Section A4.1/01 **Annex Point IIA IV.4.1**	**Analytical Method for the Characterisation of Burnt lime, Hydrated lime, Burnt dolomitic lime and Hydrated dolomitic lime and impurities therein**

		Official use only
	1 REFERENCE	
Reference	ASTM (American Society for Testing and Materials) Designation C25 – 99: "Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime" 1999. Doc. No. 492-007.	
1.1 Data protection	No	
1.1.1 Data owner	published	
1.1.2 Companies with Letter of Access	n. r.	
1.1.3 Criteria for data protection	n. r.	
	2 GUIDELINES AND QUALITY ASSURANCE	
2.1 Guideline study	The document outlines a guideline (ASTM C25 – 99) and respective round robin tests.	
2.2 GLP	No	
2.3 Deviations	n. r.	

3 MATERIALS AND METHODS

Introductory Remarks

The standard structure for this section point is believed not to be suitable to describe wet chemical analytical methods to determine the contents of lime based products adequately: Some of the data requested are not relevant for the wet chemical analytical methods to determine the contents in lime based products and other information which would be relevant is not asked for by the standard template.
Therefore, and for reasons of readability and comprehensibility, a different document structure was chosen, that fits better to the context.

The document summarised herein can be regarded as a key document for lime characterisation methods.

Typical contents of lime based products

Typical ingredients in Burnt lime, Hydrated lime, Burnt dolomitic lime and Hydrated dolomitic lime are mainly calcium, magnesium and their oxides and hydroxides.
Impurities are inorganic salts and minerals of a great variety. The impurities mainly contain minerals of silicon (silicates), aluminium, iron (pyrite), manganese, carbon (carbonates, traces of organic carbon), sulphur (sulphates, pyrite) and water.

The characterisation of lime products is complicated, as the methods to determine the different ingredients and impurities do often not directly determine the amount of a real existing species, but rather the content expressed in equivalents of the respective oxides of elements of interest. For silicon, aluminium, iron, manganese, carbon and sulphur, the equivalent content referred to their oxides is typically stated for the characterisation of the lime product.
Note that in some product descriptions for Hydrated lime both the calcium hydroxide and the respective calcium oxide equivalent concentration are stated, which consequently describes the same calcium content.

Furthermore, the analytical separation procedure is sometimes stopped at a certain stage, where further separation is considered not to be necessary, as only traces of other compounds are expected to be found. For this reason, some product characterisations are less detailed than others and they summarise all impurities except SiO_2 as “insoluble residues”.

A typical lime characterisation states all or some of the concentration values of the following list:

$Ca(OH)_2$, CaO, MgO, $CaCO_3$, CO_2, SiO_2, Al_2O_3, Fe_2O_3, Mn_3O_4, S, SO_3, insoluble residues, water / moisture, hydrated water, LOI (loss on ignition). The concentrations of these species may exceed 0.1 % w/w and they are therefore addressed in this section point. The Mn_3O_4 concentrations are lower than 0.1 % throughout the different lime product compositions, but as it is common to state this concentration for lime characterisation, it is also addressed in this section point.

The analytical methods described herein cover determinations of the concentration values of the preceding list.

The following overview follows the structure of the cited document and gives short descriptions of the analytical methods proposed. The sections of the cited document where the respective analytical methods are described are also given. The methods that describe the determination of the main contents of lime products are stated first.

Tests to determine the main components in lime based products:

Calcium oxide determination:

Section 16: Gravimetric Method for CaO determination

Calcium is separated from magnesium by means of a double precipitation as the oxalate, after the determination of the ammonium hydroxide group.

The oxalate is ignited to the oxide and re-dissolved with hydrochloric acid. Then, another ammonium hydroxide precipitation step is undertaken. Any precipitate achieved at this stage is assumed to be aluminium hydroxide, which is separated. Calcium is precipitated again as oxalate and weighed as CaO after ignited.

Section 17: Volumetric Method for CaO determination

The calcium oxalate precipitate is dissolved with dilute sulphuric acid and the liberated oxalic acid is subsequently titrated with standard potassium permanganate.

This method is suitable especially for those products that are free of interfering elements. Traces of other alkaline-earth metals and oxalate will also be titrated and calculated as calcium equivalents.

Section 31: EDTA Method for CaO and MgO determination

This method is a rapid complexometric method for determining calcium and magnesium in lime and limestone products. Ordinarily, the EDTA procedure is designed to follow routine separations, that is, single dehydration of silica and a single precipitation with ammonium hydroxide of the combined oxides of iron and aluminium. For expediency, the assay can be run directly without prior separation of the combined oxides of iron and aluminium by using the complexing action of EDTA at appropriate pH levels.
Calcium and magnesium are determined by EDTA titration after separation of silica and the ammonium hydroxide group during a routine analysis of lime and limestone. The assays may also be made after a direct HCl decomposition followed by removal of the silica and insoluble residues. If interfering elements are present in large enough quantities to cause problems, the interferences may be suppressed by the addition of complexing or masking agents such as triethanolamine or cyanide.

Magnesium oxide determination:

Section 31: EDTA Method for CaO and MgO determination; see above

Section 18: Pyrophosphate method:

The magnesium content in lime may vary from a few tenths to 2 % for high calcium limestone to as much as 22 % for Dolomitic limestone.

The pyrophosphate gravimetric method has been used successfully throughout the industry to determine magnesium within this wide range.

In this method, magnesium is doubly precipitated as magnesium ammonium phosphate from the filtrate after removal of calcium. The precipitate is ignited and weighed as magnesium pyrophosphate.

Tests to determine impurities in lime based products:

Section 8/9: Insoluble matter (over all):

Section 8: This test method is based on a double evaporation to dryness of the hydrochloric acid solution of the limestone or lime sample to convert silicon dioxide to the insoluble form. The acid-insoluble residue of a typical limestone consists of free silica and a mixture of minerals such as clay, mica, feldspar, tourmaline, barytes ($BaSO_4$), garnet, zircon, rutile etc. After dissolution in hydrochloric acid, the silica is dehydrated by a double evaporation to dryness. After each dehydration, the dry salts are re-dissolved with dilute hydrochloric acid, the solution is filtered, and the siliceous residue and other insoluble matter separated. The two papers containing the residues are combined, ignited and weighed.

Section 9: In this method the insoluble matter including silicon dioxide is determined gravimetrically as in the method described in Section 8 except that perchloric acid is used to dehydrate the silica. The procedure is more rapid that in the method described in Section 8 because only a single dehydration is necessary.

Section 10: Silicon dioxide:

Volatilisation of the SiO_2 from the insoluble residue with hydrofluoric acid and the percent SiO_2 determined by the difference in mass obtained.

Section 11: Insoluble matter other than Silicon dioxide:

The difference between the mass of insoluble matter (incl. silicon dioxide) and silicon dioxide represents the mass of insoluble matter other than silicon dioxide. The insoluble matter contains the remnants of any clay, siliceous minerals, or other refractory material present in limestone. The elemental components are mainly iron and aluminium which should be removed and added to the main filtrate from the SiO_2 separation. If the insoluble matter including silica is reported as such and no hydrofluoric acid treatment is indicated, then there is no need to make a recovery of the metals and the insoluble residue may be discarded.

Section 12: Combined Oxides (Iron, Aluminium, Phosphorus, Titanium, Manganese):

This is a group of metals that form precipitates with ammonium hydroxide which may then be ignited to their respective oxides.
They have been historically determined as a group.

The group mainly consists of oxides of:	Iron and Aluminium
and	
minor amounts of oxides of:	Titanium Phosphorous Manganese

For separate determinations, the combined oxides are usually weighed first, iron oxide is then assayed separately and aluminium oxide is finally determined by calculating the difference between the percent combined oxides and the percent Fe_2O_3. The other metal oxides are generally assumed to be present in trace amounts and can be disregarded. When necessary these traces may be analysed separately and the aluminium content may be corrected.

Section 13/14: Total Iron:

Iron in limestone is usually present as pyrite (FeS_2) with occasional occurrences of other discrete iron minerals. The amount present varies according to the location and geological history of the deposit. During lime calcination most if not all of the iron minerals present in the limestone will be converted to iron oxide or sulphate.

Section 13: Standard Method:
In this test method the total Fe_2O_3 content of the sample is determined from the ignited combined oxides by fusing the oxides with potassium pyrosulphate and leaching the melt with sulphuric acid. The iron is reduced to the ferrous state (Ion II) with stannous chloride and titrated with a standard solution of potassium dichromate.

Section 14: Total Iron by Ortho-Phenanthroline Photometric Method:
When the iron oxide content is very low, less than 0.1 %, and an accurate analysis at this low level is required, it is preferable to determine iron using procedures that have better sensitivity than the titrimetric methods. For an accurate determination of minute amounts of iron, the ortho phenanthroline method has proved invaluable.
In general, the method consists of reducing the iron to the ferrous state and then adding a slight excess of 1,10-phenanthroline, which forms a complex with ferrous iron, giving an orange-pink colour. The colour intensity is proportional to the iron content of the solution.

Section 15: Aluminium Oxide:

For the purpose of this test method, aluminium oxide is considered to be the difference between the combined oxides and Fe_2O_3. When phosphorous or titanium are determined, their oxides must also be deducted.

Subtract the percent of Fe_2O_3 obtained from the percent of combined oxides. The remainder is reported as Al_2O_3. In special cases where P_2O_5 and TiO_2 need to be reported, a correction for these oxides must be made.

Section 19: Loss on Ignition:

LOI is the loss in weight expressed as the percentage of the initial “as received” sample weight obtained after ignition of the sample at 1000 °C to constant weight. The loss in weight is due to a release of free moisture, chemically combined “lattice” or “hydroxy” water, CO_2, SO_2 and volatile pyrolytic products of any organic material that may be present.

The tared crucible containing the weighed sample is ignited to constant weight. The loss in weight is the LOI of the sample.

Section 21: Free Moisture in Hydrated lime:

The free moisture in Hydrated lime is the water that is released from the sample at a temperature of 115 to 120 °C. This distinguishes it from the hydroxyl water that is chemically bound to the lime and which cannot be liberated except at higher temperatures.

Free moisture in Hydrated lime is determined by aspirating a slow stream of CO_2-free air over the sample in an container placed inside a 115 to 120 °C oven. The loss in weight of the sample is equal to the free moisture of the Hydrated lime.

Section 22: Carbon Dioxide:

Samples of lime and Hydrated lime are analysed for CO_2 to check for the presence of carbonates, most of which are present as uncalcined limestone.

The sample is decomposed with hydrochloric acid and the liberated CO_2 is passed through a series of scrubbers to remove water and sulphides. The CO_2 is absorbed with Ascarite, a special sodium hydroxide adsorbent, and the gain weight of the adsorption tube is determined and calculated as percent CO_2.

Section 23: Sulphur Trioxide:

This test method will determine sulphur compounds mostly present as sulphates in lime and limestone, that are soluble in dilute hydrochloric acid. Iron pyrites and other sulphides will not be included because they will either be volatilised as H_2S or not react at all with the acid.

Sulphate is precipitated from an acid solution of lime or limestone with barium chloride and the SO_3 equivalent is calculated.

Section 24: Total Sulphur by Sodium Carbonate Fusion:

Sulphur in limestone is chiefly, if not wholly, present as sulphide, usually as pyrite. If the total sulphur obtained in the following test method is in excess of that present as soluble sulphate, the difference can be assumed to be present as iron disulphide.

The sample is fused with sodium carbonate and the ignited mass is leached in water and dissolved with hydrochloric acid. The solution is made ammoniacal and the hydroxide precipitate is filtered. The sulphur in the filtrate is precipitated with a 10 % solution of barium chloride. The precipitate is ignited and weighed as barium sulphate and the SO_3 equivalent is calculated.

Section 25: Total Sulphur by the Combustion-Iodate Titration Method:

This test method covers the determination of sulphur in concentrations ranging from 0.005 to 1 %. At the combustion temperature of approximately 1650 °C, complete combustion of the sulphur in the sample will take place regardless of sulphur form or sample matrix.

A major portion of the sulphur in various types of lime and limestone samples is converted to oxides of sulphur, primarily SO_2, by combustion in a stream of oxygen at the elevated temperature of a high-frequency induction furnace. During the combustion, the SO_2 is absorbed in an acidified starch-iodine solution and titrated with potassium iodate. The latter is standardised against limestone standard samples of known sulphur content to compensate for characteristics of a given apparatus and for day-to-day variation in the percentage of sulphur recovered as SO_2. Compensation is also made for the blank due to accelerators and crucibles.

Section 26: Phosphorous by Molybdovanadate Method:

This method is suitable for the determination of small amounts of phosphorous in lime and limestone samples. The procedure is based on the fact that phosphorous in its ortho form will combine with ammonium molybdovanadate to yield a yellow colour that can be measured spectrophotometrically. Total phosphate is determined after a strong oxidation decomposition with perchloric acid.

The sample is decomposed with perchloric acid, the solution filtered, SiO_2 expelled, and the insoluble residue fused with Na_2CO_3. Ammonium molybdovanadate which is then added reacts with the phosphorous in solution to form the heteropoly-phosphomolybdovanadate complex. The absorbance of this solution is measured with a photometer at 430 nm and compared against standards similarly tested.

Section 27: Manganese by the Periodate (Photometric) Method:

In this method, periodate is the oxidising agent used to convert manganous into permanganate ion whose colour can be read in a photometer at a wavelength of 545 nm. This method is capable of determining small amounts of Mn as low as 10 ppm.

The same sample solution prepared in the determinations of phosphorous by molybdovanadate (Section 26) can be used for the determination of manganese by periodate. The acid solution is oxidised to permanganate by potassium periodate. Photometric measurement is made at 545 nm.

Section 29: Free Silica

Free silica is usually present in the acid-insoluble residue of lime and limestone samples. This method is applicable to the determination of free silica when it exceeds 0.05 %.

After dissolution of a large sample of lime or limestone, the insoluble matter including SiO_2 is separated, ashed, and the oxides fused with pyrosulphate. The silicic acid is liberated from the clay minerals and the insoluble matter is dissolved in a hot solution of sodium hydroxide but the free silica is unaffected. Separation-, washing-, drying- and weighing-steps follow.

