

# **Determination of total Phosphorus, total Nitrogen and Nitrogen Fractions**

Dr. Enno Janßen

Hessisches Dienstleistungszentrum für Landwirtschaft, Gartenbau und  
Naturschutz



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## SUMMARY

The task of this desk study is to give a survey over the existing standards and the state of the art of the determination of total nitrogen (Dumas), Kjeldahl nitrogen, the nitrogen fractions and total phosphorus. The evaluation of the possibility of proposing draft standards for the fields of soil, sludge, biowaste and related wastes for the respective nutrients should be the outcome.

The assesment of the existing standards shows that partly acceptable descriptions are existing. They are related to one field only e.g. soil or e.g. sludge. The different materials require different proceedings and especially the homogeneity has to be considered. The high demands on analytical quality and the respective validation have to be satisfied.

The result of this desk study is presented in five seperate draft standards for the determination of Kjeldahl nitrogen, Kjeldahl nitrogen including nitrate and nitrite, total nitrogen (Dumas), the extraction of nitrogen fractions and total phosphorus. The necessary work to validate these standards to fulfil the high demands on analytical quality for all applications described in the corresponding scope is pronounced.

# 1. INTRODUCTION

## 1.1 General Information

The following study deals with analytical methods for the two elements nitrogen (N) and phosphorus (P) in soils, sludges, biowaste and related wastes as well as in growing media and soil improvers which often contain waste as source material. Here questions of the fertilisation effect, meaning availability for plants of these elements in the methodical contemplation and especially the methods for the assessment of their behaviour in the environment, their mobility and mobility potential as well as their translocability and their threat of being washed out shall be stressed. Due to the program of the research project not only total contents shall be contemplated, but also the analytic of element species ( $\text{NO}_3$ ,  $\text{NH}_4$ ) and the behaviour under special extraction conditions to reflect environmental situations and the behaviour under these situations. In this study only certain digestion and extraction methods and the referring final determination methods will be contemplated. The whole thematic of sample-taking and sample pre-treatment are not matter of the discussion. In the second section of the introduction the signification of different element fractions and kinds of bonds is being discussed. The third section describes the fundamental requirements on standards.

Beginning with the first section of chapter 2 the existing methods (standards) are being described and their specialties are pictured. In the second section of this chapter of the study a survey is given over possible further methodical prescriptions, which are not yet internationally standardised (possibility). In the third section an evaluation of the single existing standards especially concerning quality and state of the art of technical know-how is given. Questions of validation and thus quality standard will be central points.

In the first section of chapter 3 the state of the art and know how are being described. In the second section of this chapter methods shall be checked due to drafting a horizontal standard and it shall be shown which additional work is required to formulate the respective standards due to the demands that are made.

In the first section of chapter 4 the requirements on samples for the validation of the proposed standards are described. In the second section it shall be discussed which new fields could be worked on for standardisation. In the last section some proposals are made which points should be discussed in a more detailed way.

The proposed draft standards are summarised in chapter 5.

## 1.2 Importance of different element fractions and chemical bondings of nitrogen and phosphorus for the assessment of the environmental behaviour

At selection, evaluation and assessment of exploration methods the question is to be answered in advance which purpose the method has and which questions it can answer due to its specificity. Many methods for the analysis for nutrients especially for the analysis of soils aim at a characterisation of the soil as production site and to give fertilisation recommendations due to the analytical results. The questions of plant availability as well as the carry over of elements or element species in plants are not being emphasised for the treated question and will only be touched. For the behaviour of elements in different matrices in the environment questions of mobility potential and mobility as well as dissolubility and interchangeability as well as washing out and dislocability play the essential role. With these restrictions the chemical behaviour of the elements or their species under the special conditions of the contemplated method at a time and on the other hand the possible biochemical and physical behaviour of the elements in the environment should be appreciable.

### 1.2.1 Total Nitrogen

The content of total nitrogen is generally composed of four fractions: organically fixed nitrogen (possibly differentiated into easily and slightly soluble) proportion. The organically fixed nitrogen is calculated of the difference of total soluble nitrogen minus the three further fractions nitrate, nitrite and ammonium

Here the fraction of organically fixed nitrogen represents the addition of different components (e.g. aminosugars, aminoacids, N-containing heterocycles etc.)

Nitrite as fraction occurs rarely and only if material is developed under strongly anaerobic conditions.

The analysis of total nitrogen surely results in an important outcome as first clue and is specially required in the use of matter in the agriculture. For statements concerning the possible microbiological activity, conversion of organic substance and the release of nitrate from organically fixed nitrogen the total nitrogen is necessary to get the C/N proportion. From this proportion certain interpretations can be derived. For the evaluation of a material or the knowledge of the composition of a material the analysis of this parameter is absolutely required.

### 1.2.2 Nitrate

Nitrate normally generates easily soluble salts which can be dissolved from the respective solid. For this reason the analysis of nitrate is particularly important because it is the nitrogen compound that has got the greatest potential for wash out, elution and translocation. Hence the nitrate analysis is utmost important in soils, sludges, biological waste and related wastes. Here the quota at the total nitrogen does certainly vacillate and normally represents only a tiny fraction. In the sewage sludge e.g. nitrate plays a subdominant role. Since nitrate forms well soluble salts an extraction or elution without complex solvents is possible.

### 1.2.3 Ammonium

Ammonium has to be assessed in a differentiated way within the different materials. While it represents the most important anorganic fraction in soil after nitrogen being part of the crystalline structure and consequently fixed in the compound over crystalline powers, it occurs less solid as salt or adsorptively fixed in other materials. There exist only few slightly soluble ammonium compounds so that the extractability should not be a problem with the exception of strong adsorptive bond or insufficient reachability of the surfaces due to coarse grinding e.g. In the first case ammonium has to be exchanged with another stronger bonded ion with a similar ion radius in the latter one the grinding fineness has to be improved. Furthermore it has to be clarified in this context for both N-species, nitrate and ammonium for which evaluation the analysis is being carried out. Is a material used as soil improver or fertiliser or is it being stored at a depositing or landfill area and is consequently subject of completely different conditions and processes concerning environmental behaviour of the material itself as well as the nitrogen species that it contains. In both cases a quantitative analysis should be the first step.

### 1.2.4 Phosphorus

It is another situation with phosphorus compared to nitrogen because of the chemical behaviour of this element. In the relevant media phosphorus normally occurs in the fifth oxidation level, that means as phosphate or deriving compounds. The organically fixed part plays a rather subdominant role. In dependency from the pre-treatment of the material to exeminate and the contraion to phosphate the respective compounds are easily, less easily to slightly soluble. To record the single fractions respective gradual methods including a drastical digestion have to be existent ; the latter to determine the total phosphorus content.

In contrary to nitrogen you can speak about a certain phosphorus circulation. But this is much less dynamical and finally includes much longer periods. Furthermore this circulation is determined through completely different chemical and biochemical processes. In phosphorus sinks e.g. such as lakes and coastwaters the proportion between the phosphorus content of the sediment and the dissolved phosphorus in the water is a very broad with high contents in the sediment. In an oligotrophic body of water the biomass production is normally restricted by phosphorus during the vegetation period. The system has adjusted to this "situation of lack". So the system can get out of its balance by relative low total inputs and the alga growth can be considerably animated which results in the well known appearance of eutrophisation.

(Schernewski et.al., 1994). For this reason there should be (if possible) also standards for the simulation of environmental situations available next to the total phosphorus content determinations.

There are three basic situations to be considered:

1. The phosphorus containing material is brought on the soil as soil improver or fertiliser. In this case questions of plant availability, potential of mobility and

mobility of phosphorus as a cause of dissolution processes as well as the possible translocation in solid particles by erosion (wind, water) and the wide pore system shall be emphasised. Here, respective balances are requested where methods for the total phosphorus determination are rather needed than those that can register and quantify the single fractions. If questions concerning the behaviour in the soil are posed, methods for the examination of the different phosphorus fractions have to be applied to be able to explain the different processes of ad- and desorption as well as the different dissolution and precipitation processes.

2. The phosphorus containing material is being stored at a depositing or landfill area. Here the processes of translocation of phosphorus are completely different from the ones described in 1. The chemistry of the seeping water from the depositing area has got a central significance. This should be reflected by appropriate elution methods.

3. The phosphorus containing material is being combusted. In this case the phosphorus can occur in a modified chemical surrounding in the cinder due to its respective kind of source compound and the temperature during the combustion process. In this case the two possibilities described in 1. and 2. have to be contemplated and the appropriate methods have to be applied.

It is a difference if a landfill material, a soil improver, a fertiliser or a soil is being examined. In each case the goal has to be fixed in advance and the corresponding suitable method has to be applied. Here especially the chemistry of phosphorus and the pH-dependency of the solubility of its kinds of bondings have to be considered.

### 1.3 Requirements on standards

Within the frame of EU directives and according regulations the formulated methods shall lead to results that are loadable and comparable. Therefore they have to fulfil a high quality level. The standards will be accepted as examination methods within the scope of quality assurance and confirmation of competence (accreditations) according to EN ISO 17025 without any further check. Users as well as accreditationers and auditors have a high confidence in the quality of these standards. This confidence has also to be complied with by a high demand on the quality at the development and the validation of these standards. Under these conditions the texts have to be unambiguous and unmistakable. They have to be self-explaining not needing any further explanation. The texts have to be precise and formulated as extensive as necessary. For people who apply the standard for the first time it has to give a practical and understandable instruction. Of course its application requires a professionally trained personal. Furthermore the standards should reflect the current state of the art and scientific knowledge.

The general requirements are described in CEN & CENELEG international Regulations – Part 3.

Furthermore the described methods have to be validated by appropriate ring-tests with satisfactory results. A minimum number of laboratories should be involved but strict requirements have to be set upon the execution. The

evaluation and assessment has to be made due to EN 5725 with a special observance of normal distribution and homogeneity of the data. Data coming from different measuring methods (e.g. phosphorus with ICP-OES, with molybdenum blue or by gravimetry) must not be analyzed together. No standard can be sent off without appropriate validation data. This is the only way how to comply with the confidence into the standardised methods and how to verify the quality standard.

