South Pacific Agricultural Chemistry Laboratory Network (SPACNET)

Recommended Methods for Soil, Plant and Water Analysis

Third Edition

compiled by

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INTRODUCTION

Third Edition:
This is the third edition of this manual, updated and extended six years after the second edition. This edition has grown by some 52 pages with new methods in the soils, plants and water sections. As before (see below) the manual is aimed at laboratories with a basic level of equipment (particularly no ICP), except that a method for metals in water using graphite furnace AAS (GFAAS) has been added. This is a less expensive technique than ICP with similar detection limits.

New soil methods include a rapid method for exchangeable bases (method 129) and CEC (131) which is similar to the methods used by commercial laboratories in New Zealand carrying out soil fertility analyses. It is suitable for this purpose but possibly not for research samples. Also included are methods for measuring available (135), potentially-available (136) and total metals (138) for assessment of potential environmental pollutants.

An acid digestion method has been added for plant analyses (207), which is an alternative to the dry ash (206) method and also allows for the measurement of environmentally sensitive metals.

For waters the section on collection and preservation of water samples has been extensively rewritten and a total metals (316) method has been added. The method for AAS determination of dissolved metals (312) has been rewritten and extended and, as mentioned above, the determination of metals by GFAAS (313) is a new method.

Second Edition:
This manual describes the methods used in some of the laboratories of the South Pacific Agricultural Chemistry Laboratory Network (SPACNET). This is the second edition of the manual with a number of new methods being added. They are methods for anaerobic mineralisable-N and calcium carbonate in soils; the addition of Ca and Mg to the elements measured in Kjeldahl digests of plants and a method for Chloride in plants. In addition a section on water analysis has been added.

The methods are recommended by SPACNET as those methods which produce results useful for regional agronomic and landuse studies, soil fertility advice and now with the water methods added, information for ecological studies, particularly pollution monitoring.

Methods have been collated from the manual used at the Fiji Agricultural Chemistry Laboratory, Koronivia Research Station, Fiji for the analysis of soil, plant, animal feed, water and other agricultural samples (Daly and Wainiqolo, 1993), the soil analysis manual of Blakemore et al (1987), and methods used at the Environmental Chemistry Laboratory, Landcare Research, Palmerston North, New Zealand. The new water methods are from the above sources and also from "Standard Methods for the Analysis of Water and Wastewater, 20th Edition".

Methods were chosen for use in laboratories with a relatively low level of resources and equipment. A pH meter, EC meter, UV/Visible Spectrophotometer and a basic Atomic Absorption Spectrophotometer are the only instruments needed. In addition, for safety reasons and to avoid the cost of a specialist fume cupboard, the nitric / perchloric method for

plant analysis is not included. The alternatives, Kjeldahl digestion for N, P and K, and dry ashing for Ca, Mg and trace elements) are safer, cheaper and produce results of comparable quality.

Some soil methods are aimed at assessing fertility by measuring plant available nutrients, while others measure soil properties that are used to characterise and classify the soil.

Plant methods are to assist in the diagnosis of nutrient deficiencies or toxicities, and to monitor the effectiveness of fertilizer programmes.

Water methods are aimed at assessing suitability of water for irrigation and for pollution monitoring, and while many of the methods are also used for assessing suitability for human consumption the microbiological tests that are essential for this purpose are not included here.

So that each method is complete, all standards and reagents are given and cross-referencing has not been used between methods that use some or all of the same standards or reagents.

Most methods specify the use of two reagent blanks. If similar results are obtained for both blanks, the mean result should be used to correct the samples. If the blank results differ appreciably, the lower value should be used, but the high value indicates the possibility of random errors in the run. This should be checked by re-analysing some of the samples.

The use with each batch of samples of quality control samples with known values and defined acceptable ranges will reduce the chance of systematic errors (such as wrong standards) causing erroneous results.

SI units are used throughout, except for exchangeable bases, cation exchange capacity, and total carbon where milliequivalents (me) and normality (N) are more useful units. 1 me = 1 millimole / charge on free ion, and a 1 N solution = 1 equivalent weight / litre (where the equivalent weight = molecular weight / valency).

Because there are several methods available to produce pure water for chemical analysis the qualifiers distilled or deionised are not used and for the purpose of these methods `water' means pure water.

REFERENCES

B.K.Daly and J.L.Wainiqolo. 1993: Methods of Analysis for Agricultural Samples: Soil, Plant, Animal Feed and Water. Fiji Agricultural Chemistry Laboratory Technical Report 03/93. 115p.

L.C.Blakemore, P.L.Searle and B.K.Daly. 1987: Methods for Chemical Analysis of soils. New Zealand Soil Bureau Scientific Report 80

Standard Methods for the Analysis of Water and Wastewater. 20th Edition. (1998) American Public Health Association, Washington DC.

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SOIL METHODS

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102 SOIL SAMPLE PREPARATION

1. INTRODUCTION

Soil samples collected for chemical analysis must be dried before carrying out analyses, for ease of handling, to allow comparisons between samples of different water contents and to allow the sample to be ground. However, although most results are quoted on an oven-dry (105°C) basis, analyses are carried out on air-dried samples (dried at not more than 40°C) as oven drying causes changes in several chemical properties. To express results on an oven-dry basis, a moisture factor (method 104) is used in the calculation of results.

Samples are ground so that representative sub-samples can be taken even when small amounts are used for analyses. A <2 mm sized sample is used for most analyses, and a <0.25 mm sized sample is used for those analyses where less than 1 g sample weights are used (carbon and nitrogen). Fine grinding is not necessary if these analyses have not been requested.

If particle size analysis is required an un-dried sub-sample is retained, as air-drying can cause irreversible aggregation in some soils. Also if only pH and/or EC are to be analysed, air-drying is not required

2. APPARATUS

2.1 FORCED-AIR DRYING CABINET, with controllable temperature.

2.2 ROLLER MILL, with 2 mm sieve grinding drum; OR

2.3 ROLLING PIN &/OR WOODEN MALLET, AND FLAT SURFACE + 2 mm SIEVE, for manually reducing soil to < 2 mm.

2.4 RING GRINDER OR MORTAR AND PESTLE, for fine grinding.

3. PROCEDURE

3.1 REGISTRATION

3.1.1 Sort samples into the order of field or clients number.

3.1.2 Assign a laboratory number to each sample and record job number, laboratory number, clients number and analyses requested in the register.

3.2 DRYING

3.2.1 Empty the soil sample into a dryer tray and add a paper label with the laboratory number.

3.2.2 Break up the soil into < 1 cm lumps and mix. Remove any insects and as much as possible of the organic matter that was live at the time of sampling (e.g. live roots).

3.2.3 If necessary, take sub-sample for particle size determination. If the sample is very large a portion can be discarded after mixing.

3.2.4 Place the tray in dryer set at not more than 40°C and leave until dry; usually 48 hours.

3.3 GRINDING AND SUB-SAMPLING

3.3.1 Label a large (about 100-mL) sample container (for < 2 mm sample) and a small (about 30-50-mL) sample container (if required for < 0.25 mm sample).

3.3.2 Pour the sample into the drum of a grinder. Switch on the grinder OR Crush sample with mallet or rolling pin.

3.3.3 All of the sample including concretions must be ground, but not stones. If stones are present, they will need to be separated from the soil before they are crushed. Sieve out the stones and put the soil collected back into the grinder.

3.3.4 Thoroughly mix the ground soil.

3.3.5 Carefully sub-sample and fill the large sample container and the small sample container (if required). Discard excess.

3.4 FINE GRINDING

3.4.1 Pour soil from the small sample container into the head of the ring grinder.

3.4.2 Grind for 10 seconds to approximately < 0.25 mm. It is not necessary to use a sieve.

3.4.3 Brush out sample and return to small sample container.

3.4.4 Clean grinder using a paper towel to wipe the inside of the head and rings between samples to ensure that there is no carry-over of material. Where the soil is sticky, the head and rings will need washing between samples. Wash using a plastic brush, rinse with distilled water and dry before next sample.

OR

3.4.5 Grind sample in mortar with pestle, removing stones if necessary.

3.4.6 Sieve sample through a 0.25 mm sieve. Return unground soil to mortar and complete grinding. All of the sub sample (less stones) must be put through the sieve.

3.5 CLEANING UP

3.5.1 When all samples in set have been ground wash all grinding heads, rollers, mortars etc, in tap water, rinse with distilled water and dry well before storing.

3.5.2 Wash dryer trays and dry in drying cabinets.

3.5.3 Brush sieves well with bristle or plastic brushes.

3.5.4 Wipe out roller mills and wipe down benches with a damp cloth.

104 MOISTURE FACTOR

1. INTRODUCTION

Most results of soil chemical analysis are quoted on an oven-dry (105°C) basis, but as oven drying causes changes in several chemical properties, analyses are carried out on air-dried samples (dried at a temperature of not more than 40°C). In order to convert results to an oven-dry basis, a moisture factor is applied in the calculation of results.

It may not be necessary to always use a moisture factor. Air-dry soils typically have water contents ranging from 2-3% up to 20%, with most soils around 5%. If results are required for fertilizer advice rather than research or classification purposes, and the soils are at the low end of the range, then only a small error results from not using a moisture factor correction. It is important to realise that larger errors will result if the samples are not properly air-dried.

The moisture factor correction is not applied to results for pH and phosphate retention.

2. PROCEDURE

2.1 Make all weighings in grams to 3 decimal places.

2.2 Weigh a labelled approximately 7 cm diameter aluminium dish with lid and record the weight (W_1).

2.3 Weigh accurately a 10 - 20 g sample of soil (air-dry, < 2mm) into the dish, and record weight of dish + soil (W_2).

2.4 Dry with lid removed in an oven at 105°C for 8 - 24 hours.

2.5 Remove from oven, fit lid, cool and weigh (W_3).

Note: Because oven-dry soil rapidly picks up water vapour from the atmosphere (even in some desiccators), it is necessary to carry out weighings as soon as the dish is cool enough to handle, but before it cools to room temperature. In practice if about six dishes are removed from the oven at a time, placed on a tray and taken directly to the balance and weighed, these conditions are met.

3. CALCULATION OF RESULTS

$$\text{Moisture Factor} = \frac{\text{wt air-dry soil}}{\text{wt oven-dry soil}}$$

$$= \frac{(W_2 - W_1)}{(W_3 - W_1)}$$

Report results to 3 decimal places.

$$\text{Air-dry Water Content} = \frac{\text{wt water} * 100}{\text{wt oven-dry soil}}$$

$$= \frac{(W2 - W3) * 100}{(W3 - W1)}$$

Report results to 1 decimal place.

106 pH in H_2O, M KCl or 0.01 M $CaCl_2$

1. INTRODUCTION

The measurement of soil pH is one of the simplest determinations to make, however what is being measured is complicated. pH is a measure of the hydrogen ion activity expressed as the negative logarithm, but pH theory applies to dilute aqueous solutions of simple electrolytes. For reasons of practicality soil pH is measured in a suspension of water or dilute salt solutions and so really represents the pH of the suspension in equilibrium with the charged ions on the surfaces of soil particles.

Despite these uncertainties, soil pH is a very useful property to measure as it correlates with many other soil properties such as base saturation. Also, soil pH controls the availability of many plant nutrients, with low or very high pH causing low availability for nutrients such as phosphorus and many trace elements. At pH levels below 5.6 toxic levels of exchangeable aluminium can be present in the soil.

Water is the usual suspension medium for the soil sample, but molar potassium chloride and 0.01 M Calcium chloride are also used. These give lower values for most soils as the potassium or calcium ions replace acidic groups (positively charged H and Al ions) from cation exchange sites on soil clay particles. For some soils, M KCl pH is higher than water pH as the soil clays have a net positive charge and chloride ions from the salt replace hydroxyl groups from the ion exchange sites. KCl pH is measured to identify such soils.