Section 30: Unhydrated Oxides Calculated on As-Received Basis:

From the analytical determinations made in accordance with the preceding sections, it is possible to calculate combined water, $CaCO_3$, and $CaSO_4$ in samples of lime and Hydrated lime. Unhydrated oxides of MgO in Hydrated lime can also be calculated.

Determine the percentage of free water, LOI, CO_2, SO_3, CaO and MgO in accordance with the preceding sections. Calculate combined H_2O, calcium carbonate, calcium sulphate and unhydrated magnesium oxide.

Section 32: Total Carbon by the Direct Combustion-Thermal Conductivity Cell Method:

This test method covers the determination of carbon in lime and Hydrated lime samples having a carbon concentration in the range from 0.005 to 5 %.

All the carbon in the sample is converted to CO_2 by combustion in a stream of purified oxygen using an induction furnace. Under some conditions, CO is formed and a catalyst furnace is used to convert it to CO_2. The products of combustion are swept into the carbon analyser where the CO_2 is selectively absorbed by a molecular sieve. The CO_2 is later released and swept by a fresh stream of oxygen past a thermal conductivity cell which senses the amount of CO_2 present. The signal from the sensor is amplified and electronically converted to % Carbon which is displayed on a digital readout panel.

Section 33: Calcium Carbonate Equivalent

The calcium carbonate equivalence (CCE) test is used to determine the neutralising capability of a calcareous material and to report this value in terms of percent calcium carbonate equivalents.

Calcareous materials such as crushed limestone, Hydrated lime and pulverised slags (from the production of steel) have been used extensively as soil modifiers or agricultural liming materials. A measure of their neutralising capability can be determined through the use of this test method. Not all neutralising components of acalcareous material may be beneficial; therefore, the chemical analysis is suggested.

Section 34: pH of Alkaline Earth Solutions

This method covers the electrometric pH analysis of solutions made from a variety of lime, hydrate and limestone-bearing materials.

In this test method a sample of material is mixed with CO_2-free deionised water so that the pH of the solution can be determined electrometrically. To ensure that an accurate measurement of pH is obtained for samples with pH greater that 11.5, it is critical that all samples and buffer solutions be at 25.0 °C when measured.

Section 35: Total Carbon and Sulphur by the Combustion/Infrared Detection Method:

This test method is used for the determination of carbon or sulphur, or both, in lime and limestone. This test method has also been adapted for use with kiln flue dusts. This test method covers the determination of carbon and sulphur in an acceptable concentration range from 0.01 to 13 % carbon and from 0.005 to 3 % sulphur.

Hydrated lime, hydroxides and samples with high moisture cannot be suitably analysed for sulphur using an induction furnace unit. Significant portions of SO_2, will be trapped in the dust filter which will be moist due to the water released or produced from the combustion. Carbon results will not be similarly affected.

A sample of lime, limestone, or kiln flue dust is weighed into a ceramic crucible, accelerators are added and the crucible is placed in the furnace. In a pure oxygen environment at the high temperatures generated by the furnace, the sample is fluxed and oxidised converting carbon into CO/CO_2 and sulphur into SO_2. The combustion gases are swept through the carbon- and sulphur-infrared-detection-cells and are measured therein.

4 APPLICANT'S SUMMARY AND CONCLUSION

4.1 Materials and methods

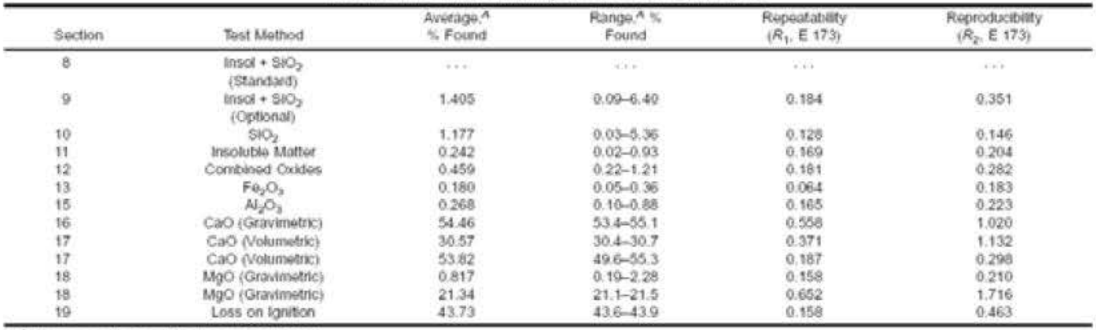
The materials and methods outlined in these standard methods are based on typical well established wet chemical procedures.

4.2 Conclusion

The above outlined methods provide a procedure to completely determine the main components and main impurities in Burnt lime, Hydrated lime, Burnt dolomitic lime and Hydrated dolomitic lime through a quantitative chemical separation process.

The precision and bias of the methods were tested in multiple laboratories. The reproducibility and repeatability of the determination of the main components has proved to be highly reliable and is summarised in the table below.

TABLE 3 Precision Summary of Classical Test Methods



Section	Test Method	Average,[A] % Found	Range,[A] % Found	Repeatability (R_1, E 173)	Reproducibility (R_2, E 173)
8	Insol + SiO_2 (Standard)	. . .	. . .	. . .	. . .
9	Insol + SiO_2 (Optional)	1.405	0.09–6.40	0.184	0.351
10	SiO_2	1.177	0.03–5.36	0.128	0.146
11	Insoluble Matter	0.242	0.02–0.93	0.169	0.204
12	Combined Oxides	0.459	0.22–1.21	0.181	0.282
13	Fe_2O_3	0.180	0.05–0.36	0.064	0.183
15	Al_2O_3	0.268	0.10–0.88	0.165	0.223
16	CaO (Gravimetric)	54.46	53.4–55.1	0.558	1.020
17	CaO (Volumetric)	30.57	30.4–30.7	0.371	1.132
17	CaO (Volumetric)	53.82	49.6–55.3	0.187	0.298
18	MgO (Gravimetric)	0.817	0.19–2.28	0.158	0.210
18	MgO (Gravimetric)	21.34	21.1–21.5	0.652	1.716
19	Loss on Ignition	43.73	43.6–43.9	0.158	0.463

[A] Average and range of the limestones tested.

4.3 Reliability 1

4.4 Deficiencies No

	Evaluation by Competent Authorities
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	29 June 2010
Materials and methods	ASTM C25-99 is a standard which identifies a series of wet methods for determination of the purity of lime products and the levels of impurities therein. These methods are therefore considered suitable for the analysis of hydrated lime (the active & therefore the product) and additional validation is not required. This application covers supply of nearly 150 products from a large number of sources and the composition will depend on the source. No definitive analysis can be given at this stage.
Conclusion	Detailed analysis must be provided at product authorisation.
Reliability	1
Acceptability	The applicant's version is considered acceptable.
Remarks	No analytical data is presented for products being supplied but this must be provided at product authorisation.
	COMMENTS FROM ...
Date	*Give date of comments submitted*
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub)heading numbers and to applicant´s summary and conclusion.* *Discuss if deviating from view of rapporteur member state*
Conclusion	*Discuss if deviating from view of rapporteur member state*
Reliability	*Discuss if deviating from view of rapporteur member state*
Acceptability	*Discuss if deviating from view of rapporteur member state*
Remarks	

Section A4.1/02 **Annex Point IIA IV.4.1**	**Analytical Method for the Characterisation of Burnt lime, Hydrated lime, Burnt dolomitic lime and Hydrated dolomitic lime and impurities therein**

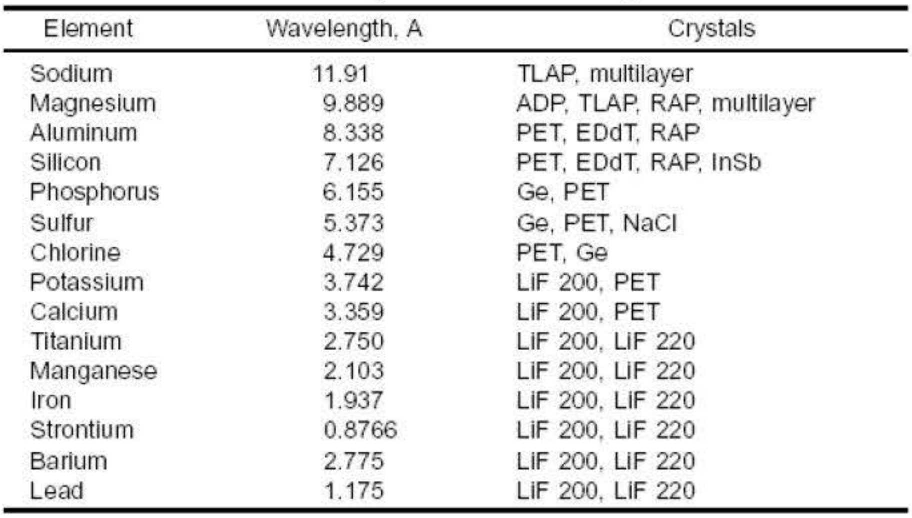
		Official use only
	1 REFERENCE	
1.1 Reference	ASTM (American Society for Testing and Materials) Designation C1271 – 99: “Standard Test Method for X-ray Spectrometric Analysis of Lime and Limestone” 1999. Doc. No. 492-003.	
1.2 Data protection	No	
1.2.1 Data owner	published	
1.2.2 Companies with Letter of Access	n. r.	
1.2.3 Criteria for data protection	n. r.	
	2 GUIDELINES AND QUALITY ASSURANCE	
2.1 Guideline study	Document outlines a guideline (ASTM C1271 – 99) and describes supporting studies	
2.2 GLP	No	
2.3 Deviations	n. r.	
	3 MATERIALS AND METHODS	
3.1 Preliminary treatment		
3.1.1 Enrichment	No enrichment or cleanup in the method involved.	
3.1.2 Cleanup		
3.2 Detection		
3.2.1 Separation method	n. r.	
3.2.2 Detector	Geiger counter, scintillation counter or equivalent. The procedure is suitable for a large number of lime components, as summarised in Table 1 (see below) of the cited document.	

Section A4.1/02

Annex Point IIA IV.4.1

Analytical Method for the Characterisation of Burnt lime, Hydrated lime, Burnt dolomitic lime and Hydrated dolomitic lime and impurities therein

TABLE 1 Analytical Lines and Crystals



Element	Wavelength, A	Crystals
Sodium	11.91	TLAP, multilayer
Magnesium	9.889	ADP, TLAP, RAP, multilayer
Aluminum	8.338	PET, EDdT, RAP
Silicon	7.126	PET, EDdT, RAP, InSb
Phosphorus	6.155	Ge, PET
Sulfur	5.373	Ge, PET, NaCl
Chlorine	4.729	PET, Ge
Potassium	3.742	LiF 200, PET
Calcium	3.359	LiF 200, PET
Titanium	2.750	LiF 200, LiF 220
Manganese	2.103	LiF 200, LiF 220
Iron	1.937	LiF 200, LiF 220
Strontium	0.8766	LiF 200, LiF 220
Barium	2.775	LiF 200, LiF 220
Lead	1.175	LiF 200, LiF 220

3.2.3	Standard(s)	External calibration with certified standard materials available from the NIST (National Institute for Standards and Technology) and other international certification agencies. See ASTM C25 – 99 (also described in the Dossier) for current listing.
3.2.4	Interfering substance(s)	Inter-element effects or matrix effects may exist for some of the elements listed (see 4.1). One way to compensate for these effects is to prepare a series of calibration curves to cover the designated concentration ranges. The composition being analysed must match closely the composition of the reference materials used to prepare the calibration curve. Alternatively mathematical corrections, derived from empirical relationships or fundamental parameter calculations, may be used.
3.3	**Linearity**	
3.3.1	Calibration range	No information given. The range depends on the used calibration standards.
3.3.2	Number of measurements	Five high calcium limestone materials were analysed by eight laboratories, performing replicate measurements on four briquetted powder specimens of high calcium limestone. The procedure is suitable for a large number of lime contents. In this round robin test, lime samples were only analysed for calcium, magnesium, silicon, iron, aluminium and manganese.
3.3.3	Linearity	A sufficient number of reference materials should be selected to cover the concentration ranges of the elements sought. Duplicate intensity measurements of each reference material should be averaged and a calibration curve should be established for each element. The curve should be established by a least squares or multiple regression fit of the X-ray intensity measurements versus the corresponding weight percent concentrations of the element in the reference materials.

3.4	**Specificity: interfering substances**	Inter-element effects or matrix effects may exist for some of the elements listed (see 4.1). One way to compensate for these effects is to prepare a series of calibration curves to cover the designated concentration ranges. The composition being analysed must closely match the composition of the reference materials used to prepare the calibration curve. Mathematical corrections, derived from empirical relationships or fundamental parameter calculations, may be used alternatively.
3.5	**Recovery rates at different levels**	not available
3.5.1	Relative standard deviation	see 3.7.1
3.6	**Limit of determination**	not available
3.7	**Precision**	
3.7.1	Repeatability	

	Average content found per sample in %	
Ca as % CaO	53,347	RSD = 0,28 % (N=32)
	53,683	RSD = 0,30 % (N=32)
	54,304	RSD = 0,23 % (N=32)
	55,599	RSD = 0,20 % (N=32)
	55,837	RSD = 0,26 % (N=32)
Mg as % MgO	0,176	RSD = 8,52 % (N=32)
	0,216	RSD = 2,78 % (N=32)
	0,637	RSD = 1,10 % (N=32)
	0,919	RSD = 1,09 % (N=32)
	1,406	RSD = 3,49 % (N=32)
Si as % SiO_2	0,054	RSD = 22,22 % (N=32)
	0,156	RSD = 5,77 % (N=32)
	0,627	RSD = 1,75 % (N=32)
	0,875	RSD = 2,97 % (N=32)
	1,866	RSD = 3,32 % (N=32)
Fe as % Fe_2O_3	0,0244	RSD = 5,33 % (N=32)
	0,0359	RSD = 5,01 % (N=32)
	0,1357	RSD = 1,69 % (N=32)
	0,1917	RSD = 1,10 % (N=32)
	0,8792	RSD = 1,56 % (N=32)
Al as % Al_2O_3	0,0463	RSD = 3,24 % (N=32)
	0,0736	RSD = 5,43 % (N=32)
	0,1142	RSD = 2,63 % (N=32)
	0,1159	RSD = 3,11 % (N=32)
	0,4404	RSD = 3,70 % (N=32)
Mn as % Mn	0,0024	RSD = 12,50 % (N=32)
	0,0035	RSD = 8,57 % (N=32)
	0,017	RSD = 21,18 % (N=32)

Section A4.1/02 Analytical Method for the Characterisation of Burnt lime, Hydrated lime, Burnt dolomitic lime and Hydrated dolomitic lime and impurities therein

Annex Point IIA IV.4.1

0,0248	RSD = 1,21 % (N=32)
0,09	RSD = 0,44 % (N=32)

3.7.2 Independent laboratory validation

Eight laboratories were involved in the round robin test.

