Determination of Exchangeable Ammonium and Ammoniacal Nitrogen in Soil Samples

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1.0 Scope

This method is suitable for the preparation and the subsequent determination of sludge and soil samples for exchangeable ammonium and ammoniacal nitrogen. The range is from 15 to 1000 mg/Kg. The validation was conducted on clay, sand, and loam matrices; and the method is accredited to ISO17025 and MCERTS for Soils. Sludge is unaccredited. (See Appendix 2 for the most recent validation data).

2.0 References and other supporting documents

2.1 WS-353 Reagent Preparation Record
2.2 WS-270 Exchangeable Ammonium Daily Reagent Blank
2.3 WS-698 Exchangeable ammonium sample run log.
2.4 SOP.7.4.27 Holding Times
2.5 Method 4500A & B, AWWA/APHA, 20th Ed., 1998 - Determination of Exchangeable Ammonium and Ammoniacal Nitrogen as N by titration on solids
2.6 CM001 Daily or Before Use Balance Checks
2.7 CM003 Calibration Checks for Auto pipettes, Dispensers and Syringes
2.8 CM006 Calibration of Volumetric Glassware
2.9 PM024 Homogenisation and Preparation of Soil Samples
2.10 WS-386 Calibration Worksheet
2.11 Methods for the Collection and Analysis of Samples from National Grid Sites

3.0 Principle

A sample of soil is shaken with potassium chloride solution, treated with magnesium oxide then steam distilled and the ammonia driven off. The ammonia is collected in boric acid and the result determined by titration against a known concentration of hydrochloric acid.

4.0 Hazards

4.1 General laboratory safety precautions to be taken at all times.

4.2 See Appendix 1 for Health, Safety and Environmental Information assessment at the end of this method before commencing.

5.0 Precision, Accuracy and Performance Characteristics

5.1 Near limit of detection spikes were performed to allow calculation of the LOD.
5.2 A summary of performance data can be found in Appendix 2 of this method. For full Validation data refer to the departmental quality records.

6.0 Apparatus

All glassware is Grade B or better unless otherwise stated.
6.1 Analytical balance calibrated as per CM001.
6.2 Top pan balance calibrated as per CM001.
6.3 2 litre volumetric flask.

6.4 1 litre beaker.
6.5 Desiccator.
6.6 25 ml measuring cylinder
6.7 50 ml measuring cylinder.
6.8 10 ml Autopipette calibrated as per CM003.
6.9 Gerhardt distillation apparatus - Vapodest 20 or equivalent.
6.10 100ml Dispenser calibrated as per CM003.
6.11 10ml Dispenser. calibrated as per CM003.
6.12 Sample containers
6.13 Muffle furnace at 650 ± 20°C.
6.14 50ml burette calibrated as per CM006.
6.15 Conical flasks
6.16 1 litre volumetric flask
6.17 Shaker (Rotatest R100) shaker set at speed 6 – 7.

7.0 Reagents

NOTE: All reagents must be of analytical grade (AR) unless otherwise specified. All reagents are to be labelled with appropriate identifiers including Name of reagent; date prepared; expiry date; and analyst's initials. This information, and the reagent batch number(s) should also be recorded on the reagent preparation log.

All reagents may be made in greater volumes by altering the weights and volumes accordingly.

7.1 Water

High purity reverse osmosis/deionised water with an electrical resistivity of 18MΩ.cm or greater.

7.2 Loamy sand 2.1
Used in both AQC and blank samples.

7.3 Ammonium Sulphate
Analytical grade available commercially.

7.4 AQC 200mg/kg as NH_4 (shelf life = 1 year)
This is Lufa soil 2.1 loamy sand (7.2) spiked with ammonium sulphate at a rate of 7.337 ± 0.05g per 10 ± 0.01kg of soil.