Ratios of soil to water used to measure pH range from 1:1 to 1:10 with 1:2.5 and 1:5 being the most common. The ratio used here is 1:5 as it allows electrical conductivity to be measured on the same extract, and for most soils gives the same answer as a 1:2.5 ratio. Conductivity needs to be measured first on the extract (if required) to avoid possible increase in EC from K^+ and Cl^- ions from the filling solution of some 'high flow' pH electrodes.

2. REAGENTS

2.1 pH 7 BUFFER, use commercially available buffers. Because prepared buffers have a limited life (a few months at most) it is preferable to use the sachet or tablet form that can be prepared when needed.

2.2 pH 4 BUFFER, 0.05 M potassium hydrogen phthalate. Dissolve 1.021 g $COOH.C_6H_4.COOK$ in water in a 100-mL volumetric flask and make up to 100 mL (or use commercial sachet or tablet).

2.3 1 M POTASSIUM CHLORIDE. Dissolve 74.55 g KCl in water, make to 1 L.

2.4 0.01 M CALCIUM CHLORIDE. Dissolve 1.11 g anhydrous $CaCl_2$ (dried at 105°C) in water and make to 1 L.

3. PROCEDURE

3.1 Weigh 10.0 g of soil (air-dry, < 2 mm) into a 200-mL screw cap glass bottle.

3.2 Add 50 mL water or M KCl or 0.01 M $CaCl_2$.

3.3 Cap and shake on an end-over-end shaker for one hour.

3.4 Calibrate pH meter with the pH 7 buffer and set slope or sensitivity with the pH 4 buffer.

3.5 Read and record pH of samples. Report results to one decimal place.

110 ELECTRICAL CONDUCTIVITY

1. INTRODUCTION

This method describes the measurement of the electrical conductivity (EC) of a 1:5 soil:water extract. The conductivity arises from ions in solution dissolved from free salts in the soil, derived from seawater, excess fertiliser or pedogenic processes. Salt levels in soil giving an EC of more than about 0.4 mS/cm can cause damage to germinating plants.

The soil:water ratio is the same as that used for pH and the conductivity can be measured before pH measurement on the same extract. The suspension is not filtered before measurement as suspended particles have a negligible affect on the conductivity, and it is more important to make the measurement quickly, as microbiological activity can change the ionic concentration.

If measurement of individual cations or anions is required the suspension can be filtered after conductivity measurement.

2. REAGENTS

2.1 POTASSIUM CHLORIDE, 0.1 M. Dissolve 7.455 g KCl (dried at 105EC) in water and make to 1 L.

2.2 POTASSIUM CHLORIDE, 0.001 M. Pipette 10 mL 0.1 M KCl into a 1-L volumetric flask and make to 1 L with water.

3. PROCEDURE

3.1 EXTRACTION

3.1.1 If pH in water is to be measured, use sample before pH measurement and go to 3.2, **OR** weigh 10.0 g of soil (air-dry, < 2 mm) into a 200-mL screw cap bottle.

3.1.2 Add 50 mL water.

3.1.3 Cap and shake on an end-over-end shaker for one hour.

3.2 MEASUREMENT

3.2.1 Check meter using the 0.1 and 0.001 M KCl solutions. At 25°C or with a temperature compensated meter these should read 12.9 mS/cm and 147 µS/cm respectively. If meter is not temperature compensated and temperature of solutions is not 25°C apply corrections according to the instrument manual.

3.2.2 Read and record conductivity of samples as mS/cm.
Note: 1 mS/cm = 1 m mho/cm = 1000 µS/cm

4. CALCULATION

Multiply results by moisture factor to correct results to oven-dry basis and report to two decimal places.

Results are usually quoted as mS/cm but an approximate total soluble salts value can be also derived using the relationship:

Soluble Salt (%) (approx.) = mS/cm x 0.35

112 ORGANIC CARBON

1. INTRODUCTION

This method is an adaptation of the Walkley and Black (1934) procedure in which the soil organic matter is oxidised by dichromate ($Cr_2O_7^{2-}$) and sulphuric acid using the heat of dilution of the sulphuric acid (about 120°C) according to the following reaction.

$$2Cr_2O_7^{2-} + 16H^+ + 3C = 4Cr^{3+} + 8H_2O + 3CO_2$$

Unreduced dichromate is titrated with ferrous ammonium sulphate using diphenylamine as a redox indicator.

Oxidation of organic matter is not complete, averaging about 77%, therefore a factor of 1.3 is applied during the calculation.

2. REAGENTS

2.1 POTASSIUM DICHROMATE, 1 N. Dissolve 49.04 g $K_2Cr_2O_7$ (dried at 105°C) in water and make to 1 L.

2.2 FERROUS AMMONIUM SULPHATE, 0.5 N in 0.5 N sulphuric acid (FAS solution). Dissolve 196 g Fe $(NH_4)_2(SO_4)_2.6H_2O$ in about 800 mL water, add 14 mL conc H_2SO_4 and make to 1 L with water.

2.3 DIPHENYLAMINE INDICATOR. Dissolve 0.5 g diphenylamine in 100 mL conc H_2SO_4.

2.4 ORTHOPHOSPHORIC ACID, Conc. sp. gr. 1.85.

2.5 SULPHURIC ACID, Conc. sp gr 1.84.

3. PROCEDURE

3.1 Weigh 0.20 g finely ground soil (air-dry, < 0.25 mm) into a dry 500-mL conical flask.

3.2 Include two reagent blanks with each batch of samples.

3.3 Add 10 mL 1 N potassium dichromate to the flask and swirl gently to disperse the soil and achieve complete wetting.

3.4 In a fume cupboard add 20 mL conc sulphuric acid and immediately swirl vigorously for one minute to thoroughly mix soil with reagents.

Note: This step and the timing of the next step are important as the oxidation of carbon is dependant on the acid being mixed rapidly to obtain the maximum temperature, and on the reaction continuing for the correct time.

3.5 Let stand for 30 minutes.

3.6 Add 200 mL water to the flask.

3.7 Add 10 mL conc. phosphoric acid and five drops of diphenylamine indicator.

3.8 Titrate the excess potassium dichromate with 0.5 N FAS solution. During the titration the indicator colour changes from pale muddy blue to dark muddy blue and flashes to brilliant green at the end point. A desk lamp to provide lateral illumination aids viewing the colour change. Record titration results (T_1 for blank and T_2 for samples). Use the mean of the two blank readings in the calculations if they agree within 0.1 mL; otherwise repeat blank determinations.

4. CALCULATIONS

Normality of FAS (N) = $10 / T_1$ **(1)**

where: T_1 = mL FAS solution for blank titration

Carbon (%) = $(T_1 - T_2) \times N \times 0.003 \times f \times 100/W \times MF$ **(2)**

where:
- T_1 = mL FAS solution for blank titration
- T_2 = mL FAS solution for sample titration
- N = normality of ferrous ammonium sulphate (from (1))
- 0.003 = weight of 1 milliequivalent carbon (g)
- f = oxidation factor (1.3)
- W = sample weight (g)
- MF = moisture factor

Therefore if 0.2 g sample is used:

Carbon (%) = (T1 - T2) x 19.5/T1 x MF (3)

Report results to one decimal place.

5. REFERENCE

Walkley, A.; Black, I.A. 1934. An examination of the Degtjareff method for determining organic matter, and a proposed modification of the chromic acid titration method. Soil Science 37: 29-38.

116 NITROGEN

1. INTRODUCTION

Total nitrogen is determined by a semi-micro Kjeldahl method (Blakemore et al., 1987) that uses digestion with conc. sulphuric acid, sodium sulphate to raise the boiling point, and copper as a catalyst to convert nitrogen in the sample to ammonium sulphate. This is carried out in 50-mL calibrated test tubes inserted in a drilled aluminium block on a hotplate.

Ammonium-nitrogen is determined in the digest by releasing the ammonia from alkaline solution by steam distillation, collection in dilute boric acid followed by titration with hydrochloric acid.

2. APPARATUS

2.1 DIGESTION TUBES, 50-mL calibrated glass test tubes.

2.2 ALUMINIUM HEATING BLOCK, 220 x 220 x 50 mm drilled with four rows of five holes (27 mm diameter, 35 mm depth).

2.3 HOT PLATE, domestic stove style single radiant element with a diameter of about 200 mm and an output of about 2 kW, mounted on a steel frame and fitted with a simmerstat.

2.4 STEAM DISTILLATION ASSEMBLY, glass system such as Parnas-Wagner or Markham, or semi-automated system such as Bucchi.

2.5 BURETTE, readable to 0.05 mL.

3. REAGENTS

3.1 SULPHURIC ACID, Conc.

3.2 KJELDAHL COPPER CATALYST TABLETS, BDH Cat No. 33064. Each tablet contains 1 g sodium sulphate and 0.1 g copper sulphate.

3.3 SODIUM HYDROXIDE SOLUTION, approx. 10 M. Carefully dissolve 400 g NaOH pellets in 1 L water, stirring constantly.

3.4 BORIC ACID, 1%. Dissolve 5.00 g H_3BO_3 in water and make to 500 mL.

3.5 HYDROCHLORIC ACID, 1 M. Prepare from standard ampoule **OR** carefully add 87 mL conc. HCl (sp gr. 1.18) to 500 mL water and make to 1 L.

3.6 HYDROCHLORIC ACID, 0.02 M. Pipette 20 mL 1 M HCl into a 1-L volumetric flask and make to volume with water.

3.7 BROMOCRESOL GREEN-METHYL RED MIXED INDICATOR. Mix 100 mL 0.1% bromocresol green (0.1 g bromocresol green dissolved in 100 mL 95% ethanol) with 20 mL 0.1% methyl red (0.1 g methyl red dissolved in 100 mL 95% ethanol).

4. PROCEDURE

4.1 DIGESTION

4.1.1 Weigh 0.50 g finely ground soil (air-dry, < 0.25 mm) into a dry 50-mL calibrated test tube.

4.1.2 Two reagent blanks should be carried throughout the following procedure.

4.1.3 Moisten the soil with a few drops of water and allow the moisture to penetrate.

4.1.4 Add one catalyst tablet.

4.1.5 Add 3 mL conc. H_2SO_4.

4.1.6 Swirl gently to mix and place on the preheated aluminium block.

4.1.7 Soils high in organic matter need careful watching to prevent loss of sample by frothing. If this occurs remove tube from rack to allow froth to settle then replace.

4.1.8 Boil the digestion mixture until it decolourises (usually a pale greenish brown or off white colour) and then carry on digestion for a further 20 - 30 minutes.

4.1.9 Remove tube from block.

4.1.10 Before the digest is completely cooled (five - six minutes after removal from block) carefully add 10 - 15 mL water and swirl to dissolve digest.

4.1.11 When cool, make to 50-mL mark with water, stopper, and shake vigorously. Allow solids to settle.

Note: If only about 5 mL water is added instead of diluting to 50 mL, the whole digest can be used for the distillation step. The advantage of making to 50 mL and taking an aliquot, is that more than one distillation and titration can be carried out, and other elements can be determined in the digest if required.

4.2 DISTILLATION AND TITRATION

4.2.1 Before analysing samples wash distillation apparatus by carrying out a distillation using water only.

4.2.2 Transfer a 20 mL sample aliquot to the steam distillation apparatus.

4.2.3 Add 10 mL 10 M sodium hydroxide.

4.2.4 Into a 100-mL conical flask add 10 mL 1% boric acid and 5-6 drops mixed indicator and place flask under the delivery tube of the condenser so that the tip is under the surface of the liquid.

4.2.5 Steam distil sample solution. The indicator in the boric acid will change colour as the ammonia begins to distil over.

4.2.6 When about 30 - 40 mL of distillate has been collected remove 100-mL flask from apparatus, rinsing the tip of the delivery tube with water into the flask.