4 APPLICANT'S SUMMARY AND CONCLUSION

4.1 Materials and methods

A briquetted powder specimen or a fused-glass disk specimen is irradiated by a high-energy X-ray beam. The secondary X-rays produced are dispersed by means of crystals and the intensities are measured by suitable detectors at selected wavelengths. Data are collected based on the time required to reach a fixed number of counts, total count for a fixed time or integration of voltage for a fixed time. Concentrations of the elements are determined by relating the measured radiation of unknown specimens to analytical curves prepared from reference materials of known composition.
The method is suitable for Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Sr, Ba and Pb, although not evaluated for minor traces (see 3.3.2 a. 3.7.1).

Remark: Typical contents of lime based products

Typical ingredients in Burnt lime, Hydrated lime, Burnt dolomitic lime and Hydrated dolomitic lime are, mainly calcium, magnesium, oxide and hydroxide.
Impurities are inorganic salts and minerals of a great variety. The typical impurities are minerals of silicon (silicates), aluminium, iron (pyrite), manganese, carbon (carbonates), sulphur (sulphates, pyrite) and water.

The characterisation of lime products is somewhat complicated, as the methods to determine the different ingredients and impurities do often not directly determine the amount of a real existing species, but rather the content expressed in equivalents of the respective oxides of elements of interest. For silicon, aluminium, iron, manganese, carbon and sulphur the equivalent content referred to their oxides is typically stated for the characterisation of the lime product.
Note that in some product descriptions for Hydrated lime both, the calcium hydroxide and the respective calcium oxide equivalent concentration is stated, which consequently describes the same calcium content.

4.2 Conclusion

The X-ray spectrometric method provides a reliable, stable and straight forward procedure to determine the main components and main impurities in high calcium lime compounds. It provides a rapid, multi-element determination with sufficient accuracy to ensure product quality. It can be assumed that this method is applicable to Dolomitic lime compounds as well.

4.2.1 Reliability 1

4.2.2 Deficiencies No

	Evaluation by Competent Authorities
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	29 June 2010
Materials and methods	ASTM C1271-99 is a standard which describes an X-ray spectrometric method for the determination of the purity of lime products and the levels of impurities therein. These methods are therefore considered suitable for the analysis of hydrated lime (the active & therefore the product) and additional validation is not required. This application covers supply of nearly 150 products from a large number of sources and the composition will depend on the source. No definitive analysis can be given at this stage.
Conclusion	Detailed analysis must be provided at product authorisation.
Reliability	1
Acceptability	The applicant's version is considered acceptable.
Remarks	No analytical data is presented for products being supplied but this must be provided at product authorisation.
	COMMENTS FROM ...
Date	*Give date of comments submitted*
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub)heading numbers and to applicant's summary and conclusion.* *Discuss if deviating from view of rapporteur member state*
Conclusion	*Discuss if deviating from view of rapporteur member state*
Reliability	*Discuss if deviating from view of rapporteur member state*
Acceptability	*Discuss if deviating from view of rapporteur member state*
Remarks	

Section A4.1/03

Annex Point IIA IV.4.1

Analytical Method for the Characterisation of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime and impurities therein

Official use only

1 REFERENCE

1.1	**Reference**	ASTM (American Society for Testing and Materials) Designation C 1301 – 95 (Reapproved 2001): "Standard Test Method for Major and Trace Elements in Limestone and Lime by Inductively Coupled Plasma-Atomic Spectroscopy (ICP) and Atomic Absorption (AA)" 1995, 2001. Doc. No. 492-010.
1.2	**Data protection**	No
1.2.1	Data owner	published
1.2.2	Companies with Letter of Access	n. r.
1.2.3	Criteria for data protection	n. r.

2 GUIDELINES AND QUALITY ASSURANCE

2.1	**Guideline study**	Document outlines a guideline (ASTM C1301 – 95).
2.2	**GLP**	No
2.3	**Deviations**	n. r.

3 MATERIALS AND METHODS

3.1	**Preliminary treatment**	
3.1.1	Enrichment	Samples are dried at 105 °C for 2 hours.
3.1.2	Cleanup	No further cleanup required.
3.2	**Detection**	
3.2.1	Separation method	n. r.
3.2.2	Detector	**ICP:** Either a scanning sequential or multi-element simultaneous type ICP, with resolution appropriate for the elements to be analysed. **AA:** Photomultiplier detector, adjustable slits, a wavelength range from 190 to 800 nm and provisions for interfacing with either a strip chart recorder or a computer. The procedure is suitable for a large number of lime components, as summarised in Table 1 (see below) of the cited document.

Section A4.1/03

Annex Point IIA IV.4.1

Analytical Method for the Characterisation of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime and impurities therein

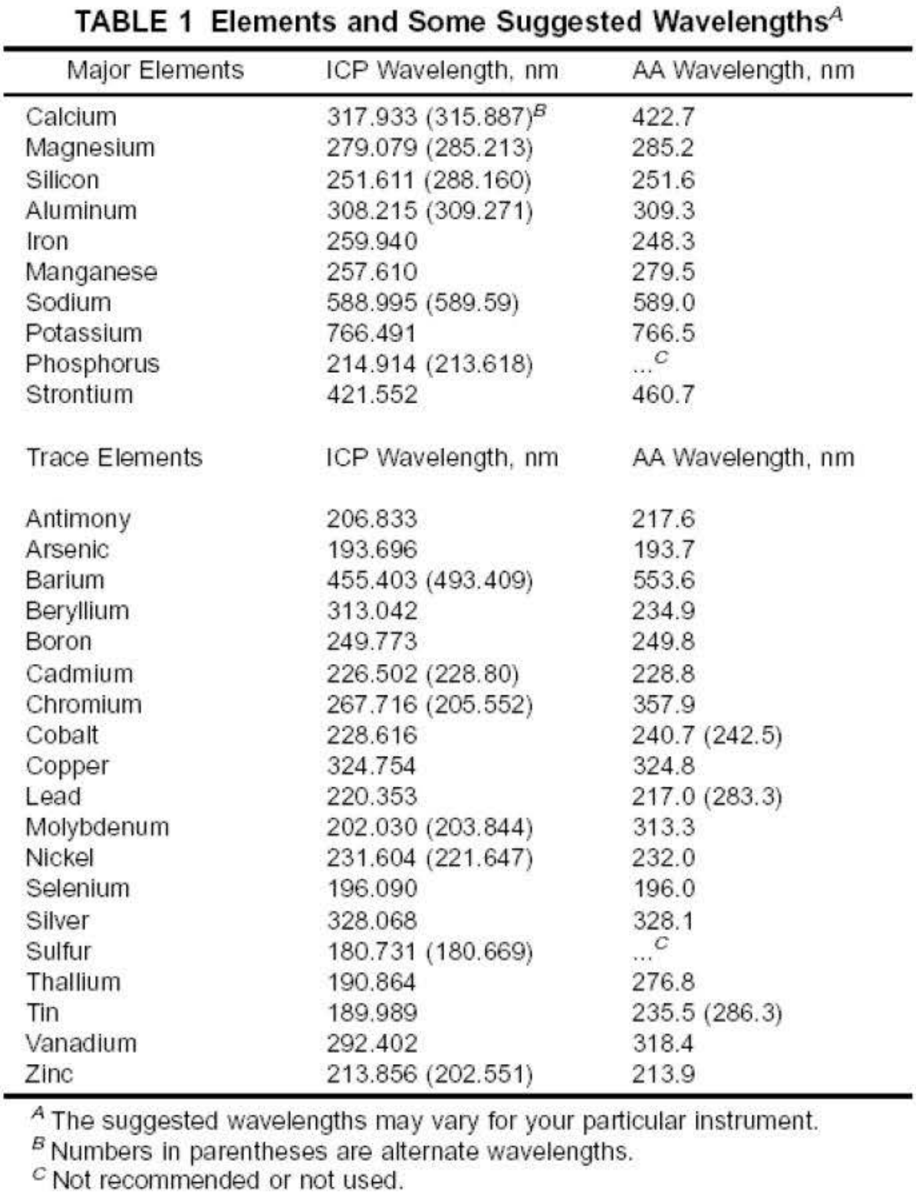


TABLE 1 Elements and Some Suggested Wavelengths[A]

Major Elements	ICP Wavelength, nm	AA Wavelength, nm
Calcium	317.933 (315.887)[B]	422.7
Magnesium	279.079 (285.213)	285.2
Silicon	251.611 (288.160)	251.6
Aluminum	308.215 (309.271)	309.3
Iron	259.940	248.3
Manganese	257.610	279.5
Sodium	588.995 (589.59)	589.0
Potassium	766.491	766.5
Phosphorus	214.914 (213.618)	...[C]
Strontium	421.552	460.7
Trace Elements	ICP Wavelength, nm	AA Wavelength, nm
Antimony	206.833	217.6
Arsenic	193.696	193.7
Barium	455.403 (493.409)	553.6
Beryllium	313.042	234.9
Boron	249.773	249.8
Cadmium	226.502 (228.80)	228.8
Chromium	267.716 (205.552)	357.9
Cobalt	228.616	240.7 (242.5)
Copper	324.754	324.8
Lead	220.353	217.0 (283.3)
Molybdenum	202.030 (203.844)	313.3
Nickel	231.604 (221.647)	232.0
Selenium	196.090	196.0
Silver	328.068	328.1
Sulfur	180.731 (180.669)	...[C]
Thallium	190.864	276.8
Tin	189.989	235.5 (286.3)
Vanadium	292.402	318.4
Zinc	213.856 (202.551)	213.9

[A] The suggested wavelengths may vary for your particular instrument.
[B] Numbers in parentheses are alternate wavelengths.
[C] Not recommended or not used.

3.2.3 Standard(s)

Standard stock solutions may be purchased or prepared from high purity metals or metal salts. Salts should be dried at 105 °C for 1 hour unless otherwise specified.

ICP calibration is most often performed using multi-element calibration standards prepared from single element stock solutions. A calibration blank is prepared at the same acid strength as that of the samples to be analysed.

A reagent blank contains all the reagents in the same concentrations as the samples to be analysed.

3.2.4 Interfering substance(s)

Prior to preparing the mixed standards, each stock solution should be analysed separately to determine possible spectral interference or the presence of impurities. Standards are combined in such a way that they are chemically compatible (no precipitation occurs) and do not cause

Section A4.1/03

Annex Point IIA IV.4.1

Analytical Method for the Characterisation of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime and impurities therein

spectral interferences.

Chemical interferences: They are most common in AA and arise from the formation of molecular compounds that cause absorbances at the wavelength of interest. This molecular band spectral overlap can be minimised by buffering the sample with matrix modifiers (a Lanthanum additive, for example), using standard addition techniques, matrix matching or by careful selection of operating conditions (for example, using a hotter nitrous oxide/acetylene flame or selecting an alternate wavelength).

Physical interferences: They are the result of inconsistencies in the introduction of the sample into the instrument, namely the transport and atomisation/nebulisation of the sample. These inconsistencies are found primarily in samples of high dissolved solid or high-acid concentrations. Physical interferences can be reduced by diluting the sample and by the use of a peristaltic pump.

Spectral interference: Spectral interference is most common in ICP and consists of overlapping and unresolved peaks. Computer software, along with the analysis of the suspected interfering element, can compensate for this effect. Using an alternate wavelength is also a solution. Another spectral interference is caused by background, both stray light and continuous spectrum (continuous argon spectrum, for example). Background correction adjacent to the analyte line will correct background spectral interference.

3.3	**Linearity**	
3.3.1	Calibration range	No information given. Range depending on the used calibration standards.
3.3.2	Number of measurements	At least 10 % of the samples analysed should be duplicates.
3.3.3	Linearity	Calibrate the instrument by aspirating the blank and standards. Most new systems are controlled by computer. The computer will establish the slope, intercept and correlation coefficients for each element.
3.4	**Specifity: interfering substances**	see 3.2.5
3.5	**Recovery rates at different levels**	not available
3.5.1	Relative standard deviation	not available
3.6	**Limit of determination**	not available
3.7	**Precision**	
3.7.1	Repeatability	not available
3.7.2	Independent laboratory validation	not available

Section A4.1/03

Annex Point IIA IV.4.1

Analytical Method for the Characterisation of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime and impurities therein

4 APPLICANT'S SUMMARY AND CONCLUSION

4.1 Materials and methods

A sample, digested by either fusion or acid, is atomised and passed into an excitation medium (a plasma in the case of ICP; a flame in the case of AA). The resulting ions are analysed by atomic spectroscopy. Elemental concentrations are determined by graphically relating the emission/absorption at specific wavelengths for an unknown sample to analytical curves made from reference standards of known composition.

Remark: Typical contents of lime based products

Typical ingredients in Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime are, obviously, mainly calcium, magnesium, oxide and hydroxide.
Impurities are inorganic salts and minerals of a great variety. The impurities mainly contain minerals of silicon (silicates), aluminium, iron (pyrite), manganese, carbon (carbonates), sulphur (sulphates, pyrite) and water.

The characterisation of lime products is somewhat complicated, as the methods to determine the different ingredients and impurities do often not directly determine the amount of a real existing species, but rather the content expressed in equivalents of the respective oxides of elements of interest. For silicon, aluminium, iron, manganese, carbon and sulfur the equivalent content referred to their oxides is typically stated for the characterisation of the lime product.
Note that in some product descriptions for Hydrated lime both, the calcium hydroxide and the respective calcium oxide equivalent concentration is stated, which consequently describes the same calcium content.

