable Ref?				Fertilizers containing ammoniacal nitrogen and all forms non-ammoniacal nitrogen	Standard laboratory	Reduction+ Digestion	Raney powder (50% Al +50% Ni) H2SO4 conc.	5 - 15 mg N			2	2	1	5	0	2
						Distillation	NaOH 50%									
						Titration	H3BO3 H2SO4 Methylred bromocresolgreen mix indicator									

Table 1

Standard/ Source	Preparation	Statistical Evaluation	Precision (r & R)	Matrix	Instrumentation Equipment	dosage	Chemistry	Sample Size	Dynamic Range	Remarks	SWOT analysis					
											Equipment costs	Operational cost	Time	Environmental impact	Application range	Global reach
AOAC 993.13 (Combustion method) ??			r = 0,11-0,26 % (w/w) R = 0,14-0,39 % (w/w)	Liquid fertilizers containing 1-67 % total nitrogen	Combustion instrument	Combustion; Conversion; Measuring	Combustion with high purity oxygen; Conversion of NOx To N2; Measuring N2 by means of Thermal Conductivity Detector		Liquid fertilizers containing 1-67 % total nitrogen	Dry reference material at 105 °C Also NH4NO3 ?	1	1	2	5	2	1

Table 2

Standard/ Source	Preparation	Statistical Evaluation	Precision (r & R)	Matrix	Instrumentation Equipment	dosage	Chemistry	Sample Size	Dynamic Range	Remarks	SWOT analysis					
											Equipment costs	Operational cost	Time	Environmental impact	Application range	Global reach
AgriLAS A Alfa01/1 (AOAC 978.02) Total NH_4NO_3-N Usable	Sample must be milled to <1.0mm		R = 0.96% (w/w)	All fertilizers, including compound fertilizers, in which nitrogen is present in nitrate form or in ammoniacal and nitrate form	Standard laboratory Kjeldahl distillation unit	Preparation; Reduction + Distillation; Titration	H_2O; Chrome(III) Chloride in reduced Zn metal 50% NaOH Received in 1% H_3BO_3; 0.1M H_2SO_4 Methylred-methylene blue mix indicator	1 – 5g sample Max: 400 mg/kg N	50 – 350 mg/kg N	This is the determination of N from NH_4NO_3 in complex fertilizer	2	2	2	5	1	2
AgriLAS A Alfa02/1 (AOAC 920.03) Total NH_4-N Usable	Sample must be milled to <1.0mm		R = 0.97% (w/w)	All fertilizers, including compound fertilizers, in which nitrogen is present in nitrate form or in ammoniacal and nitrate form	Standard laboratory Kjeldahl distillation unit	Preparation; Reduction + Distillation; Titration	H_2O; 50% NaOH Received in 1% H_3BO_3; 0.1M H_2SO_4 Methylred-methylene blue mix indicator	1 – 5g sample Max: 400 mg/kg N	50 – 350 mg/kg N	This is the determination of N from NH_4 in complex fertilizer	2	2	2	5	1	2
AgriLAS A Alfa02/3 Total NH_4-N (Colorometric) Not usable	Sample must be milled to <1.0mm		R = 0.96% (w/w)	All fertilizers, including compound fertilizers, in which nitrogen is present in nitrate form or in ammoniacal and nitrate form	Standard segmented flow analyser	Preparation; Colorimetric reaction; Detection	H_2O; Sodium phenate (8% m/v in NaOH) NaOCl (5.25% available Cl); 630nm	1 – 2.5g sample Max 400 mg/kg N	10 – 400 mg/kg N Standards 0 -400 ppm	When Urea is present, hydrolyses can take place and exact extend should be determined	2	2	2	5	0	1
AgriLAS A Alfa03/1 NO_3-N (Reduction with ferrous ion	Sample must be milled to <1.0mm		R = 0.98% (w/w)	All fertilizers, including compound fertilizers, in which nitrogen is present in nitrate form or in ammoniacal and nitrate form	Standard laboratory volumetric equipment	Preparation; Titration	HCl 0.3N Ferrous sulphate solution H_2SO_4 (c); 0.15N KMnO_4 solution (no indicator)	1 – 5g sample Max: 200 mg/kg N		Endpoint is slow, and sample should remain pink for 30s before titration is recorded	2	2	1	2	1	1

Table 3

Standard/ Source	Preparation	Statistical Evaluation	Precision (r & R)	Matrix	Instrumentation Equipment	dosage	Chemistry	Sample Size	Dynamic Range	Remarks	SWOT analysis					
											Equipment costs	Operational cost	Time	Environmental impact	Application range	Global reach
AFPC XI-16A/ AOAC 993.13	Sample Homogenizing, Sample Split, and Pulverized		r =0.21%	All fertilizers which Nitrogen is present.	LECO Truspec CN Analyzer	Combustion	Sucrose for combustion accelerant	0.1000g – 0.1050g	0.5%-50%	Liquid state is more difficult to run on LECO.	1	1	2	5	2	1
AOAC 978.02	Sample Homogenizing, Sample Split, and Pulverized			MAP, DAP, Amsul, mix fertilizer	Labconco Kjeldahl	Digestion, Distillation, Titration		0.5g-2g		We do not test Ammonium Nitrate by Kjeldahl at the moment.	2	2	2	5	1	2

Table 4: Overall evaluation result

Method	Yara rating	Statistics
EN 15476		
EN 15750 Method A = ISO 5315 ≈ AOAC 2.059 - 2.060	*	
AOAC 978.02 = AgriLASA Alfa 01/1		
AOAC 920.03 (001.10) = AgriLASA Alfa 02/1		
SN/T 0736.5		
EN 15750 B	**	
AOAC 993.13 (010.60) = AFPC XI 16A		
AgriLASA Alfa 02/3		
AgriLASA Alfa 03/1		

*AOAC 2.059-2.060 is almost identical to EN 15750 A and ISO 5315, however Hg is used in the digestion step, hence low environmental rating and also low end-rating
**EN 145750 B has less good this rating because of less good performance on operational costs and time.