4.2.7 Stop the entry of steam. The distilling flask will empty and then can be removed.

4.2.8 Titrate the distillate against 0.02 M HCl, to the neutral grey colour of the indicator. Record titres, T_1 for blanks and T_2 for samples.

5. CALCULATION OF RESULTS

$$\text{Nitrogen (\%)} = (T_2 - T_1) \times M \times 0.014 \times 100/W \times 50/v \times MF$$

where:

T_2	=	sample titre (mL)
T_1	=	blank titre (mL)
M	=	molarity of HCl
0.014	=	weight of 1 mM nitrogen (g)
W	=	sample weight (g)
V	=	aliquot of sample taken (mL). The term (50/v) is left out if whole digest is used.
MF	=	moisture factor.

For a 0.5 g sample, 0.02 M HCl titrant and 20 mL sample aliquot:

$$\text{Nitrogen (\%)} = (T2 - T1) \times 0.14 \times MF$$

Report results to two decimal places.

6. REFERENCE

Blakemore, L.C.; Searle, P.L.; Daly, B.K. 1987. Methods for Chemical Analysis of Soils. New Zealand Soil Bureau Scientific Report 80. 103 p.

118 ANAEROBIC MINERALISABLE NITROGEN

1. INTRODUCTION

Anaerobic mineralisable nitrogen is determined as the difference between the ammonium measured in two 2 M KCl soil extracts. One is extracted immediately and the other after a seven day incubation at 40°C with the soil covered by water (Keeney, 1982). Ammonium-nitrogen is determined in the extracts by releasing the ammonia from alkaline solution by steam distillation, collection in dilute boric acid followed by titration with hydrochloric acid (Blakemore et al, 1987).

The incubation is carried out in sealed containers that have as small a head space as possible after the addition of the soil and water. Universal bottles are satisfactory.

The method described below is adapted from Keeney (1982) and is based on that of Bremner (1965). It provides an index of nitrogen availability, not an estimate of true field mineralisation.

2. REAGENTS

2.1 POTASSIUM CHLORIDE, 2 M. Dissolve 149 g KCl in water and make to 1 litre.

2.2 POTASSIUM CHLORIDE, 2.5 M. Dissolve 186.3 g KCl in water and make to 1 litre.

2.3 SODIUM HYDROXIDE SOLUTION, approx. 10 M. Carefully dissolve 400 g NaOH pellets in 1 L water, stirring constantly.

2.4 BORIC ACID, 1%. Dissolve 5.00 g H_3BO_3 in water and make to 500 mL.

2.5 HYDROCHLORIC ACID, 1 M. Prepare from standard ampoule **OR** carefully add 87 mL conc. HCl (sp gr. 1.18) to 500 mL water and make to 1 L.

2.6 HYDROCHLORIC ACID, 0.01 M. Pipette 10 mL 1 M HCl into a 1-L volumetric flask and make to volume with water.

2.7 BROMOCRESOL GREEN-METHYL RED MIXED INDICATOR. Mix 100 mL 0.1% bromocresol green (0.1 g bromocresol green dissolved in 100 mL 95% ethanol) with 20 mL 0.1% methyl red (0.1 g methyl red dissolved in 100 mL 95% ethanol).

3. PROCEDURE

3.1 PREPARATION

3.1.1 After sampling do not leave samples in sealed plastic bags at room temperature for more than one to two days. Store at < 4°C.

3.1.2 Sieve field-moist sample through a 2-mm or 4-mm sieve, taking care to remove roots and macro-fauna.

3.1.3 Measure soil water content of samples, by oven-drying at 105°C for at least 16 hours a subsample of approximately 20 g of the field moist soil in a pre-weighed container. Use the following equation to express water content as percent of dry soil:

$$\text{Water Content (\% dry wt)} = \frac{\text{wt water} * 100}{\text{wt dry soil}} \quad \textbf{(1)}$$

3.1.4 Use the calculated water content to determine the weight of moist soil required equivalent to 5g oven-dry (o.d) soil. Use formula:

$$\text{Wt moist soil required (g)} = \frac{5 * (100+\%\text{water})}{100} \quad \textbf{(2)}$$

3.1.5 Weigh two 5 g oven-dry equivalent subsamples (from equation 2), one into a universal bottle for incubation and the other into a 100-mL extracting bottle.

3.1.6 Two reagent blanks should be carried throughout the following procedure.

3.2 INCUBATION

3.2.1 To the universal bottles add 10 mL water and tightly cap.

3.2.2 Place in an incubator at 40°C for seven days.

3.3 DAY ZERO EXTRACTION

3.3.1 To the subsample in the extracting bottle add 50 mL 2 M KCl.

3.3.2 Shake on an end-over-end shaker for one hour.

3.3.3 Filter through a No.42 filter paper, into tubes or vials.

3.3.4 Cap and store at < 4°C or frozen if not to be read immediately.

3.4 DAY SEVEN EXTRACTION

3.4.1 Remove universal bottles from incubator and shake to mix contents.

3.4.2 Transfer contents to 100-mL extraction bottles using 40 mL 2.5 M KCl.

3.4.3 Shake on an end-over-end shaker for one hour.

3.4.4 Filter through a No.42 filter paper, into tubes or vials.

3.4.5 Cap and store at < 4°C or frozen if not to be read immediately.

3.5 DISTILLATION AND TITRATION

3.5.1 Before analysing samples wash distillation apparatus by carrying out a distillation using water only.

3.5.2 Transfer a 20 mL sample aliquot to the steam distillation apparatus.

3.5.3 Add 3 - 5 mL 10 M sodium hydroxide.

3.5.4 Into a 100-mL conical flask add 10 mL 1% boric acid and 5-6 drops mixed indicator and place flask under the delivery tube of the condenser so that the tip is under the surface of the liquid.

3.5.5 Steam distil sample solution. The indicator in the boric acid will change colour as the ammonia begins to distil over.

3.5.6 When about 30 - 40 mL of distillate has been collected remove 100-mL flask from apparatus, rinsing the tip of the delivery tube with water into the flask.

3.5.7 Stop the entry of steam. The distilling flask will empty.

3.5.8 Titrate the distillate against 0.01 M HCl, to the neutral grey colour of the indicator. Record titres, T_1 for blanks and T_2 for samples.

4. CALCULATION OF RESULTS

Anaerobic Mineralisable N (mg/kg) = $(T_2 - T_1) \times M \times 14 \times 1000/5 \times (50+(W-5))/v$

where:

T_2	=	sample titre (mL)
T_1	=	blank titre (mL)
M	=	molarity of HCl
14	=	weight of 1 mM nitrogen (mg)
W	=	wet sample weight (g)
V	=	aliquot of sample taken (mL).

For 0.01 M HCl titrant and 20 mL sample aliquot:

Anaerobic Mineralisable N (mg/kg) = (T2 - T1) x (50+(W-5)) x 1.4

Report results to the nearest whole number.

5. REFERENCES

L.C.Blakemore, P.L.Searle and B.K.Daly. 1987: Methods for Chemical Analysis of Soils. New Zealand Soil Bureau Scientific Report 80

J.M.Bremner. 1965: Nitrogen availability indexes. in C.A.Black et al. Methods of Soil Analysis Part 2. Agronomy 9:1324-1345. American Society of Agronomy, Madison, Wisconsin.

D.R.Keeney. 1982: Nitrogen availability indices. in A.L.Page et al (ed). Methods of Soil Analysis Part 2. Chemical and Microbiological Properties: 711-733. American Society of Agronomy, Madison, Wisconsin.

122 OLSEN-AVAILABLE PHOSPHORUS

1. INTRODUCTION

This method is based on the phosphorus extraction method of Olsen et al. (1954), which uses an extraction with bicarbonate to estimate plant-available phosphorus in soil. Phosphate in solution is determined colorimetrically using the Murphy and Riley (1961) method as described by Blakemore et al. (1987). The method is similar to that used by AgResearch to produce soil P-test values for New Zealand soils (Cornforth, 1980).

2. REAGENTS

2.1 EXTRACTING REAGENT, (0.5 M $NaHCO_3$). Dissolve 42.0 g sodium hydrogen carbonate in about 980 mL water. Adjust pH to 8.5 by adding dropwise approximately 10 M sodium hydroxide (40 g NaOH dissolved in 100 mL water). Must be made up immediately before use.

2.2 SULFURIC ACID, 5 M. Carefully add 683 mL conc. H_2SO_4 to 2 L water, cool, and make to 2.5 L.

2.3 SULFURIC ACID, 1 M. Carefully add 27.3 mL conc H_2SO_4 to water, cool and make to 500 mL.

2.4 SULPHURIC ACID, 0.1 M. Dilute 100 mL 1 M H_2SO_4 to 1 L with water.

2.5 MURPHY AND RILEY REAGENT A, 1.2% ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, with 100 mg/L antimony in 2.5 M H_2SO_4.

2.5.1 Dissolve 60 g ammonium molybdate in 1 L water. The rate of solution may be increased by heating, but do not heat above 60°C. Cool.

2.5.2 Dissolve 1.334 g antimony potassium tartrate in 250 mL water.

2.5.3 Add both solutions to 2.5 L 5 M H_2SO_4. Mix well, make to 5 L with water and store in dark bottles.

2.6 MURPHY AND RILEY REAGENT B. Dissolve 1.06 g ascorbic acid in 100 mL of reagent A and mix. Prepare on day of use.

3. STANDARDS

3.1 STOCK SOLUTION (200 mg/L P). Dissolve 0.4394 g potassium dihydrogen orthophosphate, KH_2PO_4 (dried at 105°C) in water and make to 500 mL.

3.2 WORKING STOCK (20 mg/L P). Pipette 20 mL aliquot of stock solution (200 mg/L P) into a 200-mL volumetric flask and make to volume with 0.5 M $NaHCO_3$.

3.3 WORKING STANDARDS. Pipette 0, 2, 5, 10 and 20 mL of the working stock solution (20 mg/L P) into 100-mL volumetric flasks and make to volume with 0.5 M $NaHCO_3$. These standards contain 0, 0.4, 1.0, 2.0 and 4.0 mg/L P.

4. PROCEDURE

4.1 EXTRACTION

4.1.1 Weigh 1.00 g soil (air-dry, < 2 mm) into a screw cap, 50-mL polypropylene centrifuge tube.

4.1.2 Add 20 mL extracting reagent. As the amount of phosphorus extracted is time dependent, it is important that the addition of reagents and later filtering is done without delay.

4.1.3 Include two reagent blanks throughout the procedure.

4.1.4 Shake for 30 minutes using an end-over-end shaker at about 50 rpm.

4.1.5 Filter through a No.42 filter paper, into tubes or vials.

4.1.6 Cap and store in a refrigerator if not read immediately.

4.2 DETERMINATION

4.2.1 Pipette 4 mL sample filtrates or standard solutions into 25-mL stoppered tubes.

4.2.2 Add 10 mL 0.1 M H_2SO_4 to neutralise the extracting solution.

4.2.3 Mix well, and leave to stand for one - two hours with intermittent shaking to ensure complete reaction.

4.2.4 Add 4 mL Murphy and Riley Reagent B, stopper and mix well.

4.2.5 Maximum colour is produced in about one hour and is stable for 24 hours.

4.2.6 Read the absorbance on a spectrophotometer at 880 nm. Another, less sensitive peak at 660 nm can also be used if the spectrophotometer cannot be used at 880 nm.

5. CALCULATION

Prepare a standard curve of mg/L P against absorbance.

Read off unknowns as mg/L P.

Olsen P (mg/kg) = (a - b) x V/W x MF

where:
- a = P in sample solution (mg/L)
- b = P in blank solution (mg/L)
- V = volume of extracting reagent (mL)
- W = sample weight (g)
- MF = moisture factor

Therefore if 1 g sample and 20 mL extracting reagent is used:

Olsen P (mg/kg) = (a - b) x 20 x MF

Report results to nearest whole number.