A special emphasis has to be given to the purpose and the aim according to which a standard was developed. For the question of nutrient coverage there can be totally different proceedings at the sample taking as well as at the analytic for agricultural aspects like fertilisation and plant nourishment than it would be necessary for questions like elution, dislocation or total contents. This aspect has got a central importance at the horizontal standardisation according to the existing standards.

In the following the requirements on standards are represented in a summary again:

- Definition of area of purpose and application
- Description satisfactory
- Instruction sufficient and practicably understandable
- State of the art
- Execution of validation
- Data of validation satisfactory
- Calculation of statistical data according to ISO 5725

## 2. EXISTING STANDARDS OR DRAFT STANDARDS

### 2.1 Nitrogen

Table 1 gives a survey over the existing standards for nitrogen

Table 1 Existing standards for nitrogen

Standard No.	B=soil S=sludge A=waste K=soil improvers BO=biowaste	Description satisfactory	E=extraction G= total E=elution	With/ Without measuring	Validation-data available
ISO 11261	B	yes	Kjeldahl/Ti/ Cu	With	yes
ISO 13878	B	yes	Dumas	With	yes
ISO 14255	B	yes	E	with	no
ISO 14256	B	yes	E	With	no
EN 13342	S	no	Kjeldahl/ Se oder Cu	With	not satisfactory
prEN 14671 WI 308012	S	no	E	reference	no
WI 308013	S	yes	E		
EN13654-1	BO	yes	Kjeldahl	several measuring methods	yes
EN 13654-2	BO	yes	Dumas	With	yes
EN 13651	K	no	E	reference	yes, not satisfactory
EN 13652	K	no	E	Reference	yes, not satisfactory
EN 13370	W	no	E	Reference	no

Continuation of table 1 existing standards nitrogen

Standard No.	Object	matrix/ solution ratio	Extractant	Moist/field Fresh/air dried	year
ISO 11261	N in soil			air dried	1995
ISO 13878	N in soil			air dried	1998
ISO 14255	N-fractions	1:10	0,01 mol/l CaCl <sub>2</sub>	air dried	1998

Continuation of table 1 existing standards nitrogen

Standard No.	Object	Matrix/ solution ratio	extractant	Most/field Fresh/air dried	Year
ISO 14256-2	N-fractions	1:5	1 mol/l KCl	field fresh	2002
EN 13342	N in sludge			moist	2000
prEN 14671 WI 308012	Extractable ammonium		2 mol/l KCl	moist	2003
WI 308013					
EN 13654-1	N-Kjeldahl			dried	2001
EN 13654-2	N-Dumas			dried	2001
EN 13651	CAT- soluble Nutrients	1:5	Calcium chloride/DTPA	field fresh	2002
EN 13652	watersoluble nutrients	1:5	Water	field fresh	2002
EN 13370	eluable parameters		Water		2002

2.1.1 ISO 11261 Soil Quality – Determination of total nitrogen – modified Kjeldahl method

The method describes the the digestion of air dry soil samples with concentrated sulphuric acid at a temperature scarcely under 400°C. It is a modified Kjeldahl method that uses salicyl acid for the nitration with nitrate and nitrite and for the reduction of nitro compounds sodium thiosulfate. A mixture of coppersulfate and titaniumdioxide serves as catalyst. Potassium sulfate is used for the temperature raising. The distillation follows after the addition of caustic soda into a vessel with boric acid or sulphuric acid. The calculation is being given in an understandable way. The validation leads to results that are shown in table 2.

Table 2 Validation data ISO 11261

Sample No.	Nitrogen content, Average, mg/kg	s <sub>r</sub> mg/kg	s <sub>r</sub> %	s <sub>R</sub> mg/kg	s <sub>R</sub> %
1	0,98	0,06	6,1	0,27	27,0
2	3,11	0,12	3,9	0,58	18,6
3	6,70	0,19	2,8	1,07	15,9
4	10,88	0,26	2,4	0,89	8,2

s<sub>r</sub> mg/kg repeatability

s<sub>r</sub> % percentage repeatability

s<sub>R</sub> mg/kg reproducibility

s<sub>R</sub> % percentage reproducibility

Because of the modification the method includes not only organically fixed nitrogen but also nitrate and nitrite. Nitrogen being fixed in special compounds is not being completely digested. Consequently you cannot speak about a method for determination of total nitrogen.

The method is described sufficiently and checked and quality firm by a validation with a calculation by ISO 5725 at four soil samples by 14 laboratories. The repeatability and reproducibility becomes closer and is satisfactory with higher contents.

### 2.1.2 ISO 13878 Soil quality Determination of total nitrogen content by dry Combustion („elemental analysis“)

The method describes the determination of total nitrogen in soil after combustion in oxygen stream at 900°C. Air dry soil is used. The developing oxides are reduced to elementary nitrogen and the nitrogen content is measured by electrical conductance in the stream of helium. The calculation of the nitrogen content is given in an understandable way. The validation leads to results which are shown in the table 3.

Table 3 Validation data ISO 13878

Sample No.	Nitrogen content, Average, mg/kg	s <sub>r</sub> mg/kg	s <sub>r</sub> %	S <sub>R</sub> mg/kg	S <sub>R</sub> %
1	1,457	0,067	4,6	0,205	14,1
2	2,054	0,073	3,6	0,333	16,2
3	11,16	0,334	3,0	0,982	8,8

s<sub>r</sub> mg/kg      repeatability  
s<sub>r</sub> %            percentage repeatability  
S<sub>R</sub> mg/kg      reproducibility  
S<sub>R</sub> %            percentage reproducibility

The method captures the total nitrogen.

The method is described sufficiently and checked and quality firm by a validation with a calculation by ISO 5725 at four soil samples by 14 laboratories. The repeatability and reproducibility becomes closer and is satisfactory with higher contents.

2.1.3 ISO 14255 Soil quality – Determination of nitrate nitrogen, ammonium nitrogen and total soluble nitrogen in air dry soils using calcium chloride as extractant.

The method describes the extraction of nitrogen fractions (nitrate, nitrite, ammonium and soluble organic nitrogen) from air dry soil. It uses a neutral salt (0.01 mol/l calcium chloride) as extraction solution. The ratio of soil to extraction solution is 1:10. The determination of the different fractions is done in a continuous flow system with the respective chemicals. By subtraction of the content of nitrate, nitrite and ammonium from the total nitrogen content in the extraction solution the soluble part of organically fixed nitrogen can be calculated.

The description is sufficiently exact. A validation of the method is missing.

2.1.4 ISO 14256 - 1 Soil quality – Determination of nitrate, nitrite and ammonium in field moist soils using potassium chloride solution as extractant , part 1

The method describes the extraction of inorganic nitrogen fractions from field fresh soil with a neutral salt (1 mol/l potassium chloride). The ratio of soil to extraction solution is 1:5. Precise information concerning sample taking and transport as well as storing referring to the temperature are given in the method. The manual spectrometrical determining methods for nitrate, nitrite and ammonium are described in a detailed way.

The description is sufficiently exact. The results are related to dry matter.

A validation of the method is missing.

2.1.5 ISO 14256 - 2 Soil quality – Determination of nitrate, nitrite and ammonium in field moist soils using potassium chloride solution as extractant, part 2: automated method

The method describes the extraction of inorganic nitrogen fractions from field fresh soil with a neutral salt (1 mol/l potassium chloride). The ratio of soil to extraction solution is 1:5. Precise information concerning sample taking and transport as well as storing referring to the temperature are given in the method. The determination is realized with a continuous flow system with the appropriate chemicals.

The description is sufficiently exact. The results are related to dry matter.

A validation of the method is missing.

2.1.6 EN 13342 Characterization of sludges - Determination of Kjeldahl nitrogen

The standard describes the determination of nitrogen according to the Kjeldahl method in sludges by a digestion with sulphuric acid at a temperature of

scarcely under 400°C. Here selenium is added as catalyst as well as sodium sulfate to raise the boiling point.

The validation leads to results which are shown the table 4.

Table 4 Validation data EN 13342

Sample No.	Nitrogen content, Average, g/kg mT	s <sub>r</sub> mg/kg	s <sub>r</sub> %	s <sub>R</sub> mg/kg	s <sub>R</sub> %
1	28,48	2,13	12,65	2,15	16,84
2	21,87	3,5	21,47	3,22	16,3
3	27,52	0,7	7,13	1,07	9,81
4	16,28	0,65	4,79	0,718	13,58

The method is validated by four laboratories only. Furthermore the method how the statistical data are calculated is not explained.

#### 2.1.7 WI 308012 Characterisation of sludges – Pretreatment for the determination of extractable ammonia using 2 mol/l potassium chloride.

The standard draft describes the extraction of extractable ammonium with a solution of 2 mol/l potassium chloride from sludge. Here not only the soluble but also, thanks to the high cation concentration, the exchangeable ammonium is being captured. A side effect of the high salt concentration is a little tendency of the extraction solution to biological activity and thus change of the ammonium concentration.

The standard describes the extraction in a sufficiently exact way.

The standard refers to other standards where methods for the determination of ammonium are described.

A validation of the extraction is missing.

#### 2.1.8 EN 13654-1, Soil improvers and growing media – Determination of nitrogen, part 1: modified Kjeldahl method

The method describes the determination of nitrogen including nitrate and nitrite in soil improvers and growing media by a digestion with sulphuric acid at a temperature of scarcely under 400°C.. It is a modified Kjeldahl method that uses nitration of salicylic acid with nitrate and nitrite and sodium thiosulfate for the reduction of the yielded nitro compounds. The method allows the use of dry material next to fresh material. Material for the calibration is given. For the determination three different methods are referred to- distillation, continuous flow analysis or spectrometry. Their explanation is referred to by literature quoting.

The description of the realization of the Kjeldahl digestion is described in a sufficiently exact way.