7.5 Potassium Chloride
Analytical grade (Such as the Fisher or Sigma Aldrich products) available commercially.

7.6 2M Potassium Chloride Solution (shelf life = 6 months)

7.6.1 Weigh out 300 ± 2g of Potassium Chloride (7.5) in two 150g portions.

7.6.2 Dissolve in 2 litres of high purity deionised water (7.1).
7.6.3 This can be stored at room temperature and is stable for six months. Record on reagent preparation record WS-353

7.7 Magnesium Oxide Fisher (shelf life = 1 year)
7.7.1 Analytical grade available commercially.
7.7.2 This is prepared by heating at 650 °C for a minimum of 2 hours in a muffle furnace and then allowed to cool in a desiccator over silica gel.
7.7.3 Store in a screw-topped bottle in a desiccator.
7.7.4 This can be stored at room temperature and is stable for one year. Record on reagent preparation record WS-353.

7.8 Bromocresol green
Analytical grade available commercially.

7.9 Methyl red
Analytical grade available commercially.

7.10 Ethanol 95%v/v
Analytical grade available commercially.

7.11 Sodium Hydroxide – 0.1 M standard solution.
Analytical grade available commercially.

7.12 Indicator Solution (shelf life = 1 year)
7.12.1 Dissolve 0.1 ± 0.01g bromocresol green (7.8) and 0.07 ± 0.001g methyl red (7.9) in 100ml ethanol (7.10).
7.12.2 Add 0.1M sodium hydroxide (7.11) drop wise until the colour is reddish purple. Mix well.
7.12.3 This solution can be stored at room temperature and is stable for one year. Record on reagent preparation record WS-353.

7.13 Boric Acid
Analytical grade available commercially.
7.14 2 % Boric Acid Indicator Solution (shelf life = 6 months)
7.14.1 Dissolve 40 ± 0.5 g boric acid (7.13) in approximately 1800 ml of high purity deionised water in a 2-litre volumetric flask.
7.14.2 Add 40 ml of indicator solution (7.12) and make up to the 2-litre mark with high purity deionised water.
7.14.3 This solution can be stored at room temperature and is stable for six months. Record on reagent preparation record WS-353.

7.15 Decon
Available commercially.

7.16 1% Decon wash solution.
7.16.1 Add 1 ml of Decon (7.15) to 100 ml of high purity deionised water.
7.16.2 This solution can be stored at room temperature and is stable for six months.
Note: This wash solution can be made at stronger concentrations for problematic contaminants.

7.17 0.2M Hydrochloric acid
Analytical grade available commercially.

7.18 0.002M Hydrochloric Acid (shelf life = 1 month)
7.18.1 Pipette 10 ± 0.1 ml 0.2M hydrochloric acid (7.17) into approximately 800ml high purity deionised water in a 1 litre volumetric flask.
7.18.2 Dilute to the mark with high purity deionised water and mix well.
7.18.3 This solution can be stored at room temperature and is stable for one month. Record on reagent preparation record WS-353.

7.19 5M Sulphuric Acid
Available Commercially.

8.0 Calibration and Quality Control

8.1 Instrument Blank
8.1.1 Three instrument blanks are run each day. These are prepared using 50 ml of 2M potassium chloride (7.6) + 50 ml of de-ionized water (7.1).
8.1.2 Follow analysis as for samples from 10.5.1.
8.1.3 These results are plotted on WS-270
8.1.4 The average of the three titres done on WS-270 is used to blank correct all results A difference of ±0.2ml is deemed acceptable.
8.2 Process Blank
8.2.1 A process blank is run with every batch of 19 samples. This is prepared using 4 ± 0.05g of loamy sand 2.1 (7.2) and 100 ml of 2M potassium chloride (7.6). The result for this blank should be <LOD. If a positive result is obtained the batch should be failed and re-prepared.
8.2.2 Follow analysis as for samples from 10.5.1.
8.3 AQC
8.3.1 A process AQC is run with every batch of 19 samples, this is a loamy sand spiked with ammonium sulphate at a rate of 200mg/kg of NH_4.
This is prepared using 4 ±0.05g of AQC soil (7.4), and 100 ml of 2M potassium chloride (7.6).
8.3.2 Follow analysis as for samples from 10.1.4.
8.3.3 The process AQC is plotted by labware and compared with the AQC limits. When

standards are run the results should be compared with the limits shown on AQC charts stored in labware. All samples in labware are batch calculated and authorised through 'Options-Batch calculate'. If a standard falls outside the control line limits, repeat the standard and samples since the last correct standard. If two or more consecutive results lie between the warning and the control limits, this is deemed a failure, repeat the standards and samples since the last correct standard. All failures are investigated and documented in the AQC failure spreadsheet on labware.