6. REFERENCES

Blakemore, L.C.; Searle, P.L.; Daly, B.K. 1987. Methods for Chemical Analysis of Soils. New Zealand Soil Bureau Scientific Report 80. 103 p.

Cornforth, I.S. 1980. Soils and fertilisers: Soil Analysis: Interpretation. Ag Link FPP 556. NZ Ministry of Agriculture and Fisheries.

Murphy, J.; Riley, J.P. 1962. A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta 27: 31 - 36.

Olsen, S.R.; Cole, C.V.; Watanabe, F.S.; Dean, L.A. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Department Circular 939.

128 EXCHANGEABLE BASES (Ca, Mg, K & Na) – 1:50

1. INTRODUCTION

Cation exchange is the interchange between a cation in solution and another cation on the surface of any surface-active material such as clay or organic matter. In soil the principal cations found in the exchangeable form are the basic cations Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}, and the acidic cations H^{+} and Al^{3+}.

Determination of the exchangeable bases is useful because these are the forms of the elements that are considered to be plant available, by exchange with hydrogen ions from the exudates of root hairs and soil micro-organisms. Therefore the amounts of the exchangeable bases present is important for plant growth.

Molar ammonium acetate buffered to pH 7 is the most widely used solution for the extraction of exchangeable bases and determination of cation exchange capacity (CEC, Method 130).

This method includes three procedures for the extraction of exchangeable bases. The shaking extraction is used if exchangeable bases only are needed. If CEC and percentage base saturation are also needed the leaching or the automatic extractor procedure are used. In both of these methods the CEC is determined by washing excess ammonium acetate from the sample with alcohol after the first leaching, and then leaching adsorbed ammonium ions from the sample with 1 M NaCl.

The shaking extraction for exchangeable bases is adapted from the method described by Daly et al. (1984), the automatic extractor method and the leaching procedure are adapted from those described by Blakemore et al. (1987).

Solutions are diluted prior to measurement of the bases by flame spectroscopy to reduce the salt level and thus prevent nebuliser blockage. Caesium is added to eliminate ionization interference in the determination of potassium and sodium, and strontium is added to prevent chemical interference in the determination of calcium and magnesium.

2. REAGENTS

2.1 AMMONIUM ACETATE (CH_3COONH_4), 1 M, pH 7.0.

2.1.1 In a fume cupboard add 575 mL acetic acid (CH_3COOH, 99%) to about 8 L water. Mix.

2.1.2 Add 750 mL ammonia solution (NH_4OH, sp. gr. 0.91).

2.1.3 Make to 10 L with water and mix.

2.1.4 Check pH and adjust to 7.0 ± 0.05 with 2 M NH_4OH (150 mL NH_4OH (sp. gr. 0.91) made to 1 L).

2.1.5 Allow to cool before using.

2.2 ACID-WASHED SILICA SAND. Silica sand to be treated should be relatively pure (whitish), and sieved to the approximate size range 0.25 - 0.5 mm.

2.2.1 Place about 10 L of sand in a large container (a plastic bucket is suitable).

2.2.2 Wash with tap water to disperse organic matter, silt and clay, stir vigorously and remove impurities by decanting.

2.2.3 Repeat until the supernatant is clear.

2.2.4 Add 2.5 L conc. HCl to the sand and leave in a fume cupboard overnight.

2.2.5 Wash the acid from sand with large quantities of tap water, stirring and decanting as before.

2.2.6 Transfer sand to a large Buchner funnel with No. 541 Whatman filter, connected to a vacuum. Wash a number of times with distilled water until the filtrate is chloride free.

2.2.7 Dry the sand in an oven at 105°C.

2.3 MACERATED FILTER PAPER. Macerate a quantity of fast, pure filter paper (Whatman No. 31, 41, or ashless clippings are all suitable) in water, using a laboratory or food blender. Pour slurry into a large Buchner funnel and allow excess water to drain. Store moist in a closed jar.

2.4 STRONTIUM - CAESIUM SOLUTION, 7500 mg/L Sr & 25000 mg/L Cs. Dissolve 23 g $SrCl_2.6H_2O$ and 31.8 g CsCl in water and make to 1 L.

2.5 1+3 BASES DILUENT SOLUTION. Carefully add 27 mL conc. HCl to about 200 mL water, add 107 mL Sr/Cs solution and make to 1 L.

2.6 1+9 BASES DILUENT SOLUTION. Carefully add 23 mL conc. HCl to 166 mL 1 M ammonium acetate, add 90 mL Sr/Cs solution and make to 1 L.

2.7 HYDROCHLORIC ACID, 0.2 M. Carefully add 17.5 mL conc. HCl to water and make to 1 L.

3. STANDARDS

3.1 CALCIUM STOCK, 5,000 mg/L. Use commercial solution or carefully dissolve 6.243 g calcium carbonate ($CaCO_3$), dried at 105°C, in enough 1+1 HCl (approx. 5 M) to just dissolve it (about 20 mL), and make up to 500 mL with 0.2 M HCl.

3.2 MAGNESIUM STOCK, 1,000 mg/L. Use commercial solution or carefully dissolve 0.500 g magnesium ribbon (cleaned by dipping in dilute HCl, rinsed with water and dried) in 10 mL 1+1 HCl, and make to 500 mL with 0.2 M HCl.

3.3 POTASSIUM STOCK, 1,000 mg/L. Use commercial solution or dissolve 0.953 g KCl (dried at 105°C for 2 hours) in 0.2 M HCl and make to 500 mL with 0.2 M HCl.

3.4 SODIUM STOCK, 1,000 mg/L. Use commercial solution or dissolve 1.271 g NaCl (dried at 105°C for 2 hours) in 0.2 M HCl and make to 500 mL with 0.2 M HCl.

3.5 MULTIPLE WORKING STOCK SOLUTION, 500 mg/L Ca, 100 mg/L Mg, 50 mg/L K and Na. Pipette 50 mL Ca stock (5,000 mg/L), 50 mL Mg stock (1,000 mg/L), 25 mL K stock (1,000 mg/L) and 25 mL Na stock (1,000 mg/L) into a 500-mL volumetric flask, and make to volume with water. Store in an inert plastic bottle (preferably teflon).

3.6 WORKING STANDARDS. Pipette aliquots of the multiple working stock solution into 500-mL volumetric flasks according to the following table:

Working Standard	Volume of multiple working stock (mL per 500 mL)	Concentration of working standards (mg/L)			
		Ca	Mg	K	Na
0	0.0	0.0	0.0	0.0	0.0
1	5.0	5.0	1.0	0.5	0.5
2	10.0	10.0	2.0	1.0	1.0
3	25.0	25.0	5.0	2.5	2.5
4	50.0	50.0	10.0	5.0	5.0

To each flask add 10 mL conc. HCl, 40 mL Sr/Cs solution, and 125 mL 1 M ammonium acetate. Make to 500 mL with water and mix well. Store in plastic bottles.

4. PROCEDURE

4.1 EXTRACTION BY SHAKING

4.1.1 Weigh 0.80 g soil (air-dry, < 2 mm) into a 50-mL screw-cap polypropylene centrifuge tube.

4.1.2 Include two reagent blanks with each batch of samples.

4.1.3 Add 40 mL M ammonium acetate.

4.1.4 Shake on an end-over-end shaker for one hour.

4.1.5 Filter through Whatman No. 42 filter paper and ensure a clear solution is obtained.

4.1.6 Retain the solution for measurement of individual bases.

4.2 EXTRACTION BY LEACHING

4.2.1 Weigh 1.00 g soil (air-dry, < 2 mm) into a small beaker.

4.2.2 Include two reagent blanks with each batch of samples.

4.2.3 Add 2 g of acid-washed silica sand, and mix. Clayey soils may require more sand. Use the same amount of sand for blank.

4.2.4 Pack a plug of macerated filter paper into a semi-micro leaching tube held in a rack.

4.2.5 Pour in soil and sand mixture. Pour about 1 g extra sand on top of soil and sand mixture.

4.2.6 Place a 50-mL volumetric flask (receiving flask) under the leaching tube (see figure 1).

4.2.7 Add 50 mL 1 M ammonium acetate to 50-mL volumetric flask (delivery flask) and percolate through leaching tube by inverting flask in rack so that the top of the flask is inside the neck of the leaching tube.

4.2.8 When leaching is complete (usually overnight) make receiving flask to 50 mL with water and retain solution for measurement of individual bases.

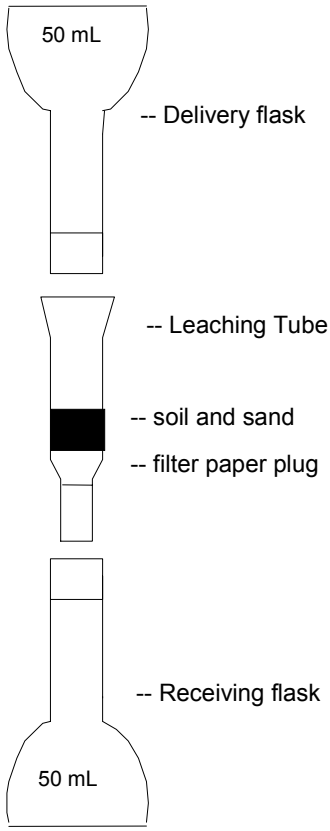

Figure 1: Leaching Setup

4.2.9 Retain NH_4^+ saturated soil in leaching tube for ethanol and sodium chloride leachings for CEC measurement (method 130).

Notes: 1. If leaching takes less than about two hours it is probable that most of the ammonium acetate has flowed through a channel rather than the soil, and low results will be obtained. Repeat leaching and use technique described in note 3 to prevent channelling.

2. To prevent Na contamination a separate set of delivery and receiving flasks should be used for the NaCl leaching.

3. In order to avoid the formation of channels or air-locks in the column of soil and sand, apply gentle suction to the outlet of the leaching tube when the ammonium acetate is first added. This can be done by attaching a short length of rubber tubing to the outlet, squeezing the whole tube and, while blocking off the end, releasing the squeezed portion. The suction is applied until the ammonium acetate just reaches the filter paper plug, then the rubber tube is removed and the receiving flask is quickly placed under the leaching tube.

4.3 EXTRACTION BY AUTOMATIC EXTRACTOR

Note. This procedure is essentially a controlled leaching, using an extractor manufactured by Concept Engineering Corp. (USA). The extraction is carried out in 60-mL plastic syringes arranged as shown in see figure 2.

4.3.1 Weigh 1.00 g soil (air-dry, < 2 mm) into a small beaker.

4.3.2 Include two reagent blanks with each batch of samples.

4.3.3 Add 2 g of acid-washed silica sand, and mix.

4.3.4 Weigh to one decimal place a complete labelled receiving syringe (W_1).

4.3.5 Pack a plug of macerated filter paper into the leaching tube and press flat using a tamper.

4.3.6 Pour in soil and sand mixture.

4.3.7 Place on apparatus and fit receiving syringe.

4.3.8 With a wash bottle add about 20 mL 1 M ammonium acetate to the leaching tube, rinsing any sample off the walls of the tube.