4.2 Conclusion

The ICP and AA spectrometric methods described in the ASTM C 1301 – 95 document provide a tool to analyse major and trace elements in lime compounds. Even minor traces like heavy metals can be determined. The procedure was accepted as an ASTM standard and involves established analytical methods.

4.2.1 Reliability	1
4.2.2 Deficiencies	No

	Evaluation by Competent Authorities
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	29 June 2010
Materials and methods	ASTM C1301-95 is a standard which describes Inductively Coupled Plasma-Atomic Spectroscopy and Atomic Absorption spectrometric methods for the determination of the purity of lime products and the levels of impurities therein. This application covers supply of nearly 150 products from a large number of sources and the composition will depend on the source. No definitive analysis can be given at this stage.
Conclusion	Detailed analysis must be provided at product authorisation.
Reliability	1
Acceptability	The applicant's version is considered acceptable.
Remarks	No analytical data is presented for products being supplied but this must be provided at product authorisation.
	COMMENTS FROM ...
Date	*Give date of comments submitted*
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub)heading numbers and to applicant's summary and conclusion.* *Discuss if deviating from view of rapporteur member state*
Conclusion	*Discuss if deviating from view of rapporteur member state*
Reliability	*Discuss if deviating from view of rapporteur member state*
Acceptability	*Discuss if deviating from view of rapporteur member state*
Remarks	

Section A4.1/04 – Analytical Method for the Characterisation of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime and impurities therein

Annex Point IIA IV.4.1

The method described herein is to determine the neutralising value of lime variants by a volumetric method.

Official use only

1 REFERENCE

1.1	**Reference**	EN 12945: "European Standard: Liming materials – Determination of neutralizing value – Titrimetric methods". Doc. No. 492-015.
1.2	**Data protection**	No
1.2.1	Data owner	published
1.2.2	Companies with Letter of Access	n. r.
1.2.3	Criteria for data protection	n. r.

2 GUIDELINES AND QUALITY ASSURANCE

2.1	**Guideline study**	Document outlines a guideline (EN 12945) and describes a supporting interlaboratory trial.
2.2	**GLP**	No
2.3	**Deviations**	n. r.

3 MATERIALS AND METHODS

3.1	**Preliminary treatment**	
3.1.1	Enrichment	No enrichment in the method involved.
3.1.2	Cleanup	The test sample should be dried to constant mass at 105 ± 2 °C. The sample is grind so that it passes the 250 µm test sieve. The thoroughly mixed sample is stored in the desiccator.
3.2	**Detection**	
3.2.1	Separation method	No separation needed.
3.2.2	Detector	The endpoint of the titration is determined by the electrochemical measurement of the pH by a suitable pH glass electrode (sensitivity at least 0.05 pH units) and a calomel or other electrode or a combined electrode. Calibration undertaken with two buffers at pH 4 and 7.
3.2.3	Standard(s)	A standard sodium hydroxide solution (0.25 mol/L) is verified by titration against 2 g potassium hydrogen phthalate ($KHC_8H_4O_4$) which is weighed at a precision of 0.001 g. For the calculation of the results an appropriate correction factor must be used. As indicator phenolphthalein should be used. A standard hydrochloric acid (0.5 mol/L) is verified by titration against sodium hydroxide. For the calculation of the results an appropriate correction factor must be used. As indicator phenolphthalein should be used. The pH-meter is calibrated as described in 3.2.2.
3.2.4	Interfering substance(s)	Limes from iron works may contain Fe(II) which must be oxidised by hydrogen peroxide to Fe(III).

Section A4.1/04 Analytical Method for the Characterisation of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime and impurities therein

Annex Point IIA IV.4.1

3.3 Linearity
Titrimetric method. No calibration against different analyte concentrations needed. Therefore no calibration curve needs to be provided.

3.3.1 Calibration range
Not relevant. See 3.3.

3.3.2 Number of measurements
Not relevant. See 3.3.

3.3.3 Linearity
Not relevant. See 3.3.

3.4 Specifity: interfering substances
Limes from iron works may contain Fe(II) which must be oxidised by hydrogen peroxide to Fe(III).

3.5 Recovery rates at different levels
Not investigated.

3.5.1 Relative standard deviation
see 3.7.1

3.6 Limit of determination
The precision of the method was established by an interlaboratory trial in eight laboratories in five countries, with different lime variants with a mean fraction of CaO of 53%. See 3.7.1 for details.

3.7 Precision

3.7.1 Repeatability

Repeatability: The absolute difference between two independent single test results obtained using the same method on identical test material in the same laboratory by the same operator using the same equipment within the shortest feasible time interval will exceed the repeatability limit (r) on average not more than once in 20 cases in the normal and correct operation of the method.
The value is: r = 2.30 % (relative) at a mean mass fraction 53 % CaO.

Reproducibility: The absolute difference between two independent single test results, obtained using the same method on identical test material in different laboratories with different operators using different equipment will exceed the reproducibility limit (R) on an average not more than once in 20 cases in the normal and correct operation of the method.
The value is: R = 12.64 % (relative) at a mean mass fraction of 53 % CaO.

Lime type	Mass fraction CaO %	Repeatability limit r % relative	Reproducibility limit R % relative
Magnesian limestone, coarse	51.4	3.22	12.69
Dolomite, fine	58.9	1.58	5.51
Dolomite, coarse	55.6	2.25	11.46
Chalk, coarse	48.6	2.80	22.3
Blast furnace slag	50.8	1.62	11.17

3.7.2 Independent laboratory validation
Eight laboratories in five countries were involved in the round robin test. See 3.7.1 for details.

Section A4.1/04

Annex Point IIA IV.4.1

Analytical Method for the Characterisation of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime and impurities therein

4 APPLICANT'S SUMMARY AND CONCLUSION

4.1 Materials and methods

Two methods are described.
Principle for both methods: The sample is dissolved in a known amount of standard hydrochloric acid. The excess acid is back-titrated with a standard sodium hydroxide solution.
The methods described can also be used to determine the alkalinity of lime variants that are not dedicated to be used as soil-conditioners, but may be used as biocides.

Method A:
Suitable for calcium-/magnesium-soil-conditioner, except limes from ironworks slags and calcium-/magnesium-soil-conditioner with a content of more than 3 % (w/w) P_2O_5.
Approximately 0.5 g Burnt lime or Hydrated lime or 1 g ground limestone or ground clay are weighed at a precision 0.001 g in an erlenmeyer flask. 50 mL standard hydrochloric acid are added under continuous stirring and the mixture is gently boiled for 10 min. After cooling to room temperature the solution is transferred quantitatively to a 250 mL beaker and the pH-electrodes are immersed and a stirrer is added. Under gentle stirring standard sodium hydroxide is titrated until the pH remains constant at 7 for at least 1 min. The consumption of sodium hydroxide solution is registered.

The neutralising value of the dried product, N_d, is given by:

$$N_d = 0.014(V_1 - 0.5V_2) \cdot 100 / m_t$$

with:
V_1: volume of hydrochloric acid standard solution in mL
V_2: volume of sodium hydroxide standard solution in mL
m_t: mass of the test portion in grams

The neutralising value of the as received product, N_{ar}, is given by:

$$N_{ar} = N_d \, m_d / m_w$$

with:
N_d: neutralising value of the dried sample
m_d: mass of the sample after drying in grams
m_w: mass of the sample before drying in grams

Method B:
Suitable for calcium-/magnesium-soil-conditioner, except calcium-/magnesium-soil-conditioner with a content of more than 3 % (w/w) P_2O_5.
Approximately 0.5 g of the analyte are weighed at a precision 0.001 g in an erlenmeyer flask. 35 mL standard hydrochloric acid are added under continuous stirring and the mixture heated and afterwards gently boiled for 10 min. The solution is diluted with water to a final volume of 100 mL and 5 mL hydrogen peroxide (30% w/v diluted to 6% w/v) solution is added. The solution is transferred quantitatively to a 200 mL graduated flask which is filled with water to the 200 mL mark. The solution is then passed through a dry filter into a dry container, discarding the initial portion. An aliquot of 100 mL of the solution is transferred to a 250 mL beaker and the pH-electrodes are immersed and a stirrer is added. Under gentle stirring standard sodium hydroxide is titrated until the pH remains constant at 4.8 for at least 1 min. The

Section A4.1/04

Annex Point IIA IV.4.1

Analytical Method for the Characterisation of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime and impurities therein

consumption of sodium hydroxide solution is registered.

The neutralising value of the dried product, N_d, is given by:

$$N_d = 0.014(0.5V_1 - 0.5V_2) \cdot 100 / m_t$$

with: V_1: volume of hydrochloric acid standard solution in mL
V_2: volume of sodium hydroxide standard solution in mL
m_t: mass of the test portion in the aliquot portion taken in grams

The neutralising value of the as received product, N_{ar}, is given by:

$$N_{ar} = N_d\, m_d / m_w$$

with: N_d: neutralising value of the dried sample
m_d: mass of the sample after drying in grams
m_w: mass of the sample before drying in grams

4.2 Conclusion

The method is based on a backtitration method, as $Ca(OH)_2$ is known to be slightly soluble in water and therefore a direct titration would be hard to conduct. $Ca(OH)_2$ is dissolved in hydrochloric acid and the excess protons that are not consumed by hydroxide are determined by titration with sodium hydroxide. The method described above allows to determine the neutralising value of lime variants with standard well established wet chemical laboratory techniques.

4.2.1 Reliability 1

4.2.2 Deficiencies No

	Evaluation by Competent Authorities
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	29 June 2010
Materials and methods	EN 12945 is a standard which describes titrimetric methods for the determination of neutralizing value. This application covers supply of nearly 150 products from a large number of sources and the composition will depend on the source. No definitive analysis can be given at this stage.
Conclusion	Detailed analysis must be provided at product authorisation.
Reliability	1
Acceptability	The applicant's version is considered acceptable.
Remarks	No analytical data is presented for products being supplied but this must be provided at product authorisation.
	COMMENTS FROM ...
Date	*Give date of comments submitted*
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub)heading numbers and to applicant's summary and conclusion.* *Discuss if deviating from view of rapporteur member state*
Conclusion	*Discuss if deviating from view of rapporteur member state*
Reliability	*Discuss if deviating from view of rapporteur member state*
Acceptability	*Discuss if deviating from view of rapporteur member state*
Remarks	

Section A4.1/05-08 — Analytical Method for the Characterisation of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime and impurities therein

Annex Point IIA IV.4.1

Official use only

1 REFERENCES

References

- DIN EN 12946: "Bestimmung des Calcium- und Magnesiumgehaltes; Komplexometrisches Verfahren" (English translation: "Determination of the calcium content and magnesium content; Complexometric method"), supplemented with the Corrigendum to DIN EN 12946. Doc. No. 492-008; A4.1/05.
- DIN EN 12947: "Bestimmung des Magnesiumgehaltes; Atomabsorptionsspektroemtrisches Verfahren" (English translation: "Determination magnesium content - Atomic absorption spectrometric method"). Doc. No. 492-009; A4.1/06
- DIN EN 12048: "Bestimmung des Feuchtegehaltes; Gravimetrisches Verfahren durch Trocknung bei (105 ± 2)°C" (English translation: "Determination of moisture content using the gravimetric method by drying at (105 ± 2)°C"). Doc. No. 492-006; A4.1/07
- DIN EN 14397 – 2: "Bestimmung von Kohlenstoffdioxid" (English translation: "Determination of carbon dioxide"). Doc. No. 492-012; A4.1/08.

1.1 Data protection	No
1.1.1 Data owner	published
1.1.2 Companies with Letter of Access	n. r.
1.1.3 Criteria for data protection	n. r.

2 GUIDELINES AND QUALITY ASSURANCE

2.1 Guideline study	Documents describe German and European standards
2.2 GLP	No
2.3 Deviations	n. r.

3 MATERIALS AND METHODS

see DOC IV for details

Section A4.1/05-08

Annex Point IIA IV.4.1

Analytical Method for the Characterisation of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime and impurities therein

4 APPLICANT'S SUMMARY AND CONCLUSION

4.1 Materials and methods

The principles of the methods described in the documents cited herein are similar to those summarised in Section A4.1/01 to A4.1/04.

4.2 Conclusion

As all necessary parameters to characterise lime products can be determined by the methods described in Section A4.1/01 to A4.1/04. The methods outlined in the documents cited herein are not described in detail in this section point. They are cited here as a justification for the methods described in detail in section points Section A4.1/01 to A4.1/04 and for the sake of completeness.

Remarks:

- In DIN EN 12947 (Mg AA) a repeatability of $r = 0.21\%$ and reproducibility of 0.25% is given. This justifies the AA methods described in Section A4.1/03 for which no such data was presented.
- The CO_2 determination described in DIN EN 14397 – 2 is based on a volumetric method, rather than on an adsorbance/gravimetric method.

4.3 Reliability

1

4.4 Deficiencies

No

	Evaluation by Competent Authorities
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	29 June 2010
Materials and methods	Four further standards are referenced as a justification for the methods described in detail in section points Section A4.1/01 to A4.1/04 and for the sake of completeness. DIN EN 12946: Determination of the calcium content and magnesium content by complexometric method. DIN EN 12947:Determination magnesium content by atomic absorption spectrometry. DIN EN 12048: Determination of moisture content by gravimetric method (drying at 105 ± 2°C). DIN EN 14397 – 2 Determination of carbon dioxide This application covers supply of nearly 150 products from a large number of sources and the composition will depend on the source. No definitive analysis can be given at this stage.
Conclusion	Detailed analysis must be provided at product authorisation.
Reliability	1
Acceptability	The applicant's version is considered acceptable.
Remarks	No analytical data is presented for products being supplied but this must be provided at product authorisation.
	COMMENTS FROM ...
Date	*Give date of comments submitted*
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub)heading numbers and to applicant´s summary and conclusion.* *Discuss if deviating from view of rapporteur member state*
Conclusion	*Discuss if deviating from view of rapporteur member state*
Reliability	*Discuss if deviating from view of rapporteur member state*
Acceptability	*Discuss if deviating from view of rapporteur member state*
Remarks	

Section A4.1/09 — Analytical Method for the Characterisation of Burnt lime and Burnt dolomitic lime: Reactivity

Annex Point IIA IV.4.1

Official use only

1 REFERENCE

Reference		EN (European Norm) 459-2:2001 "Building lime – Part 2: Test methods" Chapter 5.10. Doc. No. 272-008
1.1	**Data protection**	No
1.1.1	Data owner	published
1.1.2	Companies with Letter of Access	n. r.
1.1.3	Criteria for data protection	n. r.