The results refer to dry matter or original substance.

The validation leads to results which are shown the table 5.

Table 5 Validation data EN 13654-1

Sample No.	No. of Participants (outlier)	Nitrogen content, Average, g/kg m <sub>T</sub>	s <sub>r</sub> g/kg	s <sub>r</sub> %	s <sub>R</sub> g/kg	s <sub>R</sub> %
Bark humus	15 (0)	19,41	0,63	3,24	2,70	13,91
Biowaste	15 (2)	12,88	0,32	2,48	0,93	7,22
Clay containing Peat (fertilized)	15 (0)	9,44	0,31	3,28	0,66	6,99
Coarse peat (fertilized)	15 (1)	11,17	0,22	1,97	1,10	9,85
Composted sludge	15 (1)	29,90	0,96	3,21	2,97	9,93
Composted wood fibre	14 (1)	11,77	0,24	2,04	0,61	5,18

The statistical evaluation according to ISO 5725 leads to results which are satisfactory for a nitrogen determination according to Kjeldahl. But the figure data for s<sub>r</sub> % and s<sub>R</sub> % are taken with the factor 2.8. This was already corrected in the table 5. It is not realizable if the results from the different measuring methods were influent to a joint statistical analysis.

#### 2.1.9 EN 13654-2 Soil improvers and growing media - Determination of nitrogen – part 2: Dumas method

The method describes the determination of nitrogen according to Dumas. The sample is incinerated in a stream of oxygen at 900°C. After reduction of the nitrogen oxides into elemental nitrogen its content is determined by a conductivity measurement. It refers to the particulars of the instrument manufacturer.

In a ring test the results were reached shown in table 6.

The number of the participants is sufficient. The statistical evaluation according to ISO 5725 leads to results which are satisfactory for a nitrogen determination according to Dumas. But the figure data for s<sub>r</sub> % and s<sub>R</sub> % are taken with the factor 2.8. This was already corrected in the table 6. In the validation table data seems to be identical with the standard 13654-1.

Table 6 Validation data EN 13654-2

Sample No.	No. of Participants	Nitrogen content, Average, mg/g	s <sub>r</sub> mg/g	s <sub>r</sub> %	s <sub>R</sub> mg/g	s <sub>R</sub> %
Bark humus	10	19,5	0,45	2,30	1,32	6,77
Biowaste	12	13,21	0,36	2,73	1,10	8,33
Clay containing peat (fertilized)	11	9,2	0,25	2,72	0,63	6,85
Coarse peat (fertilized)	11	10,7	0,25	2,34	1,69	15,8
Composted sludge	15	29,90	0,96	3,21	2,97	9,93
Composted wood fibre	12	12,07	0,37	3,07	1,72	14,25

#### 2.1.10 EN 13651 Soil improvers and growing 69+media - Extraction of calcium chloride/DTPA (CAT) soluble nutrients

The method describes the extraction of nutrient elements with calcium chloride/DTPA (CAT, 0,01 mol/l calciumchloride, 0,002 mol/l DTPA) from soil improvers and growing media. The pH of the extraction solution lies at 2,65. The ratio of solution to used material is 1:5. the method is described in a sufficiently exact way for the area of the extraction and refers to the stability of the extraction solution. In appendix B different element specific methods for the determination of the different elements are given. For each element at least two methods are quoted.

The validation leads to results which are shown in the table 7. The results refer to the sample in fresh condition. An explanation how the analysis of the ring-test was made is missing (according to EN 5725 or another method) and especially if the calculation is based on different measuring methods.

Table 7 Validation data EN 13651

#### Bark humus

Analyt	No. of participants	Content, average, mg/l	s <sub>r</sub> mg/l	s <sub>r</sub> %	s <sub>R</sub> mg/l	s <sub>R</sub> %
Ammonium	19	1220,1	49,19	4,03	248,52	20,4
Nitrat	13	13,6	2,27	16,7	13,96	102,6
P	20	290,0	14,59	5,03	108,99	37,6

Continuation of table 7 Validation data EN 13651  
Biowaste

Analyt	No. of participants	Content, average, mg/l	s <sub>r</sub> mg/l	s <sub>r</sub> %	s <sub>R</sub> mg/l	S <sub>R</sub> %
Ammonium	19	192,0	9,87	5,14	79,02	41,1
Nitrat	16	33,5	1,35	4,02	27,34	81,6
P	18	42,9	1,30	3,03	12,54	29,2

Clay containing peat (fertilized)

Analyt	No. of participants	Content, average, mg/l	s <sub>r</sub> mg/l	s <sub>r</sub> %	s <sub>R</sub> mg/l	S <sub>R</sub> %
Ammonium	19	87,2	2,06	2,36	11,81	13,5
Nitrate	19	72,9	1,77	2,42	11,89	16,3
P	19	35,2	1,19	3,38	4,62	13,1

Coarse peat (fertilized)

Analyt	No. of participants	Content, average, mg/l	s <sub>r</sub> mg/l	s <sub>r</sub> %	s <sub>R</sub> mg/l	S <sub>R</sub> %
Ammonium	20	105,1	5,18	4,92	15,86	15,1
Nitrate	20	53,6	4,22	7,87	8,94	16,7
P	21	92,9	9,41	10,1	25,12	27,0

Composted sludge

Analyt	No. of participants	Content, average, mg/l	s <sub>r</sub> mg/l	s <sub>r</sub> %	s <sub>R</sub> mg/l	S <sub>R</sub> %
Ammonium	18	521,7	14,82	2,84	169,81	32,5
Nitrate	19	243,5	9,72	3,99	83,94	34,5
P	19	132,6	3,85	2,90	52,11	39,3

Composted wood fibre

Analyt	No. of participants	Content, average, mg/l	s <sub>r</sub> mg/l	s <sub>r</sub> %	s <sub>R</sub> mg/l	S <sub>R</sub> %
Ammonium	20	71,1	2,25	3,16	23,15	32,6
Nitrate	19	65,4	2,23	3,41	7,05	10,8
P	20	55,2	1,62	2,93	11,20	20,3

The number of participants is sufficient. In the present table the figures for s<sub>r</sub> % and s<sub>R</sub> % were calculated again using the data from the appendix for this standard were taken with the factor 2,8.

## 2.1.11 EN 13652 Soil improvers and growing media - Extraction of water soluble nutrients and elements

The method describes the extraction of nutrient- and other elements with water from soil improvers and growing media. The ratio of solution to used material is 1:5. The method is described in a sufficiently exact way for the area of the extraction and refers to the stability of the extraction solution. In appendix B different element specific methods for the determination of the different elements are given. For each element at least two methods are quoted.

The validation leads to results which are shown in the table 8. The results refer to the sample in fresh condition. An explanation how the analysis of the ring-test was made is missing (according to EN 5725 or another method) and especially if the calculation is based on different measuring methods.

Table 8 Validation data EN 13652

### Bark humus

Analyt	No. Of participants	Content, average, mg/l	s <sub>r</sub> mg/l	s <sub>r</sub> %	s <sub>R</sub> mg/l	S <sub>R</sub> %
Ammonium	22	764,7	23,21	3,04	260,94	34,1
Nitrat	18	25,1	1,50	5,98	45,54	181,4
P	18	236,2	6,53	2,76	67,73	28,7

### Biowaste

Analyt	No. Of participants	Content, average, mg/l	s <sub>r</sub> mg/l	s <sub>r</sub> %	s <sub>R</sub> mg/l	S <sub>R</sub> %
Ammonium	20	115,4	2,45	2,12	60,70	52,6
Nitrat	20	76,7	10,21	13,3	108,59	141,5
P	16	38,8	1,89	4,87	7,82	20,2

### Clay containing peat (fertilized)

Analyt	No. Of participants	Content, average, mg/l	s <sub>r</sub> mg/l	s <sub>r</sub> %	s <sub>R</sub> mg/l	S <sub>R</sub> %
Ammonium	18	69,7	3,09	4,43	8,96	12,86
Nitrat	23	82,7	7,69	9,30	27,39	33,12
P	20	30,8	1,16	3,77	4,09	13,28

### Coarse peat (fertilized)

Analyt	No. Of participants	Content, average, mg/l	s <sub>r</sub> mg/l	s <sub>r</sub> %	s <sub>R</sub> mg/l	S <sub>R</sub> %
Ammonium	23	76,7	6,35	8,28	19,66	25,63
Nitrat	22	57,0	5,88	10,32	9,17	16,09
P	20	88,9	4,78	5,38	21,20	23,85

Continuation of table 8 Validation data EN 13652

Composted sludge

Analyt	No. Of participants	Content, average, mg/l	s <sub>r</sub> mg/l	s <sub>r</sub> %	s <sub>R</sub> mg/l	S <sub>R</sub> %
Ammonium	20	341,0	6,35	1,86	125,57	36,82
Nitrat	22	244,3	9,67	3,96	97,85	40,05
P	18	94,3	4,85	5,14	66,90	70,9

Composted wood fibre

Analyt	No. of participants	Content, average, mg/l	s <sub>r</sub> mg/l	s <sub>r</sub> %	s <sub>R</sub> mg/l	S <sub>R</sub> %
Ammonium	22	57,9	3,19	5,51	25,87	44,68
Nitrat	22	66,6	3,08	4,62	66,60	100,0
P	21	48,5	2,49	5,13	8,09	16,68

The number of participants is sufficient. In the present table the figures for s<sub>r</sub> % and s<sub>R</sub> % were calculated again using the data from the appendix for this standard were taken with the factor 2,8.

2.1.12 EN 13370 Characterisation of waste – analysis of eluates - determination of ammonium, AOX, conductivity, Hg, phenol index, TOC, easily liberatable CN, F

The standard summarises different standards from the water analysis for the measurement of eluates and transfers them to the waste analytic. The eluates are gained with water according to the standard EN 12457 1-4. The ratio of water to waste is 1:2. Generally possible problems for the sample treatment as well as for the handling of the eluate are mentioned in the text. But it is only intimated of which special kind the problems could be and how to solve them. The production of the eluates is only mentioned in the introduction. The respective quotations in the normative references and in point 4 are missing. The disturbances mentioned in point 6 are only generally treated. In point 7 the assessment of applicability of a chosen measurement method is left to the respective laboratory without describing the exact proceeding for the applicability determination. In this case no concrete method is being described but like in a building set it is referred to standards from other fields of application that can be transferred to the waste analysis. A validation exists only in parts (ammonium, not in all samples).