4.3.9 Let stand for about 15 minutes.

4.3.10 Run extractor at maximum speed until about 5 - 10 mm of solution remains above sample.

4.3.11 Fit reservoirs to leaching tubes.

4.3.12 Add 1 M ammonium acetate to the 40-mL mark on the reservoir.

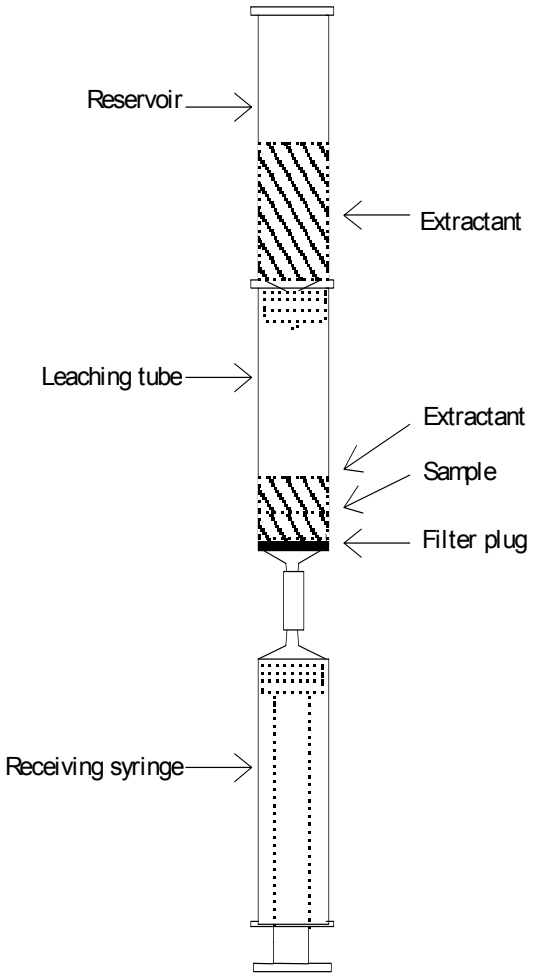

Figure 2: Syringe Arrangement on Extractor

4.3.13 Run extractor to complete extraction in about 4 hours.

4.3.14 Pull any ammonium acetate solution remaining in leaching tube into receiving syringe by hand pressure on syringe plunger.

4.3.15 Remove receiving syringes and weigh to 1 decimal place (W_2).

4.3.16 Mix sample in receiving syringe well and retain solution for measurement of individual bases.

4.3.17 Remove reservoirs and rinse with water.

4.3.18 Retain NH4+ saturated soil in leaching tube for ethanol and sodium chloride leachings for CEC measurement (method 130).

4.4 MEASUREMENT

4.4.1 Dilute 3 mL sample or blank solutions with 9 mL of the 1+3 bases diluent solution.

4.4.2 Determine exchangeable bases by flame spectroscopy using the working standards. Normally standard 4 is used as the top standard, but if samples with very low levels of exchangeable bases are measured, standard 3 can be used to give better sensitivity. If samples are too concentrated dilute 1 mL sample solution with 9 mL of the 1+9 bases diluent solution.

4.4.3 An air-acetylene flame is used for all elements. Mg is determined by atomic absorption spectrophotometry (AAS) at 285.2 nm, Ca by AAS at 422.7 nm, K by flame emission spectroscopy (FES) at 766.5 nm and Na by FES at 589.0 nm.

5. CALCULATIONS

Ca, Mg, K or Na (me/100g) = (a - b) x V/1000 x 100/W x d/z x MF

where:
- a = concentration of sample solution (mg/L)
- b = concentration of blank solution (mg/L)
- V = final volume of leachate or extractant (mL) ($V = W_2 - W_1$ for method 4.3 automatic extractor)
- W = sample weight (g)
- d = dilution (4x or 10x)
- z = equivalent weight of element (Ca = 20.04, Mg = 12.2, K = 39.1, Na = 23)
- MF = moisture factor

For 1.0 g (or 0.8 g) sample, 50 mL leachate (or 40 mL extractant) - (shaking or leaching extraction):

Ca, Mg, K or Na (me/100g) = (a - b) x 20/z x MF for 4x dilution

or = (a - b) x 50/z x MF for 10x dilution

For 1.0 g sample, V mL leachate - (automated extractor extraction):

Ca, Mg, K or Na (me/100g) = (a - b) x (W2-W1) x 0.4/z x MF for 4x dilution

or = (a - b) x (W2-W1) x 1/z x MF for 10x dilution

Report results to two decimal places.

6. REFERENCES

Blakemore, L.C.; Searle, P.L.; Daly, B.K. 1987. Methods for Chemical Analysis of Soils. New Zealand Soil Bureau Scientific Report 80. 103 p.

Daly, B.K.; Manu, V.T.; Halavatau, S.M. 1984. Soil and plant analysis methods for use at the Agricultural Research Station, Vaini, Tonga. New Zealand Soil Bureau Laboratory Report AN2.

129 EXCHANGEABLE BASES (Ca, Mg, K & Na) – 1:20

1. INTRODUCTION

Cation exchange is the interchange between a cation in solution and another cation on the surface of any surface-active material such as clay or organic matter. In soil the principal cations found in the exchangeable form are the bases Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}, and the cations H^{+} and Al^{3+}.

Determination of the exchangeable bases is useful because these are the forms of the elements that are considered to be plant available, by exchange with hydrogen ions from the exudates of root hairs and soil micro-organisms. Therefore the amount of the exchangeable bases present is important for plant growth.

Molar ammonium acetate buffered to pH 7 is the most widely used solution for the extraction of exchangeable bases and determination of cation exchange capacity (CEC, Method 144 & 145).

This method determines the exchangeable basic cations (bases) Ca, Mg, K and Na in soil and is derived from those described by Daly et al. (1984) and Blakemore et al. (1987). Cation Exchange Capacity (CEC) can be rapidly estimated by measuring the pH of the extract after extraction (see method 145). A 1:20 extraction ratio is used rather than the 1:50 in method 142. This lower ratio is used to give adequate sensitivity to the CEC estimation procedure. It is possible that for soils with high levels of calcium and magnesium the 1:20 ratio will not quantitatively extract all of these elements. As this method is generally used for soils where soil fertility and the possible need for fertilisers is being assessed, and it is low levels of bases that are important, this is an acceptable variation.

Solutions are diluted prior to measurement of the bases by flame spectroscopy to reduce the salt level and thus prevent nebuliser blockage. Caesium is added to eliminate ionization interference in the determination of potassium and sodium, and strontium is added to prevent chemical interference in the determination of calcium and magnesium.

2. REAGENTS

2.1 AMMONIUM ACETATE (CH_3COONH_4), 1 M, pH 7.0.

2.1.1 In a fume cupboard add 575 mL acetic acid (CH_3COOH, 99%) to about 8 L water. Mix.

2.1.2 Add 750 mL ammonia solution (NH_4OH, sp. gr. 0.91).

2.1.3 Make to 10 L with water and mix.

2.1.4 Check pH and adjust to 7.0 ± 0.05 with 2 M NH_4OH (150 mL NH_4OH (sp. gr. 0.91) made to 1 L).

2.1.5 Allow to cool before using.

2.2 STRONTIUM - CAESIUM SOLUTION, 7500 mg/L Sr & 25000 mg/L Cs. Dissolve 23 g $SrCl_2.6H_2O$ and 31.8 g CsCl in water and make to 1 L.

2.3 1+9 BASES DILUENT SOLUTION. Carefully add 23 mL conc. HCl to 166 mL 1 M ammonium acetate, add 90 mL Sr/Cs solution and make to 1 L.

2.4 HYDROCHLORIC ACID, 0.2 M. Carefully add 17.5 mL conc. HCl to water and make to 1 L.

3. STANDARDS

3.1 CALCIUM STOCK, 5,000 mg/L. Use commercial solution or carefully dissolve 6.243 g calcium carbonate ($CaCO_3$), dried at 105°C, in enough 1+1 HCl (approx. 5 M) to just dissolve it (about 20 mL), and make up to 500 mL with 0.2 M HCl.

3.2 MAGNESIUM STOCK, 1,000 mg/L. Use commercial solution or carefully dissolve 0.500 g magnesium ribbon (cleaned by dipping in dilute HCl, rinsed with water and dried) in 10 mL 1+1 HCl, and make to 500 mL with 0.2 M HCl.

3.3 POTASSIUM STOCK, 1,000 mg/L. Use commercial solution or dissolve 0.953 g KCl (dried at 105°C for 2 hours) in 0.2 M HCl and make to 500 mL with 0.2 M HCl.

3.4 SODIUM STOCK, 1,000 mg/L. Use commercial solution or dissolve 1.271 g NaCl (dried at 105°C for 2 hours) in 0.2 M HCl and make to 500 mL with 0.2 M HCl.

3.5 MULTIPLE WORKING STOCK SOLUTION, 500 mg/L Ca, 100 mg/L Mg, 50 mg/L K and Na. Pipette 50 mL Ca stock (5,000 mg/L), 50 mL Mg stock (1,000 mg/L), 25 mL K stock (1,000 mg/L) and 25 mL Na stock (1,000 mg/L) into a 500-mL volumetric flask, and make to volume with water. Store in an inert plastic bottle (preferably teflon).

3.6 WORKING STANDARDS. Pipette aliquots of the multiple working stock solution into 500-mL volumetric flasks according to the following table:

Working Standard	Volume of multiple working stock (mL per 500 mL)	Concentration of working standards (mg/L)			
		Ca	Mg	K	Na
0	0.0	0.0	0.0	0.0	0.0
1	5.0	5.0	1.0	0.5	0.5
2	10.0	10.0	2.0	1.0	1.0
3	25.0	25.0	5.0	2.5	2.5
4	50.0	50.0	10.0	5.0	5.0

To each flask add 10 mL conc. HCl, 40 mL Sr/Cs solution, and 125 mL 1 M ammonium acetate. Make to 500 mL with water and mix well. Store in plastic bottles.

4 PROCEDURE

4.1 EXTRACTION

4.1.1 Weigh 2.00 g soil (air-dry, < 2 mm) into a 50-mL screw-cap polypropylene centrifuge tube.

4.1.2 Include two reagent blanks and one Laboratory Control Sample per 40 samples through the following procedure.

4.1.3 Add 40 mL M ammonium acetate.

4.1.4 Shake on an end-over-end shaker for 30 minutes.

4.1.5 Filter through Whatman No. 42 filter paper and ensure a clear solution is obtained.

4.1.6 Retain solution for measurement of individual bases and pH.

4.2 MEASUREMENT

4.2.1 Dilute 1 mL sample or blank solutions with 9 mL of the 1+9 bases diluent solution into 10-ml polypropylene transport tubes. Cap and mix well

4.2.2 Determine exchangeable bases by flame spectroscopy using the working standards. Normally standard 4 is used as the top standard, but if samples with very low levels of exchangeable bases are measured, standard 3 can be used to give better sensitivity.

4.2.3 An air-acetylene flame is used for all elements. Mg is determined by atomic absorption spectrophotometry (AAS) at 285.2 nm, Ca by AAS at 422.7 nm, K by flame emission spectroscopy (FES) or AAS at 766.5 nm and Na by FES or AAS at 589.0 nm.

5. CALCULATIONS

Ca, Mg, K or Na (me/100g) = (a - b) x V/1000 x 100/W x d/z x MF

where:	a	=	concentration of sample solution (mg/L)
	b	=	concentration of blank solution (mg/L)
	V	=	volume of extractant (mL)
	W	=	sample weight (g)
	d	=	dilution (10x)
	z	=	equivalent weight of element (Ca = 20.04, Mg = 12.2, K = 39.1, Na = 23)
	MF	=	moisture factor

For 2.0 g sample, 40 mL extractant, and a 10x dilution:

Ca, Mg, K or Na (me/100g) = (a - b) x 20/z x MF

Report results to two decimal places.

6. REFERENCES

Blakemore, L.C.; Searle, P.L.; Daly, B.K. 1987. Methods for Chemical Analysis of Soils. New Zealand Soil Bureau Scientific Report 80. 103 p.

Daly, B.K.; Manu, V.T.; Halavatau, S.M. 1984. Soil and plant analysis methods for use at the Agricultural Research Station, Vaini, Tonga. New Zealand Soil Bureau Laboratory Report AN2.

130 CATION EXCHANGE CAPACITY

1. INTRODUCTION

Cation exchange is the interchange between a cation in solution and another cation on the surface of any surface-active material such as clay or organic matter. In soil the principal cations found in the exchangeable form are the basic cations Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}, and the acidic cations H^{+} and Al^{3+}.