8.4 System Suitability

8.4.1 For manual titration methods, the system suitability check (SSC) is that the burette being used has been calibrated within the last year. This is recorded on WS-386 stored in the laboratory.

9.0 Sample Preservation and Preparation

9.1 Samples are stored at 5 ± 3 Degrees C until subsampled and then stored in a fridge until extraction.

9.2 See SOP.7.4.27 for holding times.

9.3 The samples are homogenised and weighed in accordance with PM 024 – Homogenisation of soil samples.

9.4 The sample is analysed as a sub sample of the main bulk sample and in the 'as received' state without prior drying and crushing.

9.5 4 ± 0.05g of as received soil is weighed into a red topped tub this is reduced for sludge samples to 1 ± 0.05g due to the higher concentrations normally obtained, lidded and delivered to the Acid Extraction Team for preparation.

9.6 Sample Preparation

9.6.1 Make sure at the start of a run that there is sufficient potassium chloride solution made up, and in the dispenser, for the process blanks, process AQCs and a minimum of 19 samples. Set up batch for labware (ref 10.1).

9.6.2 Take the weighed 4 ± 0.05g of wet soil in the tub and add 100 ml 2M potassium chloride solution (7.6).

9.6.3 Replace lid on the sample and shake well making sure all the soil is in contact with the solution.

9.6.4 Put on Rotatest R 100 shaker with speed set at between 6 and 7 for 1 hour ± 10 minutes.

9.6.5 Whilst samples are shaking, proceed with the instrument set-up as detailed in section 10.2 When shaking is complete; allow to settle.

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10.0 Labware, Instrument and Analytical Procedure

10.1 To Set up Batch for Labware

10.1.1 Open a new batch
10.1.2 Select correct test.
10.1.3 Select prepared – SAVE.
10.1.4 Sample view
10.1.5 Manage batches.
10.1.6 Scan samples into batch or add tray to batch.

10.2 To Set up the Instrument for Gerhardt distillation.

10.2.1 Switch on the water supply to the condensers.
10.2.2 Switch on the instrument using the on/off switch at the front of the machine. A green light will appear when on.
10.2.3 Ensure the water reservoir is full of high purity deionised water.
10.2.4 "**H**" will appear in the display whilst the instrument is heating up. When ready for use "**P**" will appear in the display.

10.3 To set the Programme.

10.3.1 Press **PROG**.
10.3.2 Step 1 - press the "+" or "-" button until "**000**" appears in the time display.
10.3.3 Press **PROG**.
10.3.4 Step 2 - ensure "**000**" appears in the time display.
10.3.5 Press **PROG**.
10.3.6 Step 3 - press the "+" or "-" button until "**120**" appears in the time display.
10.3.7 Press **PROG**.
10.3.8 Step 4 - press the "+" or "-" button until "**070**" appears in the time display.
10.3.9 Press **PROG**.
10.3.10 "**P**" will now appear in the display indicating the instrument is ready for analysis.

10.4 To Purge the System

This should be done three times before and after a batch of samples.
10.4.1 Half fill a Gerhardt distillation tube with high purity deionised water and place in the appropriate position in the left side of the instrument.
10.4.2 Place an empty receiver flask in the appropriate position in the right side of the instrument.
10.4.3 Press **RUN**.
10.4.4 In the time display the seconds will count down as the instrument is running. When finished "**END**" will appear in the time display and "**Pr**" will appear in the step display.
10.4.5 Remove the distillation tube and the receiver flask.