A validation does not exist.

## 2.2 Phosphorus

The table 9 lists the existing standards for the analysis of phosphorus.

Table 9 Existing standards for phosphorus

Standard No.	B=soil S=sludge A=waste K=soil improvers BO=biowaste	Description satisfactory	E=extraction G=total E=elution	with/ without measuring	Validation data available
ISO 14869-1	B	yes	G	without	no
ISO 14869-2	B	yes	G	without	no
ISO 11263	B	yes	E	with	No
EN 13346	S	no	G	without	yes
PrEN 14672 WI 308034	S	no	G	without	yes
EN 13650	K	yes	G	without	yes
EN 13652 siehe unter Stickstoff					

Continuation Table 9 Existing standards for phosphorus

Standard No.	Object	Matrix/solution ratio	extractant	moist/field fresh/air dry/dry	Year
ISO 14869-1	Total element content		HF/HClO <sub>4</sub>	2.3 dry	2001
ISO 14869-2	Total element content		Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> LiBO <sub>2</sub>	dry	2001
EN 11263	Extractable P	1:20	Na <sub>2</sub> CO <sub>3</sub>	dry	1994
EN 13346	Total P	1:10	aqua regia	dry	2001
PrEN 14672 WI 308034	Total		Sulfuric Acid/ Salpetric Acid	moist/dry	2003
EN 13650	Total P		Aqua regia	dry	2001
EN 13652 see at nitrogen					

### 2.3.1 ISO 14869-1 Dissolution for the determination of total element content – part 1: Dissolution with hydrofluoric and perchloric acids

The standard describes the digestion of soil by means of hydrofluoro acid and perchloric acid.

After a possible pretreatment of dry ashing or pretreatment with salpetric acid for determination of the total contents of chosen elements. An advantage is the destruction of silicates and the separation of disturbing silicium by the use of hydrofluoro acid. A hint which steps have be done if the digestion has not completely effected is given. The standard is described in a sufficiently exact way. Critical points including the danger in the handling of hydrofluoro acid are mentioned. The standard ends with the production of the digestion solution and gives no hint to a special measuring method.

A validation of the digestion is not given

### 2.3.2 ISO 14869-2 Dissolution for the determination of total element content – part 2: Dissolution by alkaline fusion

The standard describes the digestion of soil by the means of alcaline fusion by di-lithiumtetraborate/ lithiummetaborate for the determination of the total contents of selected elements.

The standard is described in a sufficiently exact way. Critical points including possible dangers are mentioned. The standard ends with the production of the digestion solution and gives no hint to a special measuring method.

A validation of the digestion is not given.

### 2.3.3 ISO 11263 Soil quality – determination of phosphorus - spectrometric determination of phosphorus soluble in sodium hydrogen carbonate solution

The standard describes a method for the extraction of phosphorus from soils by the means of 0.5 molar sodium hydrogen carbonate solution at a pH of 8.5. This fraction shall reflect the availability of phosphorus and was used as basis for the calculating of the phosphorus quantity for the phosphorus fertilisation in the USA (VDLUFA, 1991). The ratio of soil to extraction solution is 1:20. The formation of a colour complex at room temperature and at high temperature(90°C, water bath) with different chemicals and the following photometric measurement are described. The calculation including the repeatability at different content levels is given.

A validation of the method is missing.

### 2.3.4 EN 13346 Determination of trace elements and phosphorus – aqua regia extraction methods

The standard describes the digestion of dried sludge by the means of aqua regia in four different methods. The ratio of sludge to acid lies between 1:8 and 1:30 for the respective variants. Data concerning the required grain size of the sludge is missing. In the description of method D the data concerning the additive of acid is missing. Different methods for the measurement are given, whereat only the standard EN ISO 11885 (ICP-OES) can be taken into consideration for phosphorus. Detailed information on the calibration of the microwave ovens is given. Information concerning possible faults at the measurement can be found in appendix C. Detailed information and ways for problem solution for the measurement of solutions after the digestion of sludge (EN ISO 11885 has been developed for the measurement of water) is not given (e.g. wave lengths for P, possible disturbing elements, ratio of disturbing element to analytical element where interferences have to be expected).

Apart from the mentioned points the standard is a detailed text.

The validation leads to results which are shown in the table 10. In column two the described methods are called A,B,C and D and the reference method is called sulfuric acid/salpetric acid.

Table 10 Validation data EN 13346

Analyt	Nb. of participants	Content, average, mg/kg	s <sub>r</sub> mg/l	s <sub>r</sub> %	S <sub>R</sub> mg/l	S <sub>R</sub> %
P	A 23	10,49	0,33	3,2	0,78	7,5
	B 7	10,82	0,22	2,0	1,30	12,0
	C 19	10,63	0,36	3,4	0,75	7,0
	D 7	11,41	0,56	4,4	1,63	14,3
	E 6	10,10	0,31	3,0	0,66	6,5

E = Sulfuric Acid/ Salpetric Acid, prEN 14672

The number of participating laboratories in some cases is not sufficient. There exist doubt if the dimension mg/kg in the head of the table was correctly chosen. For phosphorus g/kg would be the expected dimension. The results are satisfactory, but it is surprising that the results match each other so well despite the different digestion circumstances and the heavily varying proportions of acid to sludge.

### 2.3.5 prEN 14672/WI 308034 Characterisation of sludge – Determination of total phosphorus

The method describes the digestion of dried or facultatively wet sludge in a mixture of sulfuric acid/ salpetric acid under reflux. The ratio of sludge to acid is not fixed and is determined by the phosphorus content in the sludge. Three measurement methods coming from the field of water are referred to. Detailed information and ways for problem solution for the measurement of solutions

after the digestion of sludge is not given. Data concerning the required grain size for dried samples is missing.

The validation leads to results which are shown in the table 11.

Table 11 Validation data prEN 14672

Analyt	Nb. of participants	content, average, g/kg	s <sub>r</sub> g/kg	s <sub>r</sub> %	S <sub>R</sub> g/kg	S <sub>R</sub> %
P	14	19,4	0,446	2,30	1,28	6,60

The result is certainly ascertained on one sample only, but with a sufficient number of participants and is therefore satisfactory.

### 2.3.6 EN 13650 Soil improvers and growing media – Extraction of aqua regia soluble elements

The standard describes a method for the extraction of elements from soil improvers and growing media with aqua regia. The ratio of matrix to acid varies between 1:30 and 1:10. Even for boiling under reflux the standard does not prescribe a fixed proportion between acid and matrix (1 to 3g and 28 ml aqua regia). A dry material is being used. For the measurement of phosphorus content the standard ISO 11885 (ICP-OES) and the molybdenum blue method according to Hoffmann (Hoffmann, 1966) are referred to. Appropriate interferences and ways for problem solution during measuring are not described.

The validation leads to results which are shown in the tables 12.

Table 12 Validation data EN 13650

#### Bark humus

Analyt	No. Of participants	Content, average, mg/kg	s <sub>r</sub> mg/kg	s <sub>r</sub> %	S <sub>R</sub> mg/kg	S <sub>R</sub> %
P	16	10469,4	414,33	3,96	1117,25	10,67

#### biowaste

Analyt	No. Of participants	Content, average, mg/kg	s <sub>r</sub> mg/kg	s <sub>r</sub> %	S <sub>R</sub> mg/kg	S <sub>R</sub> %
P	15	2603,8	71,02	2,73	92,15	3,54

#### Clay containing peat (fertilized)

Analyt	No. Of participants	Content, average, mg/kg	s <sub>r</sub> mg/kg	s <sub>r</sub> %	S <sub>R</sub> mg/kg	S <sub>R</sub> %
P	15	975,7	45,60	4,67	100,99	10,35

Continuation of table 12 Validation data EN 13650

Coarse peat (fertilized )

Analyt	No. of participants	Content, average, mg/kg	s <sub>r</sub> mg/kg	S <sub>r</sub> %	s <sub>R</sub> mg/kg	S <sub>R</sub> %
P	17	1065,7	35,16	3,30	190,80	17,9

Composted sludge

Analyt	No. of participants	Content, average, mg/kg	s <sub>r</sub> mg/kg	S <sub>r</sub> %	s <sub>R</sub> mg/kg	S <sub>R</sub> %
P	16	9580,5	207,10	2,16	496,17	5,18

Composted wood fibre

Analyt	No. of participants	Content, average, mg/kg	s <sub>r</sub> mg/kg	S <sub>r</sub> %	s <sub>R</sub> mg/kg	S <sub>R</sub> %
P	16	1150,7	40,53	3,52	125,36	10,89

The number of participants is sufficient. In the present table the figures for s<sub>r</sub> % and s<sub>R</sub> % were calculated again using the data from the appendix for this standard were taken with the factor 2,8. The results are satisfactory.

## 2.4 Further standards and standard-like methods

Further methods exist for different questions that were worked out in different bodies of experts. Partly they have got the position of a national standard, partly they were developed in the national work of experts like e.g. the VDLUFA methods. In this context only the actual methods that are interesting for the treated questions shall be discussed.

### 2.4.1 E DIN 19746 soil quality – determination of mineral nitrogen (nitrate and ammonium) in soil profiles (N<sub>min</sub>- laboratory method) Draft

The method describes the extraction of nitrate, ammonium and the fraction of organically bound, easily soluble nitrogen with a 0,0125 mol/l containing calcium chloride solution. The method is part of the fertilisation recommendation in Germany. The soil profile is divided into three layers (0-30 cm, 31-60 cm, 61-90 cm) for the analysis. By comparing analysis of soils to their nitrogen content according to this method and the respective yields fertilisation recommendations for many different agricultural crops were derived from long-standing cultivation tests. The method includes prescriptions for the treatment of samples in course of transport, storing and sample preparation. The method is validated in Germany.