Cation exchange capacity (CEC) is defined as the total amount of cations that the soil can retain and is measured by leaching the soil with an excess of a cation such as ammonium. Molar ammonium acetate buffered to pH 7 is the most widely used solution for the extraction of exchangeable bases (method 128) and the determination of CEC.

The proportion of the cation exchange capacity that is occupied by exchangeable bases (% base saturation) is a useful fertility index and is used in soil classification systems.

Adaptations of the two extraction procedures described by Blakemore et al. (1987) (leaching and automated extractor) are used to measure CEC. Exchangeable bases are removed and the exchange sites saturated with ammonium ions by leaching with neutral molar ammonium acetate (method 128). The excess ammonium acetate is washed from the sample with alcohol. Then the adsorbed ammonium ions are then leached from the sample with molar sodium chloride and the concentration of ammonium in the sodium chloride solution measured after steam distillation to give the CEC.

2. REAGENTS

2.1 AMMONIUM HYDROXIDE, 2 M. Add 150 mL ammonia solution (sp. gr. 0.91) to water and make to 1 L.

2.2 WASH ALCOHOL, 90% ethanol. Dilute drum ethanol (usually 95%) to 90% w/w with water using a hydrometer to check strength. The amount of water required = 9.7 mL water / litre alcohol / percentage change. e.g. 10 L of 95% alcohol requires 485 mL water. Add 0.25 mL 2 M NH_4OH per litre alcohol.

2.3 SODIUM CHLORIDE, 1 M. Dissolve 585 g NaCl in water and make to 10 L.

2.4 SODIUM HYDROXIDE SOLUTION, approx. 10 M. Carefully dissolve 400 g NaOH pellets in 1 L water, stirring constantly.

2.5 BORIC ACID, 1%. Dissolve 5.00 g H_3BO_3 in water and make to 500 mL.

2.6 HYDROCHLORIC ACID, 1 M. Prepare from standard ampoule OR carefully add 87 mL conc. HCl (sp gr. 1.18) to about 500 mL water and make to 1 L.

2.7 HYDROCHLORIC ACID, 0.02 M. Pipette 20 mL 1 M HCl into a 1-L volumetric flask and make to volume with water.

2.8 BROMOCRESOL GREEN-METHYL RED MIXED INDICATOR. Mix 100 mL 0.1% bromocresol green (0.1 g bromocresol green dissolved in 100 mL 95% ethanol) with 20 mL 0.1% methyl red (0.1 g methyl red dissolved in 100 mL 95% ethanol).

3. PROCEDURE

3.1 EXTRACTION BY LEACHING

Note: This extraction follows on from the extraction of exchangeable bases by leaching (method 128 - procedure 4.2). If only CEC is required it is still necessary, before proceeding with the method described below, to carry out the ammonium acetate leaching described in method 128 (steps 4.2.1 - 4.2.9) to remove the exchangeable bases and saturate the exchange complex with NH_4^+ ions.

3.1.1 Place a 100-mL beaker under leaching tube.

3.1.2 Rinse top of leaching tube and soil three times with small amounts (< 5 mL) of wash alcohol from a wash bottle, allowing time to drain between each washing.

3.1.3 Add approximately 45 mL wash alcohol to a delivery flask and percolate through leaching tube. Discard percolate.

3.1.4 Place a 50-mL volumetric flask (NaCl receiving flask) under the leaching tube.

3.1.5 Add 50 mL M NaCl to a delivery flask and percolate through leaching tube.

3.1.6 Make receiving flask to 50 mL with water.

3.2 EXTRACTION BY AUTOMATIC EXTRACTOR

Note: This extraction follows on from the extraction of exchangeable bases by automatic extractor (method 128 - procedure 4.3). If only CEC is required it is still necessary, before proceeding with the method described below, to carry out the ammonium acetate extraction described in method 128 (steps 4.3.1 - 4.3.17) to remove the exchangeable bases and saturate the exchange complex with NH_4^+ ions.

3.2.1 Fit new receiving syringes.

3.2.2 Rinse the sides of leaching tube with about 10 mL wash alcohol from a wash bottle.

3.2.3 Run extractor at maximum speed until about 1-2 mm of wash alcohol remains above samples.

3.2.4 Rinse sides of leaching tube with another about 10 mL portion of wash alcohol and again run extractor at maximum speed until about 1 - 2 mm of alcohol is left above samples.

3.2.5 Repeat rinsing of leaching tube with a third about 10 mL portion of wash ethanol and again run extractor at maximum speed until this time about 5 - 10 mm of alcohol is left above samples.

3.2.6 Fit reservoirs and add 30 mL wash alcohol.

3.2.7 Run the extractor to complete extraction in about 1 hour.

3.2.8 Pull any alcohol remaining in leaching tube into receiving syringe by hand pressure on syringe.

3.2.9 Discard alcohol leachate.

3.2.10 Weigh to one decimal place a complete labelled receiving syringe (W_1).

3.2.11 Fit receiving syringe to leaching tube on apparatus.

3.2.12 With a wash bottle add about 20 mL M NaCl to the leaching tube.

3.2.13 Run extractor at maximum speed until about 5 - 10 mm of M NaCl is left above samples.

3.2.14 Fit reservoirs to leaching tubes.

3.2.15 Add 1 M NaCl to the 40-mL mark on the reservoir.

3.2.16 Run extractor to complete extraction in about 4 hours.

3.2.17 Pull any NaCl solution remaining in leaching tube into receiving syringe by hand pressure on syringe.

3.2.18 Remove receiving syringes and weigh to 1 decimal place (W_2).

3.2.19 Mix sample in receiving syringe well and retain solution for measurement of CEC.

3.3 DISTILLATION AND TITRATION

3.3.1 Transfer a 20 mL aliquot to the pre-washed steam distillation apparatus.

3.3.2 Add 5 mL 10 M sodium hydroxide.

3.3.3 Into a 100-mL conical flask add 10 mL 1% boric acid and five - six drops mixed indicator, and place flask under the delivery tube of the condenser so that the tip is under the surface of the liquid.

3.3.4 Start steam entry. The liquid will soon boil, and the indicator in the boric acid will change colour as the ammonia begins to distil over.

3.3.5 When about 30-40 mL of distillate has been collected remove 100-mL flask from apparatus, and rinse the tip of the delivery tube.

3.3.6 Stop the entry of steam. The distillation flask will empty and then can be removed from the apparatus.

3.3.7 Titrate the distillate against 0.02 M HCl, to the neutral grey colour of the indicator. Record titres (T_1 for blanks and T_2 for samples).

4. CALCULATIONS

4.1 CATION EXCHANGE CAPACITY

$$\text{CEC (me/100g)} = (T_2 - T_1) \times M \times V/v \times 100/W \times MF$$

where:

	T_1	=	blank titre (mL)
	T_2	=	sample titre (mL)
	M	=	molarity of HCl
	V	=	final volume of leachate or extractant (mL) ($V = W_2 - W_1$ for method 3.2 automatic extractor)
	v	=	aliquot of sample taken (mL)
	W	=	sample weight (g)
	MF	=	moisture factor

For 1.0 g sample, 0.02 M HCl, 50 mL leachate and a 20 mL aliquot - (leaching extraction):

$$\text{CEC (me/100g)} = (T2 - T1) \times 5 \times MF$$

For 1.0 g sample, 0.02 M HCl, V mL leachate and a 20 mL aliquot - (automated extractor extraction):

$$\text{CEC (me/100g)} = (T2 - T1) \times (W2 - W1) \times 0.1 \times MF$$

Report results to one decimal place.

4.2 PERCENT BASE SATURATION (%BS)

This value is derived from the sum of the individual exchangeable bases (me/100g) (method 128) and CEC.

$$\%BS = (Ca + Mg + K + Na) \times 100 / CEC$$

Report to nearest whole number.

5. REFERENCE

Blakemore, L.C.; Searle, P.L.; Daly, B.K. 1987. Methods for Chemical Analysis of Soils. New Zealand Soil Bureau Scientific Report 80. 103 p.

131 CATION EXCHANGE CAPACITY - pH DROP METHOD

1. INTRODUCTION

Cation exchange is the interchange between a cation in solution and another cation on the surface of a surface-active material such as clay or organic matter. In soil the principal cations found in the exchangeable form are the bases Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}, and the cations H^{+} and Al^{3+}. Cation exchange capacity (CEC) is defined as the total amount of cations that the soil can retain. Molar ammonium acetate buffered to pH 7 is the most widely used solution for the extraction of exchangeable bases (method 143) and the determination of CEC. The proportion of the cation exchange capacity which is occupied by exchangeable bases (% base saturation) is a useful fertility index and is used in soil classification systems.

This method is used to rapidly estimate the CEC of acid (pH < 7) soils. It does not work for soils with with free non-exchangeable cations such as Ca derived from carbonate or gypsum or other bases from soluble salts. The method does not give as high a level of accuracy as method 144, but is much quicker and cheaper to carry out and is suitable for soil fertility assessment purposes.

The pH of the ammonium acetate extract used for exchangeable bases determination (1:20 ratio, method 129) is measured and the amount of exchangeable hydrogen (or acid groups) in the soil is derived from a relationship published by Brown (1943). By adding the exchangeable H to the exchangeable bases from method 129 (both expressed as me/100 g) the CEC can be estimated.

2 PROCEDURE

2.1 Take the filtrate from step 4.1.5 in method 129 and measure pH within one hour of filtering.

NB. Many pH electrodes have a 'fast flow' reference junction. This can allow contamination of the extract with K. In practice this can be avoided by pouring off an aliquot for bases determination and making the pH measurement on the residual sample solution.

2.2 Set up pH meter and calibrate with two buffers.

2.3 Measure the pH of two reagent blanks and if not 7.00, adjust meter to read 7.00 on the second blank solution. This will mean redoing the calibration using the blank solution rather than the pH 7 buffer.

2.4 Measure pH to the nearest 0.01 and record.

3 CALCULATIONS

3.1 Read exchangeable H (in me/100g) from the following table:

pH	exch.H me/100g	pH	exch.H me/100g	pH	exch.H me/100g	pH	exch.H me/100g	pH	exch.H me/100g
6.20	43.6	6.36	32.5	6.52	22.6	6.68	13.9	6.84	6.3
6.21	42.9	6.37	31.9	6.53	22.0	6.69	13.4	6.85	5.9
6.22	42.1	6.38	31.2	6.54	21.5	6.70	12.9	6.86	5.4
6.23	41.4	6.39	30.6	6.55	20.9	6.71	12.4	6.87	5.0
6.24	40.7	6.40	29.9	6.56	20.3	6.72	11.9	6.88	4.6
6.25	40.0	6.41	29.3	6.57	19.8	6.73	11.4	6.89	4.2
6.26	39.3	6.42	28.7	6.58	19.2	6.74	10.9	6.90	3.8
6.27	38.6	6.43	28.0	6.59	18.7	6.75	10.4	6.91	3.4
6.28	37.9	6.44	27.4	6.60	18.1	6.76	10.0	6.92	3.0
6.29	37.2	6.45	26.8	6.61	17.6	6.77	9.5	6.93	2.6
6.30	36.5	6.46	26.2	6.62	17.0	6.78	9.0	6.94	2.2
6.31	35.9	6.47	25.6	6.63	16.5	6.79	8.6	6.95	1.8
6.32	35.2	6.48	25.0	6.64	16.0	6.80	8.1	6.96	1.4
6.33	34.5	6.49	24.4	6.65	15.4	6.81	7.6	6.97	1.0
6.34	33.8	6.50	23.8	6.66	14.9	6.82	7.2	6.98	0.6
6.35	33.2	6.51	23.2	6.67	14.4	6.83	6.7	6.99	0.3

NB. These values are calculated from the relationship $y = 11.4x^2 - 177.4x + 685$ which was derived from the paper of Brown (1943). This relationship was for a 1:10 extraction ratio so a multiplier of 2 was used for the 1:20 ratio method.