2 GUIDELINES AND QUALITY ASSURANCE

2.1	**Guideline study**	The document outlines a norm.
2.2	**GLP**	No
2.3	**Deviations**	n. r.

3 MATERIALS AND METHODS

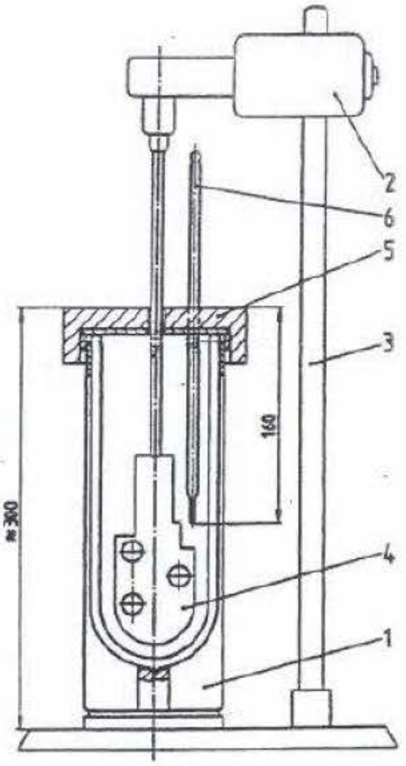
Introductory Remarks

The reactivity of Burnt lime and Burnt dolomitic lime with water is the most important characterisation parameter for Burnt lime variants used for biocidal purposes. Therefore, the determination of the reactivity is described here in Section 4.

A method to determine the reactivity of Burnt lime is given in the building lime norm 459-2:2001 and is summarised in the following.

1) **General:**
The reactivity on slaking is tested by measuring the increase in temperature which occurs on reaction with water as a function of the reaction time (wet slaking curve).
2) **Apparatus:**
The apparatus shall consist of the six parts shown in Figure 1. The weighing and feeding device shall be made of stainless steel (Figure 2). The test apparatus shall have a water equivalent of 200 J/K to 300 J/K.

Section A4.1/09 Annex Point IIA IV.4.1 Analytical Method for the Characterisation of Burnt lime and Burnt dolomitic lime: Reactivity



Key

1	Dewar vessel, 1 000 ml, internal diameter about 77 mm, internal height about 235 mm.
2	Stirrer motor, (300 ± 10) min^{-1} under load.
3	Stand and support
4	Blade stirrer made of suitable plastics[7]), diameter about 60 mm and thickness about 4 mm (see Figure 13).
5	Plastics lid with segment which can be opened, feed opening and bore for the thermometer, to fit the Dewar vessel (see Figure 14).
6	Calibrated thermometer 0 °C to 100 °C with an accuracy of 0,5 °C and a high rate of response (adjustment time from 20 °C to 60 °C less than 10 s). The penetration depth shall be about 160 mm from a suitable hole on the top edge of the lid. A recorder for the temperature measurement is recommended.

Figure 1: Apparatus for testing reactivity

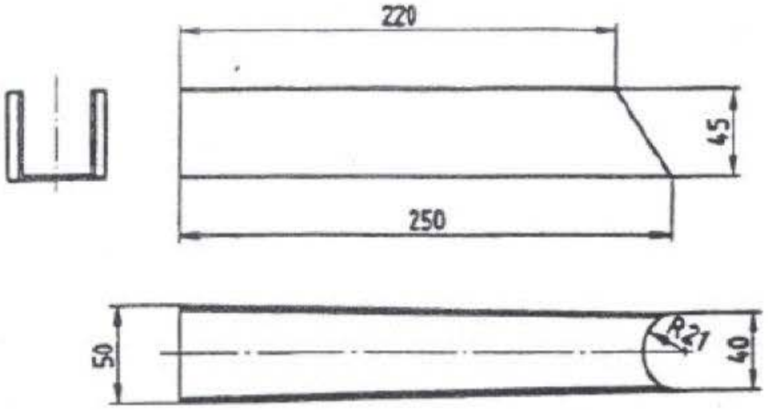


Figure 2: Weighing and feeding vessel

Section A4.1/09 — Analytical Method for the Characterisation of Burnt lime and Burnt dolomitic lime: Reactivity

Annex Point IIA IV.4.1

3) **Sample preparation:**
A sample of about 0.5 kg should be tested. To ensure that the moisture content in the sample is not altered, store it in a tightly closed container. Absorption of even small amounts of moisture influences the pattern of the wet slaking curve. Weigh out a quantity of 150 ± 0.5 g for the individual test.

4) **Procedure:**
Fill the Dewar vessel with 600 ± 1 g of distilled water at about 20 °C (T_0), insert the thermometer and blade stirrer and monitor the temperature as the blade stirrer runs at 300 ± 10 min^{-1}; the temperature shall deviate from 20 °C by not more than ± 0.5 °C. The lime sample shall also have a temperature of about 20 °C.
While the stirrer is running, introduce the weighed quantity of sample all at once into the water by means of the feeding vessel (Figure 2). This moment shall be considered to be the start of the test.
Measure the slaking temperatures after half a minute, after 1 min. and then at intervals of 1 min. up to a time of 10 min., and thereafter only at intervals of 2 min.
With very reactive limes, measure the temperature at shorter intervals, since the reaction may be completed after a few minutes.
Ensure that the contents of the vessel are thoroughly mixed completely throughout the entire duration of the test. For limes which thicken severely, it may be necessary to increase the speed of the motor after a reaction temperature of about 60 °C has been reached.

5) Evaluation:
Reference procedure: Plot the measured temperature values (°C) as a function of time (minutes) to generate the wet slaking curve as shown in Figure 3. The slaking reaction of the lime is assumed to be 100 % complete at the time when the maximum temperature (T_{max}) has been reached. By way of example, this point is shown in Figure 3. The reactivity of the lime shall be reported as the time (t_u) required for the reaction to be 80 % complete. The temperature T_u is defined as the temperature in °C at which the reaction is 80 % complete and is calculated using equation (1):

$$T_u = (0.8 \times T'_{max}) + (0.2 \times T_0) \qquad (1)$$

Having calculated T_u, the value of t_u shall be determined from the wet slaking curve as shown in Figure 3.
The fineness of the lime sample and the maximum temperature T_{max} shall also be reported. T_{max} is calculated in °C from the observed maximum temperature (T'_{max}) corrected for the water equivalent using equation (2)

$$T_{max} = (1.1 \times T'_{max}) - 2 \qquad (2)$$

Equation (2) is only valid if the apparatus has a water equivalent of 200 to 300 J/K.

6) Alternative procedure:
Plot the measured temperature values in °C as a function of time in min. (wet slaking curve, Figure 3).
The result is expressed as the time t necessary to reach the required temperature T. For instance, if the required temperature is 60 °C, t_{60} in min. will be the result.

Section A4.1/09

Annex Point IIA IV.4.1

Analytical Method for the Characterisation of Burnt lime and Burnt dolomitic lime: Reactivity

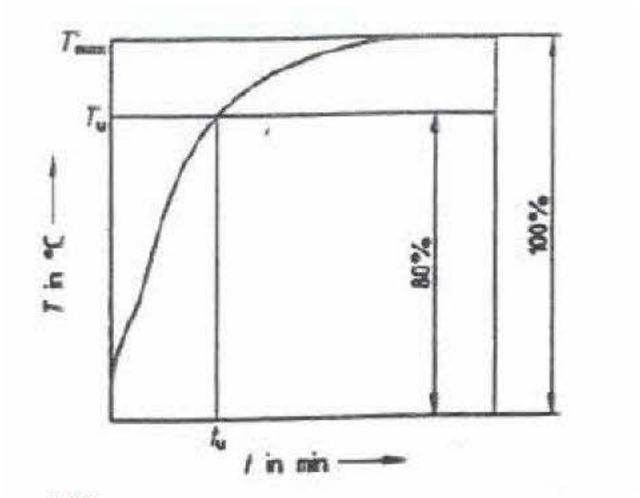


Figure 3: Example of a wet slaking curve

4 APPLICANT'S SUMMARY AND CONCLUSION

4.1	**Materials and methods**	The reactivity of Burnt lime and Dolomitic burnt lime with water can be determined via the wet slaking curve. The wet slaking curve is recorded by the measurement of the temperature raise in a dewar vessel, when Burnt lime or Burnt dolomitic lime is reacted with water. The characterisation parameters for the reactivity (t_u, T_u, T_{max} or $t_{60°C}$) can be read from the plot of the wet slaking curve.
4.2	**Conclusion**	The method described allows the determination of the reactivity of Burnt limes, which is the important characterisation parameter for Burnt lime variants used for biocidal purposes, as the temperature raise is, besides the high pH values, the active principle.
4.3	**Reliability**	1
4.4	**Deficiencies**	No

	Evaluation by Competent Authorities
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	29 June 2010
Materials and methods	EN (European Norm) 459-2:2001 "Building lime – Part 2: Test methods" Chapter 5.10 provides a method which determines the reactivity of Burnt lime and Dolomitic burnt lime with water. The temperature raise is, besides the high pH values, the active principle.
Conclusion	Acceptable
Reliability	1
Acceptability	The applicant's version is considered acceptable.
Remarks	
	COMMENTS FROM ...
Date	*Give date of comments submitted*
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub)heading numbers and to applicant´s summary and conclusion.* *Discuss if deviating from view of rapporteur member state*
Conclusion	*Discuss if deviating from view of rapporteur member state*
Reliability	*Discuss if deviating from view of rapporteur member state*
Acceptability	*Discuss if deviating from view of rapporteur member state*
Remarks	

Section A4.2a/01 Analytical Method for the Determination of the pH-value of soil

Annex Point IIA IV.4.2a

Remark: The main influences of Lime variants on soil are the change of the pH-value and the change of Ca^{2+} and Mg^{2+} contents. Therefore, analytical methods are described here in Section A4.2a, that allow the determination of the pH-value (Doc. No. 492-020; A4.2a/01) and the determination of Ca^{2+} and Mg^{2+} contents (Doc. No. 492-019; A4.2a/02) in soil.

Official use only

1 REFERENCE

1.1	**Reference**	NF ISO 10390: "French standard: Soil quality – determination of pH". Doc. No. 492-020.
1.2	**Data protection**	No
1.2.1	Data owner	published
1.2.2	Companies with Letter of Access	n. r.
1.2.3	Criteria for data protection	n. r.

2 GUIDELINES AND QUALITY ASSURANCE

2.1	**Guideline study**	Document outlines a standard norm (NF ISO 10390) and describes a supporting interlaboratory trial.
2.2	**GLP**	No
2.3	**Deviations**	n. r.

3 MATERIALS AND METHODS

3.1	**Preliminary treatment**	-
3.1.1	Enrichment	no enrichment necessary
3.1.2	Cleanup	no cleanup necessary
3.2	**Detection**	-
3.2.1	Separation method	no separation necessary
3.2.2	Detector	Potentiometric: pH-meter, with slope adjustment and temperature control; Glass electrode and reference electrode or combined electrode of equivalent performance; In case of pH values greater than 10, an electrode specifically designed for that range should be used.
3.2.3	Standard(s)	The pH meter is calibrated as specified in the manufacturer's manual, using at least two of the following buffer solutions: pH 4.00: 10.21 g potassium hydrogen phthalate in 1000 mL water pH 6.88: 3.39 g potassium dihydrogen phosphate and 3.53 disosium hydrogen phosphate in 1000 mL water pH 9.22: 3.80 g disodium tetraborate decahydrate in 1000 mL water
3.2.4	Interfering substance(s)	In samples with a high content of organic material (peat soils, pot soils etc.) the suspension effect can play a role. For calcareous soils, it is possible that carbon dioxide is absorbed by the suspension. Under these circumstances, it is difficult to reach an equilibrium pH-value.

Section A4.2a/01 Annex Point IIA IV.4.2a — Analytical Method for the Determination of the pH-value of soil

3.3 Linearity -

3.3.1 Calibration range: Depending on the buffers used; see 3.2.3 for possible ranges for calibration.

3.3.2 Number of measurements: At least two buffer solutions should be used for calibration

3.3.3 Linearity: not applicable

3.4 Specifity: interfering substances see 3.2.4

3.5 Recovery rates at different levels not applicable

3.5.1 Relative standard deviation: not applicable

3.6 Limit of determination not applicable

3.7 Precision -

3.7.1 Repeatability: The repeatability, expressed in terms of difference between the pH measurements in two separately prepared suspensions, shall satisfy the following requirements:

pH range	acceptable difference
pH < 7.00	0.15
7.00 < pH < 7.50	0.2
7.50 < pH < 8.00	0.3
pH > 8.00	0.4

3.7.2 Independent laboratory validation: An interlaboratory trial was organised in 2004 to test the procedure specified in the cited standard norm. For this interlaboratory trial, the determination of the pH of four soils was carried out by 35 laboratories. The summary of the results of the interlaboratory trial is presented in tables A4.2a/01-01 to A4.2a/01-03.

Soil samples:

1	cultivated sandy soil (Czech Republic)
2	clayey cultivated soil (Czech Republic)
3 and 4	both loamy cultivated soils (France)

Section A4.2a/01 Annex Point IIA IV.4.2a — Analytical Method for the Determination of the pH-value of soil

4 APPLICANT'S SUMMARY AND CONCLUSION

4.1 Materials and methods

Reagents:

- Water with a specific conductivity not higher the 0.2 mS/m at 25 °C and a pH greater than 5.6 (grade 2 water in accordance with ISO 3696:1987)
- Potassium chloride solution (1 mol/L)
- Calcium chloride solution (0.01 mol/L)
- Buffer solutions (see 3.2.3)

A representative test portion of at least 5 mL from the laboratory sample is mixed with five times its volume of water, potassium chloride solution or calcium chloride solution. The suspension is mixed for 60 min ± 10 min, using a mechanical shaker or mixer and allowed to stand for 1 h but not longer than 3 h afterwards. Ingress of air during standing after shaking should be avoided.