The method differs from the standard ISO 14255 in the slightly higher concentration of the extractant calcium chloride. But the more important and fundamental difference is that standard ISO 14255 starts from the assumption

of air dry material which can, as described in the standard E DIN 19746 as well as under VI.3 and also found in literature (v. Erp, 2002) lead to alterations in the composition and losses of nitrogen fractions. A connection of the two methods is theoretically imaginable. But it surely fails on the fact that both methods used two set up long-lasting experiments which led to the development of fertilisation and governmental recommendations.

#### 2.4.2 DL-method, VDLUFA method book volume I, A 6.2.1.2

The method describes the extraction of phosphorus from soils by the means of a calcium lactate solution geared to a pH of 3,6. It is described in the VDLUFA method book volume I under A 6.2.1.2 and is used in some federal states in Germany for the characterisation of plant availability of phosphorus. It is also suitable for moor soils as well as for horticultural soils and growing media. Because of its low buffer capacity it is not applicable on calcareous soils. That reduces its importance especially in comparison to the CAL-method. It is validated and the results are considered in the fertilisation requirement calculations.

#### 2.4.3 CAL-method, VDLUFA method book volume I, A 6.2.1.1

The method describes the extraction of phosphorus from soils with a solution of calcium acetate, calcium lactate, and acetic acid that is buffered at a pH of 4,1. It is described in the VDLUFA method book volume I under A 6.2.1.1 and is used as the broadest spread method for the characterisation of plant availability of phosphorus in Germany. It is also the method that has been quoted as reference method for the governmental regulations according to the German fertilisation law. It is suitable for moor soils as well as for horticultural soils and growing media. It is validated and the results are considered in the fertilisation requirement calculations. It is higher buffered compared to the DL-method. In the last years it has been completed by a pH correction for the examination of calcareous soils, so that its scope of use has been expanded.

#### 2.4.4 Determination of phosphorus in the citronic acid extraction, VDLUFA method book volume I, A 6.2.1.4

The method describes the extraction of phosphorus from soils with a 1% solution of citronic acid. Generally the method is applicable for all kinds of soils but it is mainly used for the analysis of forestry soils. The solution has got a low buffer capacity and will react on the composition of the analysed matrix even more than the methods DL and CAL and is correspondingly efficient for the phosphorus extraction.

#### 2.4.5 ISO 11466 soil quality- extraction of soluble trace elements with aqua regia (1995)

The method describes the extraction of trace elements from soils with aqua regia. The ratio of soil to aqua regia is ca. 1:10. The method itself does not describe the extraction of phosphorus but it is textually identical with the standards EN 13346 and 13650, part A. The statements given under 2.2.4 and 2.2.6 are transferable.

### 3. EVALUATION OF DRAFTING A HORIZONTAL STANDARD

#### 3.1 Assessment of the existing standards

##### 3.1.1 Nitrogen – Kjeldahl method

Table 13 Existing standards Kjeldahl methods

Norm Nr.	B=soil S=sludge A=waste K=soil Improvers BO=biowaste	Description satisfactory	Validation Satisfactory
ISO 11261	B	yes	yes
EN 13342	S	no	not satisfactory
EN13654-1	BO	yes	yes, not satisfactory

ISO 11261 Soil Quality – Determination of total nitrogen – modified Kjeldahl method

EN 13342 Characterization of sludges - Determination of Kjeldahl nitrogen

EN 13654-1 Soil improvers and growing media – Determination of nitrogen, part 1: modified Kjeldahl method

The three existing standards for the determination of the nitrogen content according to Kjeldahl descend from the fields soil, sludge as well as soil improvers and growing media. The Kjeldahl method on principle does not capture all nitrogen compounds. If no additional step like in the standards ISO 11261 and EN 13654-1 is fitted in the anorganic fractions nitrate and nitrite are not determined. Furthermore the nitrogen that occurs in organic compounds with N-N and N-O linkages (e.g. azo-, nitro- and nitroso compounds, hydrazines, hydrazones, oximes, pyrazolones, isooxazoles, dia- and triazines) is not completely recorded. In many cases the Kjeldahl method being the classical determining method for nitrogen serves as reference method. The three quoted standards are of a very different quality as the description in chapter 2 and the table 13 show.

EN 13342 describes the Kjeldahl determination without reference to nitrite and nitrate fractions (reduction of the nitrate to nitrite and subsequent nitrification of salicyl acid). Normally that is sufficient for sludge. But the standard is technically imprecise in its formulations especially in point 4 (in the digestion solution the nitrogen does not exist in a complex compound any more, but as ammonium).

Furthermore the distillation does not produce an alkaline solution of ammonium sulfate or ammonium borate. A solution like that would make redundant ammonia and a quantitative analysis would not be possible any more).

The declaration of an indicator is missing. At least for a newcomer the further explanations concerning the execution (especially concerning titration) are not sufficient. Selenium should not be used any more due to its toxicity. It can be substituted as catalyst by copper sulfate or titanium dioxide or a mixture of both. The validation is not sufficient in one or two points. In one case there are only four participating institutes. It should be at least eight. The results are not satisfactory for a Kjeldahl determination.

The two remaining standards differ in the point that one uses copper and titanium for the digestion and the other just copper alone. While ISO 11261 allows only distillation for the determination of nitrogen, EN 13654-1 does not fix a determination method for the ammonium in the digestion solution. The received validation data are comparable and satisfactory in both cases so that both standards could be available for a horizontal application. To avoid problems at the determination of ammonium in the digestion solution at the transfer on other materials from the beginning, the proceeding of standard 11261 which only allows distillation is preferred. In a standard draft the distillation should be determined in a reference method. This is nowadays being supported by the available instruments for nitrogen determination according to Kjeldahl. These systems unite the possibility to distillate and titrate in an automated course using the employed digestion glasses in one instrument.

The method allows higher amounts of material to be analysed but requires chemicals that are partly toxic and health threatening. This has to be recognised in a standard draft. Furthermore it requires a lot of personal. The fact that not all nitrogen compounds are captured reduces the quality of the method as well. It should still exist as standard, indeed.

### 3.1.2 Nitrogen - Dumas method

Table 14 Existing standards Dumas method

Standard No.	B=soil S=sludge A=waste K=soil improvers BO=biowaste	Description satisfactory	Validation Satisfactory
ISO 13878	B	yes	yes
EN 13654-2	BO	yes	yes

ISO 13878 Soil quality Determination of total nitrogen content by dry Combustion („elemental analysis“)

EN 13654-2 Soil improvers and growing media - Determination of nitrogen – part 2: Dumas method

The two standards describe the method of combustion of material for the determination of total nitrogen. At these methods the total nitrogen is captured indeed. Both standards are short and partly not sufficient concerning the text (homogeneity of samples, problems with soils rich of humus); the special handlings are described by the prescriptions of the instrument manufacturer. The two standards can be summarised to one standard as well as transferred on other material. A disadvantage is the requirement of very small amounts of test material, which presupposes an intensive preparation of the samples with effective homogenisation. The validation leads to satisfactory results for soils and biowaste. For other material the validation still has to be done.

3.1.3 Extraction methods for nitrogen fractions

Table 15 Existing standards for extraction of nitrogen fractions

Standard No.	B=soil S=sludge A=waste K=soil Improvers BO=biowaste	Description satisfactory	Validation Satisfactory
ISO 14255	B	yes	no
ISO 14256-1	B	yes	no
ISO 14256-2	B	yes	no
prEN 14671 WI 308012	S	no	no
EN 13651	K	no	no
EN 13652	K	no	no

ISO 14255 Soil quality - Determination of nitrate nitrogen, ammonium nitrogen and total soluble nitrogen in air dry soils using calcium chloride as extractant

The method bases on air dry soil samples. This can lead to a fundamental alteration of the proportions between the nitrogen fractions. Concerning the treatment of samples in course of transport and storing (cooling) no information is given. For the analytic of nitrogen fractions at the extraction one should proceed on the assumption of not dried material to avoid possible changes because of microbiological activities. That means an uninterrupted cooling chain from the moment of sample taking where the samples have to be tempered at 4°C. The ratio of matrix to solvent as given in standard 14255 is definitely sufficient for soil (1:10), but in some cases tightly bound ammonium will not be extracted even in soils. The method is proven for questions of fertilisation but leads not to a complete extraction especially of ammonium because of the low

salt concentration. Nitrate should be captured completely. Furthermore the bivalent ion calcium is not suitable as exchanger for ammonium. For these reasons and because of the fact that the method does not contain any validation data it should not be used for a horizontal standardisation.

ISO 14256 – 1 Soil quality – determination of nitrate, nitrite and ammonium in field moist soils using potassium chloride solution as extractant, part 1: manual method

ISO 14256 - 2 Soil quality – Determination of nitrate, nitrite and ammonium in field moist soils using potassium chloride solution as extractant, part 2: automated method

The two methods differ only in the part concerning the final determination. Field moist soil is used as extraction material. The concentration of the neutral salt is much higher compared to standard ISO 14255 so that also tightly bound ions can be extracted or exchanged, while the ratio of matrix to solution is half as large as in standard ISO 14255.

In part 1 a manual determination method is being explained in a detailed way. Part 2 describes an automated measuring method in a detailed way as well. The method of part 2 is state of the art especially since the different fractions are captured at the same time. The continuous flow system should be the basis of determination for a standard that has to be developed. Especially because errors can be reduced by the personal and the analysis is more controlled and reproducible on this way.

For the method is not quality proven by respective validation data these considerable work for the quality prove of the standard has to be done.

PrEN 14671/WI 308012 Characterisation of sludges- Pretreatment for the determination of extractable ammonia using 2 mol/l potassium chloride.