3.2 CATION EXCHANGE CAPACITY (CEC)

CEC (me/100g) = exch. H x MF +TEB

where: MF = moisture factor
TEB = total exchangeable bases (Ca+Mg+K+Na) from method 129

Report to nearest whole number.

3.3 PERCENT BASE SATURATION (%BS)

This value is derived from the sum of the individual exchangeable bases (method 143) and CEC.

%BS = (Ca + Mg + K + Na) x 100 / CEC

Report to nearest whole number.

4 REFERENCE

Brown, I C. 1943: Rapid method of determining exchangeable hydrogen and total exchangeable bases of soils. Soil Science 56:353-357.

132 EXCHANGEABLE ACIDITY

1. INTRODUCTION

Exchangeable acidity is the sum, in milliequivalents per 100 g, of the aluminium and hydrogen ions extracted from the soil by 1 M potassium chloride. The usual method for determining exchangeable acidity after extraction is by titration to measure the extracted aluminium plus hydrogen (Thomas, 1982). This can be followed by a measurement of aluminium either by titration of the hydroxyl ions released from $Al(OH)_3$ by adding fluoride ions (as potassium fluoride) to the solution following the first titration, or by atomic absorption spectroscopy. Hydrogen ion concentration is determined by difference.

However, as aluminium ions are generally the main component of the exchangeable acidity with little or no free hydrogen ions present in most soils, this method only describes the titration to give the combined aluminium + hydrogen value. This is sufficient for agronomic purposes, where the method is used to provide on indication of the possible immediate need for lime to overcome aluminium toxicity to plants. An exchangeable acidity > 1 me/100 g represents potential problems.

By adding exchangeable acidity to the total exchangeable bases the 'effective cation exchange capacity' (ECEC) can be calculated. This is another measure of CEC and is an estimate of the total amount of exchangeable cations the soil is holding at field pH. The four exchangeable bases plus aluminium represent virtually all the exchangeable cations normally present in soil.

The method is adapted from that described by Thomas (1982).

2. REAGENTS

2.1 POTASSIUM CHLORIDE, 1 M. Dissolve 373 g KCl in water, make to 5 L.

2.2 HYDROCHLORIC ACID, 1 M. Prepare from standard ampoule or carefully add 87 mL conc. HCl (sp gr. 1.18) to about 500 mL water and make to 1 L.

2.3 HYDROCHLORIC ACID, 0.025 M. Pipette 25 mL 1 M HCl into a 1-L volumetric flask and make to volume with water.

2.4 SODIUM HYDROXIDE, 1 M. Prepare from ampoule or dissolve 20 g NaOH in water and make to 500 mL.

2.5 SODIUM HYDROXIDE, approx. 0.025 M. Pipette 25 mL 1 M NaOH into a 1 L flask and make to volume with water.

2.6 PHENOLPHTHALEIN INDICATOR, 0.1%. Dissolve 0.10 g phenolphthalein in 100 mL 95% ethanol.

3. PROCEDURE

3.1 EXTRACTION

3.1.1 Weigh 10.00 g soil (air-dry, < 2 mm) into a No. 42 Whatman filter paper placed in a funnel.

3.1.2 Place funnel in 100-mL volumetric flask.

3.1.3 Include two reagent blanks with each batch of samples.

3.1.4 Add 10 portions of 10 mL 1 M KCl at 15-minute intervals to complete the percolation in 2½ hours.

3.1.5 After the last portion has percolated, remove funnel and make flask to volume with 1 M KCl.

3.2 TITRATION

3.2.1 Pipette 10 mL 0.025 M HCl into a conical flask.

3.2.2 Add five drops of phenolphthalein indicator, and titrate to the pink end-point with the 0.025 M NaOH to standardise the NaOH. Record titre to two dec places (T_1).

3.2.3 Pipette 25 mL sample extract into a 100-mL conical flask.

3.2.4 Add five drops of phenolphthalein indicator and titrate with the 0.025 M NaOH until the colour just turns permanently pink. Wait one minute to be sure. Record titre to two decimal place (T_2 for blanks, T_3 for samples).

4. CALCULATIONS

NaOH molarity (M) = $10 \times 0.025 / T_1$ **(1)**

Exchange Acidity (me/100g) = $(T_3 - T_2) \times M \times 100/W \times 100/v \times MF$ **(2)**

where:

	T_1	=	standardization with HCl titre (mL)
	T_2	=	blank titre (mL)
	T_3	=	sample titre (mL)
	M	=	molarity of NaOH (from (1))
	W	=	sample weight (g)
	v	=	aliquot of extract taken (mL).
	MF	=	moisture factor.

For a 10 g sample and a 25 mL aliquot:

Exchange Acidity (me/100g) = (T3 - T2) x 10/T1 x MF

Report results to one decimal place.

5. REFERENCE

Thomas, G.W. 1982. Exchangeable cations. in 'Methods of Soil Analysis'. Part 2. Page, A.L. editor. American Society of Agronomy and Soil Science Society of America. 1159 p.

134 DTPA EXTRACTABLE Fe, Mn, Cu & Zn

1. INTRODUCTION

Chelating agents are used as extractants to estimate the plant availability of trace elements in soil. The DTPA (diethylenetriamine penta-acetic acid) method of Lindsay and Norvell (1978), although designed for slightly acid or alkaline soils, is one of the more widely used. When used for acid soils, there may be insufficient capacity in the chelating agent to extract all of the extractable iron and manganese. Although 'critical' levels are published, care must be taken in interpretation of results as factors such as soil type, crop type, pH and organic matter content affect the correlation between plant response and level of trace element.

The Fe, Mn, Cu and Zn extracted by the DTPA reagent at pH 7.3, are measured by atomic absorption spectrometry.

2. REAGENTS

2.1 DOUBLE STRENGTH EXTRACTING REAGENT. Dissolve 3.93 g diethylenetriamine penta-acetic acid (DTPA), 2.94 g calcium chloride ($CaCl_2.2H_2O$) and 29.8 g triethanolamine (TEA) in about 400 mL water. Allow sufficient time for the DTPA to dissolve and dilute to about 900 mL with water. Adjust pH to 7.30 ± 0.05 with 1+1 (approx. 5 M) HCl, and then make to 1 L. This solution is stable for three - four months.

2.2 EXTRACTING REAGENT, 0.005 M DTPA, 0.01 M calcium chloride and 0.1 M TEA. Dilute 500 mL double strength extracting solution to 1 L with water. This solution is stable for three - four months from the time the double-strength extracting reagent was prepared.

3. STANDARDS

3.1 CONCENTRATED STOCK SOLUTIONS, 1,000 mg/L Zn, Fe, Mn or Cu.

3.2 WORKING Zn & Cu STOCK SOLUTION, 200 mg/L Zn & Cu. Pipette 20 mL 1,000 mg/L Zn and 20 mL 1,000 mg/L Cu into the same 100-mL volumetric flask, and make to volume with water.

3.2 WORKING STANDARDS. Into four 100-mL volumetric flasks pipette aliquots of the working Zn & Cu stock solution and the 1,000 mg/L Fe and Mn solutions according to the following table:

Stock Solution	mL stock solution added			
	Std 0	Std 1	Std 2	Std 3
200 mg/L Zn & Cu	0	1	2	5
1000 mg/L Fe	0	1	2	5
1000 mg/L Mn	0	1	2	5

Add 50 mL double strength extracting solution to each flask, and make to volume with water. Keep under refrigeration.

Standards have the following concentrations:

Element	Standard concentrations (mg/L)			
	Std 0	Std 1	Std 2	Std 3
Fe	0	10	20	50
Mn	0	10	20	50
Cu	0	2	4	10
Zn	0	2	4	10

4. PROCEDURE

4.1 EXTRACTION

4.1.1 Weigh 10.00 g soil (air-dry, < 2 mm) into a screw cap polypropylene centrifuge tube.

4.1.2 Include two reagent blanks with each batch of samples.

4.1.3 Add 20 mL of extracting reagent.

4.1.4 Shake for two hours on an end-over-end shaker.

4.1.5 Centrifuge at 2000 rpm for 15 minutes and filter through No. 1 Whatman filter paper to obtain a clear filtrate.

4.2 DETERMINATION

4.2.1 Concentrations of Fe, Mn, Cu and Zn in the samples are determined directly in the filtrate within one day of extraction, using atomic absorption spectrometry. Determine Fe at 248.3 nm, Mn at 279.5 nm, Cu at 324.8 nm and Zn at 213.9 nm.

4.2.2 Dilute extracts which have a higher concentration than the top standard with extracting reagent. Include dilution factor in calculation.

5. CALCULATION

Fe, Mn, Cu or Zn (mg/kg) = (a - b) x V/W x MF

where:
- a = Fe, Mn, Cu or Zn in sample solutions (mg/L)
- b = Fe, Mn, Cu or Zn in blank solutions (mg/L)
- V = volume of extracting reagent (mL)
- W = sample weight (g)
- MF = moisture factor.

For a 10 g sample and 20 mL extracting reagent:

Fe, Mn, Cu or Zn (mg/kg) = (a - b) x 2 x MF

Report results to nearest whole number.

6. REFERENCE

Lindsay, W.L.; Norvell, W.A. 1978. Development of a DTPA soil test for zinc, iron, manganese and copper. Soil Science Society of America Journal 42: 421-428.

135 0.01M $Ca(NO_3)_2$ EXTRACTABLE METALS

1 INTRODUCTION

The accumulation of heavy metals in soils is a concern because of the potential threat of metal accumulation in the food chain and toxic effects on plants and soil fauna. Arsenic, copper, nickel and zinc may adversely affect plant growth and soil microbial activity. Chromium and lead are very strongly retained by the solid phase in most soils so their accumulation poses somewhat smaller risks. Cadmium is an element of major concern in that it can reach concentrations in crops that are a danger to human and animal consumers at levels well below those where phytotoxicity is expressed.

Metals accumulate in soil through a number of ways, including fertiliser use, industrial pollution and the deposition of wastewater, biosolids and greenwastes. Guidelines have been developed to control metal contamination of soil from sewage biosolids (NZWWA 2003); however these are estimated solely on the basis of total soil metals concentrations. This measure does not reflect the fact that many soil properties and constituents, including pH, texture, organic matter, oxides and clay minerals, greatly influence the bioavailability of metals in any given soil. Metal bioavailability to plants and micro-organisms is function of the:

- bioavailability of dissolved metal species in the soil solution (Intensity factor, *I*),
- ability of the soil to buffer or maintain metal concentrations in the soil solution (Quantity factor, *Q*)

McLaughlin et al (2000) propose an alternative 2-pronged approach for assessing metal pollution of soil. This involves using a dilute neutral salt extractant to estimate soluble metals and provide an indication of ***immediate*** metal bioavailability (reflecting *I*) as well as using chelators such as EDTA or DTPA to estimate labile metal pools, and so ***potential*** bioavailability (reflecting *Q*).

Historically, a number of neutral salt extractants at different concentrations have been used to assess metal bioavailability, with the most common being calcium chloride, calcium nitrate and ammonium nitrate. Calcium nitrate extraction has been used most often in New Zealand biosolids studies, and it is the method used by McLaren et al (2005) that is described here. Extracts are analysed either by flame or graphite furnace atomic absorption spectrometry (FAAS/GFAAS) depending on metal levels.

2 REAGENTS

2.1 DOUBLE STRENGTH EXTRACTING REAGENT 0.02M $Ca(NO_3)_2$. Dissolve 4.72 g of calcium nitrate $Ca(NO_3)_2$ in water and then make to 1 L. Prepare fresh each use.

2.2 EXTRACTING REAGENT 0.01M $Ca(NO_3)_2$. Dilute 500 mL double strength extracting solution to 1 L with water. Prepare fresh each use.