The pH-meter is calibrated as specified in the manufacturer's manual using the buffer solutions (see 3.2.3) at 20 °C.

The pH is measured in the suspension at 20 °C ± 2 °C immediately after or whilst being stirred. The stirring should be at such a rate to achieve a reasonable homogenous suspension of the soil particles, but entrainment of air should be avoided. The pH is read after stabilisation of the value and noted to two decimal places. If a swinging needle pH meter is used, the second decimal place should be estimated.

4.2 Conclusion

The standard specifies an instrumental method for the routine determination of pH using a glass electrode in a 1:5 (volume fraction) suspension of soil in water (pH in H_2O), in 1 mol/L potassium chloride solution (pH in KCl) or in 0.01 mol/L calcium chloride solution (pH in $CaCl_2$).

The International standard is applicable to all types of air-dried soil samples, pre-treated for example in accordance with ISO 11484.

4.2.1 Reliability: 1

4.2.2 Deficiencies: No

Section A4.2a/01 Analytical Method for the Determination of the pH-value of soil

Annex Point IIA IV.4.2a

	Evaluation by Competent Authorities
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	29 June 2010
Materials and methods	NF ISO 10390 provides a method which allows the determination of the pH-value and can be used in cojuction with standard NF X 31-108.
Conclusion	Acceptable
Reliability	1
Acceptability	The applicant's version is considered acceptable.
Remarks	
	COMMENTS FROM ...
Date	*Give date of comments submitted*
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub)heading numbers and to applicant´s summary and conclusion.* *Discuss if deviating from view of rapporteur member state*
Conclusion	*Discuss if deviating from view of rapporteur member state*
Reliability	*Discuss if deviating from view of rapporteur member state*
Acceptability	*Discuss if deviating from view of rapporteur member state*
Remarks	

Table A4.2a/01-01: Results of the interlaboratory trial for the determination of the pH in H_2O

Sample No.	**1**	**2**	**3**	**4**
Number of laboratories retained after eliminating outliers	35	33	32	33
Number of outliers (laboratories)	0	2	3	2
Number of accepted results	70	66	84	66
Mean value	5.72	7.60	8.08	6.40
Repeatability value ($r = 2.8 s_r$)	0.08	0.12	0.10	0.10
Reproducibility value ($R = 2.8 s_R$)	0.79	0.45	0.42	0.38

Table A4.2a/01-02: Results of the interlaboratory trial for the determination of the pH in KCl

Sample No.	**1**	**2**	**3**	**4**
Number of laboratories retained after eliminating outliers	35	35	34	33
Number of outliers (laboratories)	0	0	1	2
Number of accepted results	70	70	88	66
Mean value	5.00	7.13	7.38	5.87
Repeatability value ($r = 2.8 s_r$)	0.08	0.08	0.08	0.14
Reproducibility value ($R = 2.8 s_R$)	0.47	0.37	0.36	0.25

Table A4.2a/01-03: Results of the interlaboratory trial for the determination of the pH in $CaCl_2$

Sample No.	**1**	**2**	**3**	**4**
Number of laboratories retained after eliminating outliers	33	33	32	34
Number of outliers (laboratories)	2	2	3	1
Number of accepted results	66	66	64	68
Mean value	5.16	6.98	7.45	5.81
Repeatability value ($r = 2.8\ s_r$)	0.07	0.06	0.06	0.09
Reproducibility value ($R = 2.8\ s_R$)	0.37	0.25	0.32	0.33

Section A4.2a/02 — Analytical Method for the Determination of Ca^{2+} and Mg^{2+} in soil

Annex Point IIA IV.4.2a

Remark: The main influences of Lime variants on soil are the change of the pH-value and the change of Ca^{2+} and Mg^{2+} contents. Therefore, analytical methods are described here in Section A4.2a, that allow the determination of the pH-value (Doc. No. 492-020; A4.2a/01) and the determination of Ca^{2+} and Mg^{2+} contents (Doc. No. 492-019; A4.2a/02) in soil.

Official use only

1 REFERENCE

1.1	**Reference**	NF X 31-108: “Soil quality – Determination of ammonium acetate extractable Ca++, Mg++, K+ and Na+ cations – Agitation method””. Doc. No. 492-019.
1.2	**Data protection**	No
1.2.1	Data owner	published
1.2.2	Companies with Letter of Access	n. r.
1.2.3	Criteria for data protection	n. r.

2 GUIDELINES AND QUALITY ASSURANCE

2.1	**Guideline study**	Document outlines a standard norm (NF X 31-108)
2.2	**GLP**	No
2.3	**Deviations**	n. r.

3 MATERIALS AND METHODS

3.1	**Preliminary treatment**	-
3.1.1	Enrichment	no enrichment necessary
3.1.2	Cleanup	no cleanup necessary
3.2	**Detection**	-
3.2.1	Separation method	no separation necessary
3.2.2	Detector	Atomic Emission Spectrophotometry (AES) Atomic Absorption Spectrometry (AAS) Wavelengths: Potassium = 766.5 nm (emission and absorption) Sodium = 589,0 nm (emission and absorption) Calcium 422,7 nm Magnesium = 285,2 nm
3.2.3	Standard(s)	Potassium solution of 0.500 g/L in K_2O equivalents: 0.793 potassium chloride are dissolved in 1L of water. Sodium solution of 0.500 g/L in Na_2O equivalents: 0.943 sodium chloride are dissolved in 1L of water. Calcium solution of 1.000 g/L in CaO equivalents: 1.785 $CaCO_3$ are added to a 1L volumetric flask. Hydrochloric acid (see 4.1) is added

Section A4.2a/02 Annex Point IIA IV.4.2a — Analytical Method for the Determination of Ca^{2+} and Mg^{2+} in soil

		successively until the dissolution is complete (theoretically 36 mL). The volume is adjusted to 1L and the flask should be shaken well. Magensium solution of 1.000 g/L in MgO equivalents: 0.603 g of Magnesium are added to a 1L volumetric flask. Hydrochloric acid (see 4.1) is added successively until the dissolution is complete (theoretically 50 mL). The volume is adjusted to 1L and the flask should be shaken well.
3.2.4	Interfering substance(s)	The operator should verify that the instrumental conditions assure the specificity of the measured signal.
3.3	**Linearity**	-
3.3.1	Calibration range	For calibration standard solutions are obtained from the stock solution (see 3.2.3) by dilution according to table A4.2a/02-01.
3.3.2	Number of measurements	not specified Please note in the original standard norm only general conditions (no quantitative conditions) for the validity of the test are stated, which the operator should take care of.
3.3.3	Linearity	The validity of the calibration curve should be verified by the relation between the value of the signal and the concentration of the standard solution.
3.4	**Specificity: interfering substances**	It should be ensured that the calibration solutions and the sample solutions have identical behaviour during measurements.
3.5	**Recovery rates at different levels**	not applicable: no fortification in this method
3.5.1	Relative standard deviation	not applicable: no fortification in this method
3.6	**Limit of determination**	Not specified in the standard norm. But based on common knowledge of AAS performance a Limit of determination of 1mg/kg soil for Magnesium and 5 mg/kg for Calcium could be achieved.
3.7	**Precision**	-
3.7.1	Repeatability	The operator should verify that the instrumental conditions assure a repeatability and reproducibility of the measurements according to the objective of the study.
3.7.2	Independent laboratory validation	not performed

Section A4.2a/02 Annex Point IIA IV.4.2a — Analytical Method for the Determination of Ca^{2+} and Mg^{2+} in soil

4 APPLICANT'S SUMMARY AND CONCLUSION

4.1 Materials and methods

Reagents:

- Water with a specific conductivity not higher than 0.5 µS/m
- Ammonium acetate with a content of K_2O, Na_2O and MgO of less than 0.5 mg/kg and a CaO content of less than 2.5 mg/kg.
- Hydrochloric acid (1 mol/L)
- Ammonia (1 mol/L)
- Acetic acid (1 mol/L)
- Lanthanum trichloride hexahydrate

77.0 g ammonium acetate are dissolved in 900 mL water. The pH value is adjusted to 7.00 ± 0.05 by adding small amounts of acetic acid or ammonia, respectively. The solution is transferred to a 1L volumetric flask which is filled to the 1L mark with water and shaked well.

A defined amount of soil is extracted by a respective amount of extraction solution in an appropriate vessel, according to the following table:

Mass of soil sample	Extraction volume	Vessel size
2.5 g	50 mL	75 – 100 mL
5.0 g	100 mL	125 – 150 mL
10.0 g	200 mL	250 – 300 mL

The extraction suspension should be shaken for at least 1h at 20 °C. Afterwards the mixture is filtered and filtrate is transferred to an appropriate tightly closed vessel.

Blanks: Blank samples are prepared under the same conditions as described above, but without soil. For MgO, Na_2O and K_2O the concentrations in the blank samples should not exceed 0.05 mg/L and for CaO the concentration should not exceed 0.2 mg/L.

Water is used for dilution of the samples for atomic emission spectrophotometry and a solution of 0.5 g of $LaCl_3x6H_2O$ in 1L of water is used for the dilution of the samples for atomic absorption spectrometry. The following dilution rates should be used:

1/10 (V/V) for K and Na for AES and AAS

1/20 (V/V) for Mg for AAS

1/50 (V/V) for Ca for AAS

The calibration, test and blank samples are measured consecutively. Verify that the results for the blank samples do not exceed the values given above (under the paragraph **Blanks**).

Interpretation of the results:

The concentration T of the respective element expressed in grams / 1000 g soil is given by:

$T = A * f * 0.02$ [g/kg]

with

Section A4.2a/02 Analytical Method for the Determination of Ca^{2+} and Mg^{2+} in soil

Annex Point IIA IV.4.2a

A = concentration of the oxide equivalent in the test solution expressed in mg/L

f = dilution factor

In case the results need to be expressed in relation to the dry soil (T'), the following correction needs to be applied:

$T' = T * (100 / (100 – H))$

with

H = concentration of residual water in the soil sample (according to NF ISO 11485) expressed in mass % of the sample mass.

4.2 Conclusion	The standard norm specifies a method that allows the determination of extractable cations in soil. The soil is extracted by solution of ammonium acetate. The cations are detected by atomic emission spectrophotometry or atomic absorption spectrometry.
4.2.1 Reliability	1
4.2.2 Deficiencies	No

	Evaluation by Competent Authorities
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	29 June 2010
Materials and methods	NF X 31-108 provides a method which determines ammonium acetate extractable Ca++, Mg++, K+ and Na+ cations by Atomic Emission Spectrophotometry and Atomic Absorption Spectrometry.
Conclusion	Acceptable
Reliability	1
Acceptability	The applicant's version is considered acceptable.
Remarks	This method, or any other, cannot determine whether the source of the residue is from biocidal use. Given the use of burnt lime allows for application of the treated sewage or manure to agricultural land (as a replacement for agricultural liming) the normal requirement for analysis of the active/residues in soil would seem unnecessary.
	COMMENTS FROM ...
Date	*Give date of comments submitted*
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub)heading numbers and to applicant's summary and conclusion.* *Discuss if deviating from view of rapporteur member state*
Conclusion	*Discuss if deviating from view of rapporteur member state*
Reliability	*Discuss if deviating from view of rapporteur member state*
Acceptability	*Discuss if deviating from view of rapporteur member state*
Remarks	

Table A4.2a/02-01: Examples of concentrations of calibration solutions for the different elements

Element	Quantities of the stock solutions in 1L [ml] (concentrations of the oxide equivalent [mg/L])	Quantity of ammonium acetate per litre [g]
Potassium	0 – 5.0 – 10 – 20 – 30 (0.0 – 2.5 – 5 – 10 – 15)	77
Sodium	0 – 5.0 – 10 – 20 – 30 (0.0 – 2.5 – 5 – 10 – 15)	77
Calcium	0 – 100 – 200 – 300 – 400 (0 – 100 – 200 – 300 – 400)	77
Magnesium	0 – 5.0 – 10 – 20 – 30 (0.0 – 2.5 – 5 – 10 – 15)	77

Section A4.2b/01 — Analytical Method for the Determination of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime components in air

Annex Point IIA IV.4.2b

Official use only

1 REFERENCE

Reference	W. S. Cain, A. A. Jalowayski, M. Kleinman, N.-S. Lee, B.-R. Lee, B.-H. Ahn, K. Magruder, R. Schmidt, B. K. Hillen, C. B. Warren and B. D. Culver, "Sensory and Associated Reactions to Mineral Dusts: Sodium Borate, Calcium Oxide, and Calcium Sulfate", *J. Occ. Env. Hygiene* **2004**, *1*, 222-236. Doc. No. 592-020.
1.1 Data protection	No
1.1.1 Data owner	published
1.1.2 Companies with Letter of Access	n. r.
1.1.3 Criteria for data protection	n. r.

2 GUIDELINES AND QUALITY ASSURANCE

2.1 Guideline study	No
2.2 GLP	No
2.3 Deviations	n. r.

3 MATERIALS AND METHODS

Remarks:

According to the TNsG on data requirements, an analytical method in air must be provided if the substance is volatile (i.e. if the vapour pressure is >= 0.01 Pa) or sprayed, or occurrence in air is otherwise probable.

- The lime based products are not volatile (vapour pressure < 0.01 Pa). Spray applications only involve large droplets which are not respirable.
- Occurrence of dust is possible in some applications.

The cited document describes a study on the sensory and associated reactions to calcium oxide, calcium sulphate and sodium borate. It is also described how the dust concentrations of calcium oxide in air can be measured. This method is described in the following:

A known amount of dust containing air is conveyed over a filter. The filter is weighed and the concentration is calculated through the mass difference. For samples of a mixture of calcium sulphate and calcium oxide, the filter is weighed and the percentage of calcium oxide is determined by a pH-measurement. This entails making an aqueous solution of 5% dissolved solids based upon the amount of dust on the filter. The pH of this solution reflects the proportion of calcium oxide when compared against standard curves that contain various proportions of calcium oxide and calcium sulphate.