The standard describes an extraction method with relatively high salt concentrations (2mol/l) in the extractant. This method also captures adsorbed ammonium. Since the standard refers to fresh material and describes how the samples shall be treated and stored it seems to be suitable for the development of a new standard. This extraction can also capture nitrate and nitrite.

Though neither the extraction method is quality proven nor a standardised measurement is prescribed. That makes considerable validation work necessary. A standardised, problem adapted measurement method is a condition for satisfactory validation data. At least the quoted measurement methods from the area of water condition have to be implemented and checked at the matrix that shall be examined. One could fall back on the experiences from the standard ISO 14256-2 with the continuous flow system for this extraction method.

## EN 13651 Soil improvers and growing media - Extraction of calcium chloride/DTPA (CAT) soluble nutrients

The method differs from the methods treated in this chapter because it does not use neutral salt but works at a low pH of 2,65 containing also a complex builder. But the latter fact is not relevant for nitrogen. The extraction solution has got a low buffer capacity. That can lead to change of the pH in course of the extraction. The method is well described for the area of the extraction. However it allows different measurement methods for the single nutrients that come from the field of water and that are quoted. A discussion of the possible influence of the measurement by extracted matrix and its treatment is not made. A comment if different measurement methods were evaluated together at the validation is not given.

Even after the correction the validation data comes to a partly unsatisfactory result for nitrate and ammonium in all six materials which were examined. Additionally the span between repeatability and reproducibility is too wide. This indicates either a problem at the control of the methodology by the different laboratories, being the result of the different use of measurement methods or could make the conclusion possible that the single subsamples were homogeneous within themselves (low repeatability) but not among each other. The partly very high percentage reproducibilities ( e.g. 102.6 and 81.6 %) are unsatisfactory.

The method is being used routinely for the determination of trace elements in soil improvers and growing media as well as in agricultural soils in Germany and other countries. According to newest experiences in the purview of VDLUFA in Germany (VDLUFA 2003) the method is at least for questions of fertilisation not suitable for the main nutrient elements (N, P, Mg and K). This is being seconded by the validation data.

## EN 13652 Soil improvers and growing media - Extraction of water soluble nutrients and elements

The method describes the extraction of nutrients from soil improvers and growing media with water. The extraction solution has got a low buffer capacity. That can lead to change of the pH in course of the extraction which means a change of extraction efficiency. The method is well described for the area of the extraction. The table 16 shows a comparison of the results according to the standards EN 13651 and EN 13652.

The results show that water extracts less ammonium and approximately comparable amounts of nitrate. However the watery extract leads to higher percentage reproducibility. As it was already told for the standard EN 13651 the method allows different measurement methods for the single nutrients that come from the area of water and are quoted. A discussion of the possible influence of the measurement by extracted matrix and its treatment is not made. A comment if different measurement methods were evaluated together at the validation is not given.

Table 16 Comparison of the results according to the standards EN 13651 and EN 13652, average mg/l and S<sub>R</sub> %

	Bark humus	Biowaste	Clay containing peat	Coarse peat	Comp. Sludge	Comp. Wood fibre
Ammon. EN 13651	1220,1 20,4%	192,0 41,1%	87,2 13,5%	105,1 15,1%	521,7 32,5%	71,1 32,6%
Ammon. EN 13652	764,7 34,1%	115,4 52,6%	69,7 12,9%	76,7 25,6%	341,0 36,8%	57,9 44,7%
Nitrate EN 13651	13,6 102,6%	33,5 81,6%	72,9 16,3%	53,6 16,7%	243,5 34,5%	65,4 10,8%
Nitrate EN 13652	25,1 181,4%	76,7 141,5%	82,7 33,1%	57,0 16,1%	244,3 40,1%	66,6 100,0%

As it was already told for the standard EN 13651 even after the correction the validation data comes to a partly unsatisfactory result for nitrate and ammonium in all six materials which were examined. Additionally the span between repeatability and reproducibility is too wide. This indicates either a problem at the control of the methodology by the different laboratories, being the result of the different use of measurement methods or could make the conclusion possible that the single subsamples were homogeneous within themselves (low repeatability) but not among each other. The partly very high percentage reproducibility ( e.g. 181.4 and 141.5 %) are unsatisfactory.

#### 3.1.4 Methods for the determination of N-fractions in eluates

Table 17 gives a survey over the existing standards for the determination of N - fractions in eluates.

Table 17 Existing standards for elution of N-fractions

Norm No.	B=soil S=sludge A=waste K=soil Improvers BO=biowaste	Description satisfactory	Validation Satisfactory
EN 13370	A	no	No

EN 13370 Characterisation of waste - analysis of eluates - determination of ammonium, AOX, conductivity, Hg, phenol index, TOC, easily liberatable CN, F

As it was already described in the chapter 2 the standard for the eluate analysis summarises different measurement methods from the water analytic as determination methods. A discussion of possible sources of error because of matrix influences is completely missing. The given information gives not enough guidance for the newcomer. He has to do a lot of own work for the validation of the measurement of the eluates. These validation work has to be done at the

development of the standard already, so that a common quality standard can be assumed if different laboratories are using the standard. For the area of nitrogen fractions a validation of nitrate and nitrite for wastes is completely missing. The results for ammonium are incomplete. In two samples (sewage sludge and artificial eluate) ammonium is measured with two different methods. The results are significantly not comparable according to the posed criteria. Under these circumstances the standard is, at least without considerable further validation work, not suitable for a horizontal standardisation.

### 3.1.5 Determination of total phosphorus contents

Table 18 gives a survey over the existing standards for the determination of total phosphorus.

Table 18 Existing standards for the determination of total phosphorus

Standard No.	B=soil S=sludge A=waste;K=soil improvers BO=biowaste	Description satisfactory	Validation satisfactory
ISO14869-1	B	yes	no
ISO14869-2	B	yes	no
EN 13346	S	no	yes
PrEN 14672 WI 308034	S	no	yes
EN 13650	K	yes	yes

ISO 14869-1 Dissolution for the determination of total element content - part 1: Dissolution with hydrofluoric and perchloric acids

ISO 14869-2 Dissolution for the determination of total element content – part 2: Dissolution by alkaline fusion

The two standards come from the field of soil meaning especially geology. They have to be perceived as an entity and complement one another for especially the standard 14869-1 recommends the use of the standard 14869-2 at the occurrence of problems. They contain a step for the oxidation of the organic components as well as a step for the complete digestion of the mineral components and following solution of the salts. These proceedings are transferable to other areas of application.

A disadvantage is the little amount of test sample and the fact that one has to use dry material. This could lead to problems for some wastes because the production of a homogeneous subsample can cause severe difficulties at least in some cases. Also the required grain size could be not reachable in single cases.

The two methods are suitable for a horizontal standardisation, but a validation for the determination of phosphorus including all matrices being under consideration. In general one should query if a process as described in the standards ISO 14869-1 and –2 for the determination of phosphorus has to be

prescribed. The very drastical methods using perchloric acid and hydrofluoric acid on the one side and lithium borate on the other side are definitely necessary for the digestion of other elements but not implicitly for phosphorus. The possibly additionally captured P-contents compared to the methods according to the standards ISO 131346 and 13650 as well as prEN 14672 are being evaluated as very low and therefore irrelevant. If multi element methods shall be described in the digestion technique as well as in the following measuring technique both methods are suitable including phosphorus.

EN 13346 Determination of trace elements and phosphorus - aqua regia extraction methods

EN 13650 Soil improvers and growing media - Extraction of aqua regia soluble elements

The two preceding standards extract the respective matrix with aqua regia. The standard EN 13346 includes an identical method as the standard 13650 in method A. But it also permits the extraction in a micro system (B) and in microwave systems of different construction type (C,D). The standard discussed in section 2.4.5 (ISO 11466) is taken into consideration too. The description and hints to possible dangers are very detailed and nearly identical in both standards.

The validation data of both standards as well as the comparison of the different extraction systems of the standard 13346 lead to satisfactory results. It has to be clarified if so many different digestion methods like boiling under reflux in macro- and micro scale, digestion by microwave with and without pressure, should be discussed parallelly and equally. The methods A-D lead to a very much differing proportion of matrix to acid quantity (1:10 to 1:30). Consequently the digestion efficiency might differ. That is definitely not too important for phosphorus but plays an important role if the method shall be used as multi element method.

In practice today the aqua regia extraction is already used not only for determination of phosphorus but also especially for the heavy metal and trace element analysis including mercury, selenium, antimony and arsenic determination as the standard digestion method. So the validation work in course of the horizontal standardisation should be done with aqua regia extraction by boiling under reflux for the multi element method including phosphorus. Here a fixed proportion of matrix to acid should be a coercive claim of the draft standard that has to be described while one can decide quite freely about the used sample quantity for the boiling under reflux. Preferring boiling under reflux the amount of test sample is not limited to small amounts in the region of mg. In this case no problem exists with homogeneity. Validation work is necessary.

## prEN 14672/WI 308034 Characterisation of sludge - Determination of total phosphorus

The mentioned method describes a digestion of dried sludge by the means of a mixture of salpetric acid and sulfuric acid. Background is the fact that some phosphates might not be digested at the extraction at the temperature of aqua regia e.g. and the sulfuric acid also might transform hardly soluble phosphates which can occur into soluble orthophosphates. That is why this standard is, similar to the Kjeldahl method for nitrogen, very useful as reference standard. Apart from the points mentioned in the chapter 2 the method is described in a sufficient way. The validation leads to satisfactory results. It should be adapted as standard for horizontal standardisation. Extensive validation work is necessary.

### 3.1.6 Extraction of phosphorus fractions

Table 19 gives a survey over existing standards for the extraction of phosphorus fractions.