10.5 Sample Distillation

10.5.1 Dispense 5 ml boric acid solution (7.14) into a plastic sample container.

10.5.2 Place the plastic sample container in the right side of the instrument, making sure the plastic tubing is in the container and under the surface of the boric acid.
10.5.3 Measure 50 ml of the prepared potassium chloride extract (9.6) and 50 mls de-ionised water from a 50 ml measuring cylinder into a Gerhardt distillation tube.
10.5.4 Add one scoop (approximately 0.5g) of magnesium oxide (7.7) to the distillation tube immediately before distillation begins.
10.5.5 Place the distillation tube in the left side of the instrument and press **RUN**.
10.5.6 In the time display the seconds will count down as the instrument is running. When finished "**END**" will appear in the time display and "**Pr**" will appear in the step display.
10.5.7 Remove the distillation tube and the plastic tub and titrate (10.6).
10.5.8 The distillation tube should be rinsed between samples with deionised water. This should be replaced with every batch, or if contamination is suspected.
10.5.9 After distilling and cooling, clean the sample tube using a bottle brush and de-ionised water. Rinse thoroughly with de-ionised water, this should remove any deposits but if not add 5M sulphuric acid (7.19), rinse with 1% Decon solution (7.16) then rinse thoroughly with de-ionised water.
Note: The magnesium oxide must not be added in advance of distillation as this initiates the release of ammonia as a gas and any loss of gas will lead to a lowering of results.

10.6 Titration of Distillate

10.6.1 Pour the distillate from the plastic sample cup into a conical flask, ensuring all the sample is rinsed from the tub with deionised water.
10.6.2 Note the initial burette reading before beginning titration.
10.6.3 Titrate dropwise with 0.002M hydrochloric acid until the solution changes from blue green through amethyst to a bright pink colour.
10.6.4 Note the final burette reading and enter the data on to work sheet WS-698.
10.6.5 On completing worksheet, enter results into the labware batch by selecting options – Results entry by test.
10.6.6 Copy results into corresponding labware sections and select save.
10.6.7 The manual results should be transcription checked before being committed.
10.6.8 Change status to ready for QC checking and save.
10.6.9 Run Batch Calculate, Trend and Chart and Batch checks then Authorise.

10.7 Maintenance of Distillation Apparatus

10.7.1 The entire system should be acid washed monthly; this is done by distillation of sulphuric acid. A distillation tube is approximately half filled with DI water, to which is carefully added 40ml of 5M Sulphuric Acid (7.19). This then runs through the distillation procedure. Following the acid wash, the instrument is cleaned by distilling at least 3 times with DI Water.
10.7.2 As required, the distribution head, condenser and Viton cone is removed and soaked overnight in a Decon solution.
10.7.3 At the end of every run, take a damp cloth over the Viton cone, to remove any

crystallization.

11.0 Expression of results

11.1 All results are expressed as mg/kg of ammonia, either as N or as NH_4

$$\text{Ammonium (in mg/kg as } NH_4) = \frac{(\text{titre} - \text{blank titre}) \times \text{molarity of HCl} \times \text{Rmm } NH_4 \times 1000}{\text{sample weight (g)}} \times \frac{\text{mls KCl}}{\text{aliquot}}$$

$$\text{mg/kg as } NH_4 = \frac{(\text{titre} - \text{blank titre}) \times 0.002 \times 18 \times 1000}{\text{sample weight (g)}} \times \frac{100}{5}$$

This can be reduced to

$$\text{mg/kg as } NH_4 = \frac{(\text{titre} - \text{blank titre}) \times 72}{\text{sample weight}}$$

$$\text{Ammonium mg/kg as N} = \frac{(\text{titre} - \text{blank titre}) \times \text{molarity of HCl} \times \text{RRM N} \times 1000}{\text{sample weight}} \times \frac{\text{mls KCl}}{\text{aliquot}}$$

$$\text{mg/kg as N} = \frac{(\text{titre} - \text{blank titre}) \times 0.002 \times 14 \times 1000}{\text{sample weight}} \times \frac{100}{50}$$

This can be reduced to

$$\text{mg/kg as N} = \frac{(\text{titre} - \text{blank titre}) \times 56}{\text{sample weight}}$$

N.B. Samples are corrected for moisture content when report is issued.

12.0 Training Questions

12.1 What are the acceptability criteria for the Instrument reagent blank?
12.2 Why should sufficient potassium chloride for the whole batch be present in the dispenser before prep of the batch begins?
12.3 How is the end point of the titration determined?
12.4 Where should the dried Magnesium oxide be stored when not in use?
12.5 What is used as a system suitability check for this analysis?