Section A4.2b/01 — Analytical Method for the Determination of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime components in air

Annex Point IIA IV.4.2b

4 APPLICANT'S SUMMARY AND CONCLUSION

4.1	**Materials and methods**	The principle of the determination of calcium oxide in air is based on conveying an air stream over a filter and weighing the filter afterwards. It is also described, that it is possible to distinguish the calcium oxide content from the calcium sulphate content by measuring the basicity through a calibrated pH-metric method.
4.2	**Conclusion**	It is assumed that similar methods are suitable to determine dust concentrations of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime in air and to distinguish from other dusts by measuring their basicity.
4.3	**Reliability**	1 – 2
4.4	**Deficiencies**	No

	Evaluation by Competent Authorities
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	13 July 2010
Materials and methods	The method does not give much detail regarding the sampling and analysis of samples. Validation data are not included.
Conclusion	Detailed analysis may be provided at product authorisation.
Reliability	2
Acceptability	The applicant’s version is considered acceptable.
Remarks	Whether or not measurement of residue in air is required will depend on a combination of factors such as particle size, method of application and degree of enclosure. This should be addressed at product authorisation.
	COMMENTS FROM ...
Date	*Give date of comments submitted*
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub)heading numbers and to applicant's summary and conclusion.* *Discuss if deviating from view of rapporteur member state*
Conclusion	*Discuss if deviating from view of rapporteur member state*
Reliability	*Discuss if deviating from view of rapporteur member state*
Acceptability	*Discuss if deviating from view of rapporteur member state*
Remarks	

Section A4.2c

Annex Point IIA IV.4.2c

Analytical Method for the Determination of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime components (Ca^{2+}, Mg^{2+} and OH^-) in water

JUSTIFICATION FOR NON-SUBMISSION OF DATA

Official use only

Other existing data [X] **Technically not feasible [ ]** **Scientifically unjustified [ ]**

Limited exposure [ ] **Other justification [ ]**

Detailed justification:

This Section point is covered by read-across to analytical methods for Ca^{2+}, Mg^{2+} and pH-values available for the Lime variants.

The difference between the determination of Lime residues in water and the analytical methods for Lime products themselves is that the step to dissolve the Lime products is not necessary since they are already dissolved in water.

Short summary of the methods in Sections 4.1/01 and 4.1/03:

> **Section 4.1/01:** ASTM (American Society for Testing and Materials) Designation C25 – 99: "Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime" 1999. Doc. No. 492-007.
>
> > This method is based on standard wet chemical separation procedures and specific quantitative determination procedures. For Ca^{2+} and Mg^{2+} the well established complexometric titration method with EDTA is described in detail, which is also applicable for the determination of Ca^{2+} and Mg^{2+} in water. For the determination of OH^- ions, which occur when Lime products are dissolved in water, a potentiometric pH-determination is provided.
>
> **Section 4.1/03:** ASTM (American Society for Testing and Materials) Designation C 1301 – 95 (Re-approved 2001): "Standard Test Method for Major and Trace Elements in Limestone and Lime by Inductively Coupled Plasma-Atomic Spectroscopy (ICP) and Atomic Absorption (AA)" 1995, 2001. Doc. No. 492-010.
>
> > ICP and AAS are the most common standard procedures to routinely determine Ca^{2+} and Mg^{2+} traces in water. Especially for very low concentrations these methods are very suitable, because of their high sensitivity. These methods are also applicable for the determination of the typical minor elements in Lime products. Detection limits for AAS typically range from mg/L to µg/L for the flame technique and µg/L to ng/L for the graphite tube technique. The sensitivity of the ICP method is comparable to the sensitivity of the AAS flame method for some elements and comparable to the sensitivity of the AAS graphite tube technique for others. Detection limits are also apparatus depended.

For detailed descriptions of the methods mentioned above, please refer to the respective study summaries in Section A4.1.

	Evaluation by Competent Authorities
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	29 June 2010
Evaluation of applicant's justification	Acceptable, additional methods are not required.

Conclusion	The applicant’s version is considered acceptable.
Remarks	
	COMMENTS FROM OTHER MEMBER STATE *(specify)*
Date	*Give date of comments submitted*
Evaluation of applicant's justification	*Discuss if deviating from view of rapporteur member state*
Conclusion	*Discuss if deviating from view of rapporteur member state*
Remarks	

Section A4.2d Analytical Method for the Determination of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime components in animal and human body fluids and tissues

Annex Point IIA IV.4.2d

JUSTIFICATION FOR NON-SUBMISSION OF DATA

Official use only

Other existing data [ ] **Technically not feasible [ ]** **Scientifically unjustified [ ]**

Limited exposure [ ] **Other justification [X]**

Detailed justification:

According to the Technical Notes on Data Requirements data must be submitted “Where an active substance is classified as toxic or highly toxic [...]“. None of the stated Lime products is classified as toxic. Nevertheless, it should be refered to medical standard procedures for the determination of calcium and magnesium in blood.

	Evaluation by Competent Authorities
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	2 July 2010
Evaluation of applicant's justification	The applicant’s version is considered acceptable.
Conclusion	Accept
Remarks	
	COMMENTS FROM OTHER MEMBER STATE *(specify)*
Date	*Give date of comments submitted*
Evaluation of applicant's justification	*Discuss if deviating from view of rapporteur member state*
Conclusion	*Discuss if deviating from view of rapporteur member state*
Remarks	

Section A4.3/01 — Analytical Method for the Determination of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime components (Mg^{2+} and Ca^{2+}) in food stuff

Annex Point IIIA IV.1

			Official use only
		1 REFERENCE	
1.1	**Reference**	DIN EN (Deutsche Norm; Entwurf) 15505 "Foodstuffs – Determination of trace elements – Determination of sodium, magnesium and calcium by flame atomic absorption spectrometry (AAS) after microwave digestion; German version prEN 15505:2006", Doc. No. 492-022; A4.3/01. Only Calcium and Magnesium are addressed in the following study summary.	
1.2	**Data protection**	no	
1.2.1	Data owner	published	
1.2.2	Companies with letter of access	n. r.	
1.2.3	Criteria for data protection	n. r.	
		2 GUIDELINES AND QUALITY ASSURANCE	
2.1	**Guideline study**	The document outlines a norm and the results of a round robin test.	
2.2	**GLP**	no	
2.3	**Deviations**	n. r.	
		3 MATERIALS AND METHODS	
3.1	**Preliminary treatment**	--	
3.1.1	Enrichment	no enrichment described	
3.1.2	Cleanup	no cleanup described	
3.2	**Detection**	--	
3.2.1	Separation method	no separation described	
3.2.2	Detector	Atomic Absorption Spectrometry (AAS) Wavelengths: Calcium = 422.7 nm Magnesium = 285.2 nm	
3.2.3	Standard(s)	external calibration; Magnesium [mg/L]: 0.05, 0.1, 0.2, 0.4 mg/L each containing 1% Lanthanum Calcium [mg/L]: 0.5, 1.0, 2.0, 4.0 mg/L each containing 1% Lanthanum	
3.2.4	Interfering substance(s)	No interfering substances cited	
3.3	**Linearity**	--	
3.3.1	Calibration range	Magnesium [mg/L]: 0.05, 0.1, 0.2, 0.4 mg/L each containing 1% Lanthanum	

Section A4.3/01 **Annex Point IIIA IV.1**	**Analytical Method for the Determination of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime components (Mg^{2+} and Ca^{2+}) in food stuff**

		Calcium [mg/L]: 0.5, 1.0, 2.0, 4.0 mg/L each containing 1% Lanthanum
3.3.2	Number of measurements	Not applicable Method is an norm; validity data is provided based on a round robin test and summarised in tables A4.3/01-01 and A4.3/01-02
3.3.3	Linearity	not applicable Method is an norm; validity data is provided based on a round robin test and summarised in table A4.3/01-01 and A4.3/01-02
3.4	**Specificity: interfering substances**	In general AAS is a highly specific method but depending on specific matrices adjustments might be necessary.
3.5	**Recovery rates at different levels**	Not applicable Measurement of spiked samples is not described.
3.5.1	Relative standard deviation	Not applicable Measurement of spiked samples is not described.
3.6	**Limit of determination**	The method is suitable for the determination of Magnesium content of at least 250 mg/kg dry weight and for the determination of Calcium content of at least 2000 mg/kg dry weight. The method is not applicable for wheat bran.
3.7	**Precision**	Non-entry field
3.7.1	Repeatability	see table A4.3/01-01
3.7.2	Independent laboratory validation	see table A4.3/01-01

Section A4.3/01

Annex Point IIIA IV.1

Analytical Method for the Determination of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime components (Mg^{2+} and Ca^{2+}) in food stuff

4 APPLICANT'S SUMMARY AND CONCLUSION

4.1 Materials and methods

Principle:

The samples are digested in closed vessels in a mixture of nitric acid and hydrogen peroxide in a microwave oven. The solution obtained is diluted with water and the content of magnesium and calcium is determined by atomic absorption spectrometry using matrix modifiers.

Reagents:

General: The concentrations of Calcium and Magnesium in the reagents used should not influence the test results.

(1) Nitric acid: at least 65% with a density of 1.4 g/mL (in case the nitric acid is not pure enough, it needs to be purified by distillation according to EN 13805.

(2) Diluted nitric acid solution 1 (2.7 % w/w):

42 mL nitric acid (1) are diluted with water to 1000 mL

(3) Diluted nitric acid solution 2 (0.65 % w/w):

Nitric acid (1) and water are mixed in a volume ratio of 1:99

(4) Hydrochloric acid 37 % (w/w)

(5) Hydrogen peroxide 30 % (w/w)

(6) Caesium chloride to be used in AAS

(7) Caesium chloride solution:

31.75 g CsCl (6) are dissolved in water and diluted to 250 mL. This solution is stable in the fridge for at least 6 months.

(8) Lanthanum oxide (III) (La_2O_3) for AAS

(9) Lanthanum solution

14.66 g La_2O_3 are weighed in a 250 mL beaker and are moistured with 10 mL of water. Then, 62.5 mL hydrochloric acid (4) are added. The solution is transferred to a 250 mL volumetric flask which is filled up to the mark. This solution is stable for one month.

(10) Magnesium and Calcium stock solution:

Commercially available stock solution with 1000 mg/L of the respective element should be used.

(11) Magnesium standard solution:

1 mL Magnesium stock solution (10) is diluted in a volumetric flask with 0.65 % nitric acid (3) to 100 mL. The solution is stable for one month.

(12) Calcium standard solution:

1 mL Calcium stock solution (10) is diluted in a volumetric flask with 0.65 % nitric acid (3) to 100 mL. The solution is stable for one month.

Procedure:

For the determination of Calcium and Magnesium, the solutions are used which were obtained by the microwave digestion according to EN

Section A4.3/01
Annex Point IIIA IV.1

Analytical Method for the Determination of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime components (Mg^{2+} and Ca^{2+}) in food stuff

13805 and 13804.

To an appropriate amount of sample solution, 5% Lanthanum solution (9) is added. This volume is diluted with 0.65% Nitric acid to obtain an end concentration of Calcium and Magnesium in the linear range of the calibration curve (see 3.2.3). In case the concentrations of the sample solutions are lower, the lowest point of the calibration curve can be adapted accordingly. The 5% Lanthanum solution is added to reach an end concentration for La of 1%.

Before each measurement, the AAS apparatus is adjusted according to the manufacture's manual.

Calculations:

The element content (w) is calculated as mass fraction of Calcium or Magnesium per kg sample according to the following equation:

$w = (a*V*F) / (m*1000)$

with

a = concentration of the element in the sample solution [mg/L]

V = volume of the digestion solution after filling up [mL]

F = dilution factor of the sample solution [1]

m = the sample mass [g]

4.2 Conclusion

This standard norm provides a method to determine Calcium and Magnesium in different food stuff matrices. The method is based on the well established atomic absorption spectrometry, which is a common technique to determine Calcium and Magnesium. The results of the round robin test show that the method is valid. It has to be taken into consideration that the natural background of Calcium and Magnesium in food stuffs could be high.

4.2.1 Reliability	1
4.2.2 Deficiencies	No

Section A4.3/01 Analytical Method for the Determination of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime components (Mg^{2+} and Ca^{2+}) in food stuff

Annex Point IIIA IV.1

	Evaluation by Competent Authorities
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	29 June 2010
Materials and methods	DIN EN 15505 is a standard which describes a method to determination the levels of trace elements in foodstuffs by flame atomic absorption spectrometry.
Conclusion	Acceptable
Reliability	1
Acceptability	The applicant's version is considered acceptable.
Remarks	The method is not able to determine whether the residue is a consequence of the biocidal use of lime.
	COMMENTS FROM ...
Date	*Give date of comments submitted*
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub)heading numbers and to applicant´s summary and conclusion.* *Discuss if deviating from view of rapporteur member state*
Conclusion	*Discuss if deviating from view of rapporteur member state*
Reliability	*Discuss if deviating from view of rapporteur member state*
Acceptability	*Discuss if deviating from view of rapporteur member state*
Remarks	

Table A4.3/01-01: Mean values, repeatability* and reproducibility for Magnesium**

Sample	**Mean [mg/kg]**	**r [mg/kg]**	**R [mg/kg]**
Simulated food (D)	665	70	129
Simulated food (F)	618	76	120
milk powder, lyophilised	859	51	111
hackled fish, lyophilised	749	50	144
apple, dried	251	15	32
Chocolate cake	284	16	32

Table A4.3/01-02: Mean values, repeatability* and reproducibility for Calcium**

Sample	**Mean [mg/kg]**	**r [mg/kg]**	**R [mg/kg]**
milk powder, lyophilised	9450	940	1670
hackled fish, lyophilised	3830	253	635

*The repeatability is the absolute difference of two independent results (double blind), obtained with the same method, with identical samples, in the same laboratory with the same operator and the same apparatus in a short time frame. In less than 5% of all cases, the repeatability is > r.

**The reproducibility is the absolute difference of two independent results (double blind), obtained with the same method, with identical samples, in different laboratories with the different operators and the different apparatus. In less than 5% of all cases, the reproducibility is > R.