Table 19 Existing standards for the extraction of phosphorus fractions

Norm Nr.	B=soil S=sludge A=waste K=soil improvers BO=biowaste	Description satisfactory	Validation Satisfactory
ISO 11263	B	yes	no
EN 13651	K	no	no
EN 13652	K	no	no

ISO 11263 Soil quality - determination of phosphorus - spectrometric determination of phosphorus soluble in sodium carbonate solution

The method describes the extraction of phosphorus from soils at a pH of 8.5. It was developed especially for neutral and calcareous soils and shall reflect the availability of phosphate (VDLUFA, 1991). The extraction solution is not very stable and needs a regular check of the pH. By the means of this extraction solution secondary phosphate precipitation and/or di- and adsorption processes are avoided because the concentration of the suitable cations (Fe, Al, Ca) are very low in the extract. The method is described in a sufficient way, but the validation is missing.

EN 13651 Soil improvers and growing media - Extraction of calcium chloride/DTPA (CAT) soluble nutrients

EN 13652 Soil improvers and growing media - Extraction of water soluble nutrients and elements

The two standards work at pH of 2,65 and 7,0 respectively, together with the standard ISO 11263 they cover a wide range of pH. A disadvantage is that the buffering capacity of the three solvents differs a lot and is sometimes very little. This may lead to a change of the pH during extraction and in consequences of that of not well defined phosphorus fractions. This question had to be taken into consideration intensively at a horizontal standardisation. A pH-stepped extraction for phosphorus would make sense. It would have to be clarified if other, more stable buffer systems lead to better results. The results of the validation of these standards do partly not fulfill the criteria that were set in chapter 2 and an explanation is missing, but the biggest part of the results fulfills them. For the reasons mentioned before and taking the facts under 3.1.3 into consideration there is a considerable demand for research and analysis if the three mentioned standards are being standardized over all mentioned matrices. The better way is to find other, pH stable buffer systems and to validate them.

### 3.2 State of the art and knowledge

For the international standardisation it makes only sense to enter those extraction and determination methods that are commonly available and can be executed without considerable expenditure by additional institutions. The neutron activation analysis e.g. is definitely very helpful in some cases but requires a nuclear reactor.

#### 3.2.1 Nitrogen according to Kjeldahl

There have been no fundamental innovations published for the determination of nitrogen according to Kjeldahl in the last time. The method is subdivided into two parts:

- a. the digestion
  - b. the determination
- a. As described by Kjeldahl the digestion is done with sulfuric acid adding a salt for the boiling point elevation and a catalyst. It has not changed (Hoffmann, 1997). Changes were made for the use of the catalysts. The toxic mercury as well as selenium are today being replaced by copper and/or titanium (Ugrinovits, 1982). Also the instruments changed. In modern instruments the digestion glasses are used for the distillation at the same time. Modern Kjeldahl instruments work half automated. (Munsinger et al. 1982).
  - b. The determination of the ammonium that was built at the digestion is being made classically by distillation as ammonia and a following titration. Further possibilities of ammonium determination are given by flow injection resp. continuous flow analysis or by spectrometric methods.

Distillation and titration should be the reference method in any case because they avoid the matrix problems that may occur in other determination methods.

### 3.2.2 Total nitrogen according to Dumas

Modern element analysers make the determination of total nitrogen according to Dumas. They work completely automated after weighing of test material. A disadvantage is the little amount of test material. Possible homogeneity problems should be solved by the description of respective steps for sample preparation. There is no comparable alternative to element analysers.

### 3.2.3 Extraction methods for ammonium, nitrate and nitrite

For the extraction of ammonium, nitrate and nitrite there are plenty of extraction methods that all serve a special purpose. They were mainly developed for questions of fertilisation. For the questions treated here, mainly the total contents are of interest. For nitrate and nitrite a watery extraction would be sufficient, because both do not form any slightly soluble salts that occur in a considerable concentration. For ammonium the extraction is a bit more difficult because it can partly occur bound. In this case it is necessary to use a salt solution that exchanges the ammonium from its bond. For this procedure potassium chloride is especially suitable. It is therefore useful to describe a method that includes potassium chloride as extractant and that captures nitrate and nitrite simultaneously.

### 3.2.4 Total phosphorus

A lot of different methods exist for the determination of phosphorus in its different kinds of linkage. On the one side there are the two standards for the total digestion by the means of perchloric acid and hydrofluoric acid resp. as alkaline fusion with lithiumborates (ISO 14869-1 und ISO 14869-2). Furthermore there exists the standard prEN 14672 which describes the digestion with sulfuric acid and salpetric acid.

The two methods mentioned first for the total digestion are not suitable for the routine analyst and request very well qualified personal because of the dangerousness of the used chemicals (perchloric acid and hydrofluoric acid). These two methods should be in the background if there are really doubts that the used methods do not capture the phosphorus in its entirety. They could be worked at for the horizontal standardisation at a later time if the demand is realized.

The most common method for the determination of phosphorus that is being used in many laboratories for environmental analysis is the digestion with aqua regia in the different variations (EN 13346 and EN 13650).

The introduction of the Röntgen Fluorescence Analysis (RFA) as standardised method is in discussion. Modern instruments allow a reliable determination of phosphorus. The problem with this technique still is the very high dependency of the measurement on the matrix. It should be discussed if this analytic method that could also be used as in situ analytic is being equipped with a set of reference material that would make the calibration a lot easier.

For the determination of total phosphorus of the discussed materials at this time the aqua regia for the horizontal standardisation is being suggested. Here the aqua regia extraction under reflux in an open system should be the reference method.

### 3.3 Proposals for draft standards for the horizontalisation from the collection of existing standards for the areas soil, sludges and biowaste and related wastes

Table 20 gives a survey over the need and the possibility of horizontal standardisation at this time.

Table 20 Methods for the horizontal standardisation

Kjeldahl N	Kjeldahl	Dry or moist material	Validation necessary
Modified Kjeldahl N	Kjeldahl	dry or moist material	Validation necessary
Total N	Combustion Dumas	dry or moist material	Validation necessary
N-fractions	Extraction with KCl	Moist material	Validation necessary
Total P	H <sub>2</sub> SO <sub>4</sub> / HNO <sub>3</sub>	Dry material	Validation necessary
Total P	Aqua regia	Dry or moist material	Validation necessary

#### 3.3.1 Kjeldahl nitrogen

The method according to Kjeldahl has been modified and adapted in many aspects in course of the years. In practice especially the toxic catalysts mercury and selenium were replaced by copper and titanium. There are also technical developments which collect and automate the several steps of the method (digestion, distillation and titration). One problem remains. By modification nitrite and nitrate can be recorded but nitrogen in special kinds of bonds evades from the digestion in some cases. That is why one always has to speak about Kjeldahl- nitrogen using this method and not about total nitrogen. Since the relation to Kjeldahl- nitrogen consists of many regulations, tables and prescriptions it is necessary to include this method into the horizontal standardisation. Here two variations should be described and exist next to each other:

1. „classical” Kjeldahlmethod, not capturing nitrate and nitrite
2. modified Kjeldahlmethod, including nitrite and nitrate

The two methods could be treated in one standard together, while the additional step for the capturing of nitrite and nitrate is being installed as a module. Here the disadvantage exists that queries might become necessary in cases of doubt to clarify if nitrite and nitrate were recorded as well.

Because of clarity and plainness it is pleaded for the editing of two equal standards.

The necessary works for validation as well as works concerning the questions of homogeneity have to be executed.

Formulating the standards one has to take into consideration that the used quantity of sulfuric acid leads to a different consumption of acid for the different materials. The table 21 shows that only for soil and is definitely transferable.

Table 21 Amounts of sulfuric acid consumption by various materials during Kjeldahl digestion (Bremner 1960)

Material	Acid consumption ml of 36 mol/l H <sub>2</sub> SO <sub>4</sub> /g of material
Soil organic C	10.0
Soil organic matter	5.8
Al <sub>2</sub> O <sub>3</sub>	1.63
Fe <sub>2</sub> O <sub>3</sub>	1.04
Clay	0.60
CaCO <sub>3</sub>	0.55
Silt	0.33
Sand	0
Salicylic acid	6.76
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	0.58
Reduced Fe	1.50

Consequently at the description of the Kjeldahl method one has to observe that the consumption of sulfuric acid is only seen through the material for its oxidation. If the salt concentration is being considerably elevated in course of the process the temperature in the digestion solution could rise over 400°C causing the possible threat of nitrogen losses (Bremner et al. 1982). This has to be checked as well. The used quantity of sulfuric acid seems to be too low in the two passed standards compared to other validated methods (VDLUFA a, 1991). This has to be checked in a further step of the project.

If the reaction with salicyl acid and sodium thiosulfate for the capturing of nitrite and nitrate is being set ahead of the intrinsic Kjeldahl digestion the mentioned points have to be taken into consideration according to the table 21.

Furthermore one has to decide if the method is being described as macro method with digestion glasses with a content of 250, 500 or more ml, in a

semimicro scale or in a micro scale with digestion glasses with a content of 30 to 50 ml. The application of the micro scale is desirable because the consumption of chemicals can be reduced. Anyhow this is dependent on the sample preparation and the obtained homogeneity of the material. In any case the weighed quantity has to be adapted to the expected nitrogen content of the sample and the reached homogeneity. The acid quantity including salt and catalyst have to be attuned to this data.

To avoid an influence on the variance of the result because of the determination of the ammonium content in the digestion solution, the approved distillation/titration as determination method is taken up as reference method.

The necessary work for validation as well as the work concerning the questions of homogeneity have to be executed. Table 22 gives a survey over the work to be done.

Drafts for the determination of Kjeldahl - nitrogen and the determination of Kjeldahl - nitrogen with the module for the capturing of nitrate and nitrite in soils, sludges, biowaste and related wastes can be found in the appendix.

Table 22 Necessary work and sample, Kjeldahl nitrogen

Scientific investigation	Homogeneity	Round robin test Validation	Material aquisition	Materialproperty
X	X	X	X	Dry or moist

### 3.3.2 Total Nitrogen

To capture the total nitrogen the combustion according to Dumas is the method being used today and represents the state of the art. As it was already said in VI.2 the problem with this method is the required homogeneity of the samples since one has to work with very little amounts of test material. In this context the biggest problem will definitely be the wastes with their high variability. Despite these restrictions it should be tried to summarize and prepare the horizontal standardisation for the two existing standards ISO 13878 and EN 13654-2. Here corresponding validation work as well as questions of the sample preparation of the material to reach required homogeneity have to be executed. Table 23 gives a survey over the necessary tasks.