13.0 Appendices

1. Health, Safety and Environmental Information.
2. Performance data.

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14. Authorised and approved for adequacy.

Note, the authorisation required varies between 'white' and 'pink' copies, please see below:

ORIGINATED BY:	**…….....**	**Method Owner/Team Leader/Technical Specialist***
DATE:	**……...**	**(White copy)**
CHECKED BY:	**…….....**	**Trained Analyst**
DATE:	**……...**	**(White copy)**
CHECKED BY:	**…….....**	**Technical Specialist (White copy)/Team Leader (White & Pink copy)**
DATE:	**……...**	
CHECKED BY:	**…….....**	**Lab Manager**
DATE:	**……...**	**(White & Pink copy)**
AUTHORISED BY:	**.....**	**Operations/Technical Manager or Technical Services Manager***
DATE:	**……...**	**(White copy)**
SIGNED BY:	**…….....**	**Quality Manager**
DATE:	**……...**	**(White & Pink copy)**

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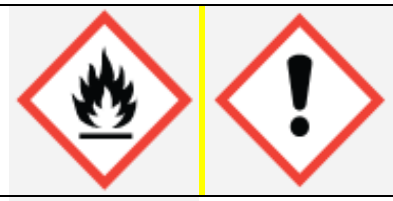
APPENDIX 1

HEALTH, SAFETY AND ENVIRONMENTAL CONTROLS

As a result of the Risk Assessments carried out on this activity, the following requirements concerning control measures, checks and precautions must be observed to ensure the activity is carried out safely and without risk to health.

CHEMICAL HAZARD INFORMATION

Name	Pictograms	Signal Word	H- Statements
Ethanol		Danger	H225 - Highly flammable liquid and vapor. H319 - Causes serious eye irritation.
Sodium hydroxide 0.1M Hydrochloric acid 0.2M Sulphuric acid 5M		Danger	H314 - Causes severe skin burns and eye damage.
Boric acid		Danger	H360FD - May damage fertility or the unborn child.
Ammonium sulphate Bromocresol green Loamy sand Magnesium oxide Methyl red Potassium chloride	Non-hazardous.		

Health and Safety risks from the chemicals used can be found in Safety Data Sheets. It is recommended to use the CoSHH spreadsheet as SDSs can give conflicting advice.

PERSONAL PROTECTIVE EQUIPMENT

The following PPE must be worn whilst conducting this test:

Lab Coat/Overalls	X	Safety Glasses	X
Disposable Gloves	X	Face Shield	
Dust Mask		Ear Defenders	
Other – specify	Heat resistant mit	Other - specify	

See CoSHH spreadsheet for the types of nitrile glove suitable for use when carrying out work with hazardous chemicals. Care should be taken when working near the muffle furnace, and removing samples from the furnace.
Disposable nitrile gloves give very limited protection, particularly from organic liquids. They should be checked regularly for holes and tears and changed frequently during the day as contaminants may permeate through to the skin.
Keep PPE clean, ensure that it is in good condition and, if necessary, check that it is functioning correctly.

OTHER CHECKS AND PRECAUTIONS
The following checks must be made, and precautions taken before and during the test:

TAKE EXTRA CARE WHEN HANDLING VAPODEST TUBES-THEY CAN BECOME VERY HOT

REFER TO THE DOCUMENT "HAZARDOUS CONTAMINANTS IN SAMPLES"

Check that fume extraction is on and working correctly.
Take extra care when working near hot surfaces.
Ensure that any guards are properly fitted and effective.
Ensure that gloves are used and disposed of correctly, so that chemicals and contaminants on their surfaces are not transferred to other items, particularly computer keyboards/mouse and phones.
Apply good standards of housekeeping – keep the working area tidy, keep containers closed.
Ensure chemicals are stored and labelled correctly, particularly those that are flammable, toxic or corrosive. Labelling must include any intermediate and waste containers if appropriate.

Use appropriate carriers when carrying containers of chemicals and solvents.
Guards or interlocks on the vapodests must be in place.
Ensure the pressure outlet valve is channelled away from the working environment.
Sample jars containing potassium chloride are disposed of separately.