Section A4.3/02

Annex Point IIIA IV.1

Analytical Method for the Determination of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime components (Mg^{2+} and Ca^{2+}) in animal feeding stuff

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1 REFERENCE

1.1	**Reference**	DIN EN (Deutsche Norm; Entwurf) 15510 “Animal feeding stuffs – Determination of calcium, sodium, phosphorus, magnesium, potassium, iron, zinc copper, manganese, cobalt, molybdenum, arsenic, lead and cadmium by ICP-AES; German version prEN 15510:2006”, Doc. No. 492-021; A4.3/02. **Remark:** Only the determinations of Calcium and Magnesium in organic feed stuffs are addressed in the following study summary.
1.2	**Data protection**	No
1.2.1	Data owner	published
1.2.2	Companies with letter of access	n. r.
1.2.3	Criteria for data protection	n. r.

2 GUIDELINES AND QUALITY ASSURANCE

2.1	**Guideline study**	The document outlines a norm and the results of a round robin test.
2.2	**GLP**	No
2.3	**Deviations**	n. r.

3 MATERIALS AND METHODS

3.1	**Preliminary treatment**	--
3.1.1	Enrichment	no enrichment described
3.1.2	Cleanup	after the digestion the solutions are filtered
3.2	**Detection**	--
3.2.1	Separation method	no separation described
3.2.2	Detector	ICP-AES

Wavelengths:

	Wavelength [nm]	Interference
Calcium	315.887	Co
	317.933	Fe, V
	393.366	
Mg	279.079	
	279.553	
	285.213	Fe

3.2.3	Standard(s)	External calibration
3.2.4	Interfering substance(s)	No interfering substances cited
3.3	**Linearity**	--

Section A4.3/02

Annex Point IIIA IV.1

Analytical Method for the Determination of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime components (Mg^{2+} and Ca^{2+}) in animal feeding stuff

3.3.1	Calibration range	The calibration solutions are prepared from the stock solution (see 4.1 Reagents (10) adjusting the concentration range to the expected concentration of the test solution.
3.3.2	Number of measurements	Not applicable Method is an norm; validity data is provided based on a round robin test and summarised in tables A4.3/02-01 and A4.3/02-02
3.3.3	Linearity	not applicable Method is an norm; validity data is provided based on a round robin test and summarised in table A4.3/02-01 and A4.3/02-02
3.4	**Specificity: interfering substances**	In general ICP-AES is a highly specific method but depending on specific matrices adjustments might be necessary.
3.5	**Recovery rates at different levels**	Not applicable Measurements of spiked samples are not described.
3.5.1	Relative standard deviation	Not applicable Measurements of spiked samples are not described.
3.6	**Limit of determination**	The limit of detection of this method depends on the sample matrix and on the apparatus used. The method is not suitable for the determination of very low element concentrations. A limit of detection of 3 mg/kg should usually be achieved.
3.7	**Precision**	Non-entry field
3.7.1	Repeatability	see table A4.3/02-01 and A4.3/02-02
3.7.2	Independent laboratory validation	see table A4.3/02-01 and A4.3/02-02

Section A4.3/02

Annex Point IIIA IV.1

Analytical Method for the Determination of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime components (Mg^{2+} and Ca^{2+}) in animal feeding stuff

4 APPLICANT'S SUMMARY AND CONCLUSION

4.1 Materials and methods

Principle:

For the determination of Calcium and Magnesium in feed stuffs, for organic feed stuffs, a test amount of the sample is reduced to ashes and dissolved in hydrochloric acid. The standard norm covers also the determination of Calcium and Magnesium in mineral material mixtures. These methods are not relevant for this Section point and are therefore not summarised.

The concentrations of Calcium and Magnesium are determined by atomic emission spectrometry with inductive coupled plasma by utilising external calibration or the method of standard addition.

Reagents:

General: Only reagents of an approved purity and water of the quality 2 according to EN ISO 3696 should be used.

(1) Nitric acid: at least 65% (w/w) with a density of 1.42 g/mL

(2) Diluted nitric acid:
1 volume unit nitric acid (1) is mixed with 1 volume unit of water

(3) Diluted nitric acid 5 % (w/w):
160 mL nitric acid (2) are added to a 1000 mL volumetric flask and filled up to the mark

(4) Diluted nitric acid 2 % (v/v):
20 mL nitric acid (1) are added to a 1000 mL volumetric flask and filled up to the mark

(5) Hydrochloric acid:
at least 30 % (w/w) and a density of 1.15 g/mL

(6) Diluted hydrochloric acid:
1 volume unit hydrochloric acid (5) is mixed with 1 volume unit of water

(7) Hydrochloric acid 1 % (w/w):
60 mL hydrochloric acid (5) are added to a 1000 mL volumetric flask and filled up to the mark

(8) Magnesium and Calcium stock solution:
Commercially available stock solution with 1000 mg/L of the respective element should be used.

(9) Magnesium / Calcium standard solution:
Multiple element standard solution can be used. 40.0 mL of each stock solution (8) is added to a 1000 mL volumetric flask. 60 mL of hydrochloric acid (6) is added the flask is filled up to mark.

Procedure:

Feeding stuff that can be milled:

The sample should be milled with a mill or a mortar until a particle size of 1 mm or less is achieved.

Section A4.3/02

Annex Point IIIA IV.1

Analytical Method for the Determination of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime components (Mg^{2+} and Ca^{2+}) in animal feeding stuff

Liquid feeding stuff:

Liquid feeding stuff must be dried at 70 °C ± 5 °C for 16 h or must be lyophilised. The sample weight should be recorded before and after drying.

Wet digestion with 1 % hydrochloric acid:

Ca. 1 g (to 1 mg exactly) of the prepared sample is weighed in a 250 mL beaker. 20 mL of hydrochloric acid (6) and ca. 100 mL water is added. The beaker is covered with a watchglass and the mixture is boiled for 30 min. After cooling the solution is decanted to a 500 mL volumetric flask, rinsing the beaker and the watchglass several times. The volumetric flask is filled up to the mark. After homogenisation the solution is filtered over a dry fluted filter into a dry vessel. The first filtrate portion should be used for rinsing of the glassware and should then be discarded. If the determination is not performed immediately, the vessel containing the solution should be tightly closed.

Parallel to the extraction, blank solutions should be prepared in the same manner, but without feeding stuff samples.

If the expected concentration of the element is less than 1 mg/kg, 6 mL hydrochloric acid, 70 mL water and a 100 mL volumetric flask should be used.

Reducing to ashes and dissolution in 1 % hydrochloric acid

Ca. 5 g (to 1 mg exactly) of the prepared sample is weighed in a crucible. The weighed in sample is reduced to ashes in a to 450 °C pre-heated oven until a white or grey ash is obtained (small amounts of carbon do not interfere). The ash is transferred to a 250 mL beaker containing 30 mL hydrochloric acid (6). 100 mL water is added.

The beaker is covered with a watchglass and the mixture is boiled for 30 min. After cooling the solution is decanted to a 500 mL volumetric flask, rinsing the beaker and the watchglass several times. The volumetric flask is filled up to the mark. After homogenisation the solution is filtered over a dry fluted filter into a dry vessel. The first filtrate portion should be used for rinsing of the glassware and should then be discarded. If the determination is not performed immediately, the vessel containing the solution should be tightly closed.

Parallel to the extraction, blank solutions should be prepared in the same manner, but without feeding stuff samples.

If the expected concentration of the element is less than 1 mg/kg, 6 mL hydrochloric acid, 70 mL water and a 100 mL volumetric flask should be used.

Wet digestion with 5 % nitric acid:

Ca. 2 g (to 1 mg exactly) of the prepared sample is weighed in a 100 mL beaker. 16 mL of nitric acid (2) and ca. 70 mL water is added. The beaker is covered with a watchglass and the mixture is boiled for 30 min. After cooling the solution is decanted to a 100 mL volumetric flask, rinsing the beaker and the watchglass several times. The volumetric flask is filled up to the mark. After homogenisation the solution is filtered over a dry fluted filter into a dry vessel. The first filtrate portion should be used for rinsing of the glassware and should

Section A4.3/02

Annex Point IIIA IV.1

Analytical Method for the Determination of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime components (Mg^{2+} and Ca^{2+}) in animal feeding stuff

then be discarded. If the determination is not performed immediately, the vessel containing the solution should be tightly closed.

Parallel to the extraction, blank solutions should be prepared in the same manner, but without feeding stuff samples.

Determination:

Before operation of the ICP-AES-System, the spectral lines, sensitivity, detection- and quantification limits, linearity and interference must be determined. Relevant spectral line are as follows:

	Wavelength [nm]	Interference
Calcium	315.887	Co
	317.933	Fe, V
	393.366	
Magnesium	279.079	
	279.553	
	285.213	Fe

Method with external calibration:

The blank sample solution, the calibration solutions and the test solutions are introduced separately in increasing concentrations and the emission of the element to detect is measured. The tests should be run in duplicate. After each measurement, water or 2 % diluted nitric acid (4) is introduced.

Method with standard addition:

The blank sample solution, the test solutions and the standard addition are introduced separately in increasing concentrations and the emission of the element to detect is measured. The tests should be run in duplicate. After each measurement, water or 2 % diluted nitric acid (4) is introduced.

Calculations:

- External calibration:

In case of a linear calibration curve, determined with one blank sample solution and one calibration solution, the calibration function can be expressed as follows:

$S_{st} = c_{st} * b + a$

with

S_{st} = net signal of the calibration solution

c_{st} = concentration of the calibration solution [mg/L]

The element concentration c_f in the filtrate of the sample, in milligrams per litre, can be calculated by the slope b and the y-axis intersection a by:

$c_f = (S_f – a) / b$

with S_f = the net signal of the sample solution.

Section A4.3/02

Annex Point IIIA IV.1

Analytical Method for the Determination of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime components (Mg^{2+} and Ca^{2+}) in animal feeding stuff

- Multiple standard additions:

In case of multiple standard additions for the determination of the element concentration in the sample solution, regression methods on the basis of the linear model for the variable y as a function of x, need to be utilised. In general this model can be described as:

$y_i = a + b * x_i$

In the special case of three standard additions:

$y_i = S_i$ (for i = 1, 2, 3)

$x_i = c_S * Vi$ (for i = 1, 2, 3)

with

c_S = concentration of the standard solution [mg/L]

V_i = different volumes of the standard solution added [L]

S_i = net signal after the different standard additions

The values of a and b can then be calculated as follows:

$$b = \frac{n \cdot \sum x_i y_i - \sum x_i \sum y_i}{n \cdot \sum x_i^2 - \left(\sum x_i\right)^2}$$

$$a = \frac{\sum y_i - b \cdot \sum x_i}{n}$$

with n = the number of measured solutions (n = 4 in the case of three standard additions)

The element concentration $c_{f,}$ in milligrams per litre, of the filtrate of the sample can be calculated as follows:

$c_f = (a / b) / V_f$

with V_f = the volume of the filtrate of the sample used for the preparation of the sample solution [L]

Calculation of the element content in the sample:

The content of the element in sample or the mass fraction of the element w_{elem}, expressed in milligrams element per kilogram feeding stuff, is calculated according to the following equation:

$w_{elem} = V_t * (c_f – c_{bl}) / m$

with

c_f = concentration of the filtrate of the sample, determined according to one of the three methods described above [mg/L]

c_{bl} = concentration in the blank sample [mg/L]

m = mass of the sample used for extraction, corrected for the water content [kg]

Section A4.3/02 — Analytical Method for the Determination of Burnt lime, Hydrated lime, Dolomitic lime and Hydrated dolomitic lime components (Mg^{2+} and Ca^{2+}) in animal feeding stuff

Annex Point IIIA IV.1

V_t = the complete volume of the extract (filtrate of the sample) [L]

In case the sample solution was diluted, the dilution factor must be considered.

If the sample was dried, the result needs to be related to the fresh sample mass, considering the loss of moisture.

For Calcium and Magnesium, the result should be stated in % (w/w).

4.2 Conclusion	This standard provides a method to determine Calcium and Magnesium in different feeding stuff matrices. The method is based on the well established atomic emission spectrometry, which is a common technique to determine Calcium and Magnesium concentrations. The results of the round robin test show that the method is valid. It has to be taken into consideration that the natural background of Calcium and Magnesium in feeding stuffs could be high.
4.2.1 Reliability	1
4.2.2 Deficiencies	No

	Evaluation by Competent Authorities
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	29 June 2010
Materials and methods	DIN EN 15510 is a standard which describes a method to determination the levels of trace elements in foodstuffs by ICP-AES spectrometry.
Conclusion	Acceptable
Reliability	1
Acceptability	The applicant's version is considered acceptable.
Remarks	The method is not able to determine whether the residue is a consequence of the biocidal use of lime.
	COMMENTS FROM ...
Date	*Give date of comments submitted*
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub)heading numbers and to applicant's summary and conclusion.* *Discuss if deviating from view of rapporteur member state*
Conclusion	*Discuss if deviating from view of rapporteur member state*
Reliability	*Discuss if deviating from view of rapporteur member state*
Acceptability	*Discuss if deviating from view of rapporteur member state*
Remarks	

Table A4.3/02-01: Mean values, repeatability* and reproducibility for Calcium**

Sample	**Mean [%]**	**r [%]**	**R [%]**
Pig feeding stuff (1)	1.09	0.07	0.15
Sheep feeding stuff (1)	1.00	0.05	0.16
Phosphate (1)	10.78	0.47	1.34
Minerals pre-mixture (1)	21.78	1.25	2.58
Minerals mixture (1)	2.43	0.17	0.56
Minerals mixture (2)	14.6	0.7	2.9

Table A4.3/02-02: Mean values, repeatability* and reproducibility for Magnesium**

Sample	**Mean [%]**	**r [%]**	**R [%]**
Pig feeding stuff (1)	0.21	0.02	0.05
Sheep feeding stuff (1)	0.38	0.02	0.07
Phosphate (1)	11.12	0.66	1.73
Minerals pre-mixture (1)	0.36	0.03	0.06
Minerals mixture (1)	10.31	0.50	1.03

* The repeatability is the absolute difference of two independent results (double blind), obtained with the same method, with identical samples, in the same laboratory with the same operator and the same apparatus in a short time frame. In less than 5% of all cases, the repeatability is > r.

** The reproducibility is the absolute difference of two independent results (double blind), obtained with the same method, with identical samples, in different laboratories with the different operators and the different apparatus. In less than 5% of all cases, the reproducibility is > R.