A corresponding draft for the determination of total nitrogen according to the combustion method of Dumas in soils, sludges, biowaste and related wastes can be found in the appendix.

Table 23 Necessary work and sample quality, Dumas method

Scientific Investigation	Homogeneity	Round robin test Validation	Material aquisition	Materialproperty
	X	X	X	Dry , < 2 mm

### 3.3.3 Total Phosphorus

To work at methods for the determination of total phosphorus at present one could validate the digestion with salpetic acid/sulfuric acid (prEN 14672/ WI 308034) for the five materials next to the digestion with aqua regia. Even though the results of validation for the four different variants A-D of the aqua regia extract in the standard EN 13346 lead to an excellent consistency there should be no description of different proceedings for the aqua regia digestion because this could lead to problems in some cases. If the phosphorus determination with an aqua regia extract under reflux is being compared with phosphorus determination in a microwave under pressure (e.g.) one could receive diverging results in single cases. If this proceeding is being followed even so, the validation of the methods has to be done all the thoroughly and the assessment of the results has to follow strictest scales.

In contrary to the nitrogen determination the digestion of soils, sludge, biowaste and related wastes the phosphorus determination and the following measurement should not be realized apart from the determination of other elements. The utilization of the possibility of measuring several elements together (multi element analysis) is state of the art and practice in many laboratories. Phosphorus can be determined with other non-metals and metals e.g. with ICP-OES and ICP-MS. Here special matrix interferences have to be described and be taken into consideration. This situation has to be considered at the digestion. Next to the boiling under reflux digestion in the microwave oven is the best method in many cases for the standardisation of multi element proceedings. For the microwave digestion the digestion in a closed system should be preferred in any case. Since the digestion conditions, the contact to the side of the digestion vessel, ratio of material to acid and pressure conditions play an important role, both methods (boiling under reflux and microwave digestion) should be described separate from each other as it was already explained. The extraction by aqua regia by boiling under reflux is the reference method.

The standard prEN 14672 leaves the determination method open and refers to a photometric determination method and the chromatography of ions. These are no methods that are suitable for the multi element analysis and they are not state of the art for the phosphorus determination according to this extraction. To avoid an influence of the variance of the result because of the determination of the phosphorus content in the extraction solution, the determination with ICP-OES as reference method is being suggested (EN ISO1885). Since sulfuric acid normally causes problems in the nebulizing systems as well as in the course of the further measuring process of the methods mentioned above, the emphasis should be on the extract with aqua regia. Anyways there should be made parallel analysis using the digestion with salpetic acid and sulfuric acid to confirm the statement that both methods lead to similar results. After this comparing test one has to decide if the aqua regia extract alone is sufficient for the total phosphorus determination or if the standard prEN 14672 has to be described parallelly. In this case research work which define the area of application and the demarcation of the two standards in an exact way is necessary.

At the measurement an unannotated adoption of the standards from the field of water quality has to be avoided because this could lead to severe errors at the measurements. Especially here the validation work has to begin. Table 24 gives a survey over the necessary work.

A corresponding draft for the determination of total phosphorus according to the aqua regia extraction in soils, sludges, biowaste and related wastes can be found in the appendix.

Table 24 Necessary work and sample quality , total phosphorus

Scientific Investigation	Homogeneity	Round robin test Validation	Material aquisition	materialpro- perty
X	X	X	X	Dry, < 0.5 mm

### 3.4 Extraction and elution methods for ammonium, nitrite, nitrate and phosphorus

As it was already mentioned at the description and assesment of the methods under IV and VI as well as under VII.3 several standards could be edited for a horizontal standardisation with complementary validation work referring to the state of the description. The elution methods shall not be described here because this is done in the work package “elution” which was created only for this task. Before the formulation of standard drafts it would be absolutely necessary that the experts from the different areas discuss and come to a common result, if the extraction method is suitable for the respective matrix and if the results are interpretanionable.

When these multistage clarifying processes between the body of experts has lead to a result the respective text drafts have to be prepared resp. the neccesary validation work has to be done.

The questions of phosphorus extraction are already mentioned in chapter II and it is refered to them. The three described standards are not suitable to describe a pH-dependent, differentiated phosphorus extraction because of their differing but all in all low buffer capacity.

Only from the area of extraction the standards ISO EN 14256-1 and ISO EN 14256-2 and prEN 14671 for the extraction of ammonium seems to be suitable to be expanded beyond the application to soil or sludge horizontally to other matrices right at this time. Ammonium should be exhaustively extractable by the extractant 2 mol/l KCl, so that one could speak about total ammonium determination in this case. The validation data not only for sludge (today’s field of application) but also for all matrices had to be prepared. Here also the questions should be followed which KCl concentration is actually sufficient for a quantitative extraction. Furthermore it has to be clarified what time a quantitative extraction takes since it concerns not only a pure extraction but also an exchange process that does not have to execute spontaneously. Here it

should also be scrutinized if a repeated extraction might be necessary. Table 25 gives a survey over the necessary work.

Since nitrite and nitrate are not fixed to the matrix normally forming easily soluble salts the standard could be expanded on these two parameters as it was done in the standard ISO 14256.

A corresponding draft for the determination of ammonium, nitrate and nitrite after extraction with KCl (2 mol/l) in soils, sludges, waste, biowaste and related wastes can be found in the appendix.

Table 25 Necessary work and sample quality, extraction of nitrogen fractions

Scientific Investigation	Homogeneity	Round robin test Validation	Material acquisition	Material property
X	X	X	X	Moist

## 4. CRITICAL POINT AND RECOMMENDATIONS

The in chapter 3.3 discussed and in chapter 5 presented proposals of draft standards demand an intensive work on validation to describe the range of application especially in the lower range and the precision.

### 4.1 Requirements on samples for the validation of the proposed standards

The samples for the validation for the determination of Kjeldahl nitrogen, total nitrogen and total phosphorus according to the methods described in the prefix have to be homogeneous. Using these methods normally quantities over 5 g dry matter cannot be weighed, sometimes it is even much less than 5g. Each participant of the round robin tests needs at least 100 g dry matter/method and laboratory for the validation. For the determination of nitrogen fractions fresh material has to be used (cooled at 4°C). For the other determinations (Kjeldahl-nitrogen, total nitrogen, total phosphorus) besides fresh or field moist material also dried material can be used. Normally a material is used that was grinded to a grain size < 2mm. If severe inhomogeneity occurs the material has to be grinded < 0.5 mm or even finer. Here pre-tests with the respective methods or analytes that are suitable for the homogeneity test (e. g. Cu, Mg) are necessary.

Validations are necessary for the Kjeldahl methods, total nitrogen and total phosphorus methods as well as for the determination of nitrogen fractions. Consequently samples are needed in a sufficient quantity for soils, sludge, biowaste and related wastes. Here it is furthermore necessary to make differentiated types for the different matrices available. That means different soils, sludges, biowaste and related wastes. Different scopes of concentration have also to be covered to define a span of content scope for the area of utilization especially in the lower area and to be able to define the boundary of determinability. This would have to be completed in the scope and working area.

The proposal is to make three different types and three different scopes of concentration available for each matrix (see table 26).

Table 26 Necessary sample number and amount for validation and additional investigation

Soil 1	low analyte concentration	100 g dry matter/participant
	Middle analyte concentration	100 g dry matter/participant
	High analyte concentration	100 g dry matter/participant
Soil 2	low analyte concentration	100 g dry matter/participant
	Middle analyte concentration	100 g dry matter/participant
	High analyte concentration	100 g dry matter/participant
Soil 3	low analyte concentration	100 g dry matter/participant
	Middle analyte concentration	100 g dry matter/participant
	High analyte concentration	100 g dry matter/participant

This system is transferable on sludge, biowaste and related wastes. If moist or field fresh material is required the respective amount of dry matter has to be distributed.

#### 4.2 Outlook on new fields for standardisation

The standards proposed in chapter VIII base on the state of the art and existing standards. They describe methods that have already been introduced in the praxis and have proved their suitability. Next to them it should be queried if at such an important step as the standardisation over several matrices a second step should be done: the consideration of newer techniques. That means that next to the necessary works concerning methodology and validation further research expenditure has to be done.

The total element determination would have to be apparatusively executed in a way that they could be done in situ directly following the sample taking. Total phosphorus could be captured with X-Ray Analysis. This technique could be connected directly with the sample taking. Anyhow it contains a difficulty concerning the calibration since it normally reacts very heavily on the matrix.

For the determination of phosphate fractions one could either chose extraction solutions with a high buffer capacity and consequently stable pH in course of the extraction, or one could try a percolation method with pH control.

Furthermore one could enter developments for the determination of the C/N ratio by NIR-spectroscopy. Anyhow this would require an intensive research work on all matrix fields.

#### 4.3 Key points for Discussion

Next some questions will be discussed that arose in the desk study.

1. Which phosphorus fractions are interesting next to the total contents?
2. Which buffer systems have a high buffering capacity and can be used without essential pH change for the extraction for all matrices?
3. Are the different microwave systems comparable concerning their digestion- resp. extraction efficiency?
4. Is the extraction method with 2 mol/l KCl suitable for the whole matrix palette to cover the total contents of nitrite, nitrate and ammonium? Which concentration and time is required for the different materials?
5. Which validation data (scale of repeatability and reproducibility) are sufficient to meet the quality demand of international standards?
6. For which materials has the digestion with sulfuric acid/salpetric acid to be preferred to the aqua regia digestion for the total phosphorus content determination?
7. Which quantity of sulfuric acid is required for the Kjeldahl digestion?
8. Are the extractions with aqua regia under reflux and that in a vessel heated in a micro wave oven comparable?

## 5. DRAFT STANDARD (CEN TEMPLATE)

See Annex to this study

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