For hazardous spills contact the company spill team.

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APPENDIX 2

Method Validation Data

Mini Validation July 2008

Method	Exchangeable Ammonium in Soil
Matrices Spiked	Loamy sand
Spiking Solution	Ammonium Sulphate 10000mg/kg as NH4
Method of spiking	20% spike; 2mls of spike + 100g sample. 80% spike; 8mls of spike + 100g sample.
LOD data	Calculated LOD 14.98 mg/l
IRM/AQC	200 mg/kg as NH4
Precision	6.52
Bias	-4.07
Uncertainty	(2*6.52) + 4.07 = 17.11
Analyst	J Selbie
Method Validation date	July 2008

Summary of Limit of Detection

For full NS 30 validation results, please refer to F:\MethDev\Test method Information\TM024 NH4 in soils. Current limits of detection are specified below.

Note: whenever performance testing is re-evaluated, this information should be amended.

Method	Calculated LOD	Reportable LOD
Manual Titration	14.98 mg/kg	15 mg/kg

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Full Validation May 2005

ALCONTROL LAND VALIDATION DATA

LABORATORY	CHESTER	PARAMETER	Exchangeable Ammonia
START DATE	May-05	ANALYTICAL METHOD	Vapodest
COMPLETED DATE	June-05	MATRIX	SPIKE & RECOVERY DATA
UNITS	mg/kg NH4	DATA SET	SUMMARY

ANALYTE	REQUIRED TARGETS		SANDY SOIL 20% SPIKE				SANDY SOIL 80% SPIKE			
	PREC'N	BIAS	EXPECTED VALUE	MEAN SPIKE REC	PREC'N	BIAS	EXPECTED VALUE	MEAN SPIKE REC	PREC'N	BIAS
units	%	%	mg/kg	mg/kg	%	%	mg/kg	mg/kg	%	%
Exchangeable Ammonia	10	20	386	336	4.0	-13.0	1543	1300	2.7	-15.7

ANALYTE	REQUIRED TARGETS		CLAY SOIL 20% SPIKE				CLAY SOIL 80% SPIKE			
	PREC'N	BIAS	EXPECTED VALUE	MEAN SPIKE REC	PREC'N	BIAS	EXPECTED VALUE	MEAN SPIKE REC	PREC'N	BIAS
units	%	%	mg/kg	mg/kg	%	%	mg/kg	mg/kg	%	%
Exchangeable Ammonia	10	20	386	332	6.8	-13.9	1543	1289	4.3	-16.5

ANALYTE	REQUIRED TARGETS		LOAMY SOIL 20% SPIKE				LOAMY SOIL 80% SPIKE			
	PREC'N	BIAS	EXPECTED VALUE	MEAN SPIKE REC	PREC'N	BIAS	EXPECTED VALUE	MEAN SPIKE REC	PREC'N	BIAS
units	%	%	mg/kg	mg/kg	%	%	mg/kg	mg/kg	%	%
Exchangeable Ammonia	10	20	386	342	4.6	-11.3	1543	1329	4.0	-13.8

COMMENTS

All the spike and recovery data meets MCERTS Criteria.

ALCONTROL LAND VALIDATION DATA

LABORATORY	CHESTER	LABORATORY	Exchangeable Ammonium
START DATE	August-05	START DATE	Vapodest
COMPLETED DATE	August-05		
MATRIX	SAND	MATRIX	LOD Single batch
UNITS	mg/Kg NH4	UNITS	BETWEEN BATCH DATA

ELEMENT	Spike Value	1	2	3	4	5	6	7	8	9	10	11	MEAN	S_t	SPIKE REC (%)	Target Criteria (see page 3) RSD_w	Target Criteria (see page 3) BIAS(%)	LOD as NH4 mg/Kg
	mgKg															<10%	<20%	
Ex Ammonia	30	24.43	29.57	24.43	24.43	27.00	25.72	28.29	28.29	23.14	24.43	28.29	26	2.2	87	8.3	-12.7	6.52
Ex Ammonia	50	42.43	42.43	42.43	45.00	45.00	43.72	46.29	43.72	46.29	41.14	46.29	44	1.8	88	4.1	-11.9	5.48