3 STANDARDS

3.1 STOCK SOLUTIONS, 1,000 mg/L. Use commercial solutions for all elements.

3.2 MULTIPLE INTERMEDIATE STOCK, 50 mg/L. Pipette 5 mL of the 1,000 mg/L stock solution of each element into a 100-mL volumetric flask and make to volume with deionised water. Prepare fresh as required.

3.3 WORKING STANDARDS. 0, 0.25, 0.50, 1.00 and 2.50 mg/L. Pipette 0, 0.50, 1.00, 2.00 and 5.00 mL of multiple intermediate stock into 100-mL flasks. Add 50 mL of double strength extracting reagent (reagent 2.1) and make to volume with deionised water. Prepare fresh each use.

4 PROCEDURE

4.1 EXTRACTION

4.1.1 Weigh 5 g soil (air-dry, < 2 mm) into a screw cap polypropylene centrifuge tube.

4.1.2 Include two reagent blanks and one Laboratory Control Sample per 40 samples through the following procedure.

4.1.3 Add 30 mL of 0.01M $Ca(NO_3)_2$ extracting reagent.

4.1.4 Shake for two hours on an end-over-end shaker.

4.1.5 Centrifuge at 2000 rpm for 15 minutes and filter through Advantec Toyo 5C filter paper to obtain a clear filtrate.

4.2 DETERMINATION

4.2.1 Measure metal concentrations in the filtrates using flame AAS as soon as possible to avoid microbial growth. Dilute those extracts that have a higher concentration than the top standard with extracting reagent. Extracts with very low metal concentrations may require analysis by graphite furnace AAS or ICP if available.

5 CALCULATIONS

$$\text{Metal (mg/kg)} = (a - b) \times V/W \times MF$$

where:

a	=	metal in sample solution (mg/L)
b	=	metal in blank solution (mg/L)
V	=	volume of sample extract (mL)
W	=	sample weight (g)
MF	=	moisture factor

For a 5 g sample and 30 mL extract volume:

Metal (mg/kg) = (a - b) x 6 x MF

Report results to nearest whole number.

6 REFERENCES

McLaren, R.G., Clucas, L.M. and Taylor, M.D. 2005. Leaching of macronutrients and metals from undisturbed soils treated with metal-spiked sewage sludge. 3. Distribution of residual metals. Australian Journal of Soil Research 43: 159-170.

McLaughlin, M.J., Hamon, R.E., McLaren, R.G., Speir, T.W. and Rogers, S.L. 2000. Review: A bioavailability-based rationale for controlling metal and metalloid contamination of agricultural land in Australia and New Zealand. Australian Journal of Soil Research 38: 1037-1086.

New Zealand Water and Wastes Association. 2003. Guidelines for the safe applications of biosolids to land in New Zealand. Volume 2: Technical Manual.

136 EDTA-EXTRACTABLE METALS

1. INTRODUCTION

The 0.005M DTPA soil test was developed to identify inadequate supplies of plant-available micronutrient metals in slightly acid and alkaline soils but has since found widespread use with acid soils, reduced soils and metal-contaminated soils. In such soils, however, neither the buffered alkaline pH nor the metal chelating capacity may be appropriate. (Haynes & Swift 1983.)

EDTA has been used successfully as an extractant for micronutrient metals under many soil conditions. In their study comparing DTPA and EDTA using New Zealand soils, Haynes & Swift (1993) found that 0.04M chelate concentrations extracted considerably greater quantities of metal than did 0.005M concentrations. Furthermore, when the pH of extraction was adjusted over the range 4.5 to 7.5, EDTA was found to be far less sensitive to the pH during extraction than DTPA.

The EDTA test for micronutrients has been more popular than DTPA in New Zealand, and work has been done calibrating laboratory soil tests against plant responses. O'Connor (1995) looked at EDTA-extractable cobalt levels in soils and in plant tissue in the central North Island and Southland; while Haynes (1995) reported on a study of copper, manganese and zinc levels in soils used for winter wheat in Canterbury.

The EDTA test is also used in assessing metal pollution of soil. McLaren, Clucas and Taylor (2005) used 0.04M EDTA extraction to measure arsenic, cadmium, chromium, copper, nickel lead and zinc in biosolids and soils to which biosolids or sewage sludge has been applied. Chelators such as EDTA can be used to estimate labile metal pools, or potential bioavailability, as opposed to dilute neutral salt extractants such as calcium nitrate which only estimate soluble metals and provide an indication of immediate metal bioavailability. The stronger chelating extractants are able to desorb metal ions from exchange sites on the solid phase into soil solution but, unlike acid digestions which measure total metal, do not extracting metals bound firmly within crystal lattices which are unlikely to ever become bioavailable.

Metals which can be measured in the extracts by atomic absorption spectrometry include arsenic, cadmium, chromium, copper, iron, manganese, nickel, lead and zinc.

2 REAGENTS

2.1 DOUBLE STRENGTH EXTRACTING REAGENT, 0.08 M EDTA. Dissolve 29.78 g of disodium dihydrogen ethylenediaminetetra-acetic dihydrate in 1 L of water.

2.2 EXTRACTING REAGENT, 0.04 M EDTA. Dilute 500 mL of double strength extracting reagent (reagent 2.1 above) to about 900mL with water. Adjust to pH 6.0 using 15 M NaOH, then make to 1L.

3 STANDARDS

3.1 STOCK STANDARDS, 1,000 mg/L Cd, Cr, Cu, Fe, Mn, Ni, Pb & Zn.

3.2 INTERMEDIATE STANDARD, 50 mg/L Cd, Cr, Cu, Ni, Pb & Zn. Pipette 5 mL of the 1000 mg/L stock solution of each element into a 100-mL volumetric flask and make to volume with deionised water. Prepare fresh as required.

3.3 WORKING STANDARDS. Into four 50-mL volumetric flasks pipette aliquots of the 1,000 mg/L Fe and Mn standards (standards 3.1 above) and 50 mg/L intermediate standard (standard 3.2 above) according to the following table. Only add Fe and Mn stock if these metals are being determined.

	mL stock solution added			
Stock solution	Std 0	Std 1	Std 2	Std 3
1000 mg/L Fe & Mn	0	1.0	2.5	5.0
50 mg/L Cd, Cr, Cu, Ni, Pb & Zn	0	0.8	2.0	4.0

Add 25 mL double strength extracting solution to each flask, and make to volume with water. Keep under refrigeration. Standards containing the following levels:

	Standard concentrations (mg/L)			
Element	Std 0	Std 1	Std 2	Std 3
Fe & Mn	0	20	50	100
Cd, Cr, Cu, Ni, Pb & Zn	0	0.8	2	4

4 PROCEDURE

4.1 EXTRACTION

4.1.1 Weigh 10.00 g soil (air-dry, < 2 mm) into a screw cap polypropylene centrifuge tube.

4.1.2 Include two reagent blanks and one Laboratory Control Sample per 40 samples through the following procedure.

4.1.3 Add 25 mL of extracting reagent.

4.1.4 Shake for two hours on an end-over-end shaker.

4.1.5 Centrifuge at 2000 rpm for 15 minutes and filter through Advantec Toyo 5C filter paper to obtain a clear filtrate.

4.2 DETERMINATION

4.2.1 Measure metal concentrations in the filtrates as soon as possible to avoid microbial growth. Determine Fe and Mn at their secondary wavelengths (372.0 and 403.0 nm respectively) and the other metals at their primary wavelengths using atomic absorption spectrophotometry with the short path burner to further reduce sensitivity.

4.2.2 Dilute extracts which have a higher concentration than the top standard with extracting reagent.

5. CALCULATIONS

EDTA-extractable metal (mg/kg) = (a - b) x V/W x MF

where:
- a = metal in sample solutions (mg/L)
- b = metal in blank solutions (mg/L)
- V = volume of sample extract (mL)
- W = sample weight (g)
- MF = moisture factor

For a 10 g sample and 25 mL extract volume:

EDTA-extractable metal (mg/kg) = (a - b) x 2.5 x MF

Report results to nearest whole number.

6. REFERENCES

Haynes, R.J. 1995. Micronutrient status of a group of Canterbury cropping soils and its relationship with plant response to applied Cu and Zn. In Fertiliser Requirements of Grazed Pastures and Field Crops: Macro and Micro-Nutrients. (Editors: L.D. Currie and P. Loganathan) Occasional Report No. 8, Fertiliser and Lime Research Centre, Massey University, Palmerston North, pp 292-299.

Haynes, R.J. and Swift, R.S. 1983. An evaluation of the use of DTPA and EDTA as extractants for micronutrients in moderately acid soils. Plant and Soil 74, 111-122.

McLaren, R.G., Clucas, L.M. and Taylor, M.D. 2005. Leaching of macronutrients and metals from undisturbed soils treated with metal-spiked sewage sludge. 3. Distribution of residual metals. Australian Journal of Soil Research 43: 159-170.

O'Connor, M.D., Morton, J.D., Waller, J.E., Hawke, M.F. and Addison, B. 1995. Soil and plant cobalt status in farm surveys in the central North Island and Southland. In Fertiliser Requirements of Grazed Pastures and Field Crops: Macro and Micro-Nutrients. (Editors: L.D. Currie and P. Loganathan) Occasional Report No. 8, Fertiliser and Lime Research Centre, Massey University, Palmerston North, pp 286-291.

138 TOTAL METALS

1. INTRODUCTION

Hydrofluoric acid (HF) is the only treatment capable of total dissolution of the silicate components of soil to release metals into solution for analysis, but HF is a very dangerous reagent to work with. Mineral acids on the other hand are safer, but while vigorous enough to dissolve the metals not bound to silicate phases, they do not dissolve silica and silicates totally. Their usage is therefore referred to as "pseudo" total digestion techniques.

Cook et al (1997) compared procedures for digestion of sediments, and concluded that strong mineral acid methods and HF digestions were broadly equivalent for copper and zinc, while HF digestions produced higher concentrations for other metals. They found that that the most commonly used strong acid digestions gave comparable results for Cd, Cr, Cu, Ni, Pb and Zn. Interestingly, they also noted that even HF does not always provide absolute total results compared to XRF analysis. Of the mineral acids, sulphuric acid matrices lead to complex interferences in flame AAS, hydrochloric acid matrices are not suitable for graphite furnace AAS due to analyte volatilisation losses prior to atomisation, and perchloric acid can be explosive when used with samples high in organic matter.

The method described in this procedure is that of Kovacs et al (2000), and is very similar to EPA SW 846 Method 3050B Acid digestion of sediments, sludges and soils. It uses nitric acid and hydrogen peroxide to dissolve "almost all elements that could become environmentally available" and results in a matrix suitable for analysis by either flame or graphite furnace AAS depending on analyte levels.

2. SCOPE

2.1 This method is applicable to sludges, sediments and soils.

2.2 Samples prepared by this method can be analysed by flame atomic absorption spectrometry, graphite furnace atomic absorption spectrometry or ICP depending on the metal levels and availability of equipment.

3. INTERFERENCES

3.1 Soil grinding should not be done with metal equipment with the exception of tungsten carbide mills. Otherwise use agate or ceramic mortar and pestles to reduce sample size.

3.2 In sample preparation, cleanliness is of prime concern. The work area, including bench top and fume hood should be regularly cleaned in order to eliminate environmental contamination.

3.3 This digestion procedure may not be vigorous enough to destroy some metal complexes, particularly those bound to silicate phases.

3.4 All metals are not equally stable in the digestate, particularly since hydrochloric acid is not used in this method. The digestate should therefore be analysed as soon as possible.

3.5 Specific interferences in the atomic absorption determination step are discussed below:

3.5.1 Cadmium - No major interferences have been reported in the air-acetylene flame.

3.5.2 Chromium - Cobalt, iron and nickel have been found to cause depression of chromium absorbance. This can be overcome by use of an oxidising air-acetylene flame or preferably a nitrous oxide-acetylene flame. Interference has also been found in the air-acetylene flame from copper, barium, aluminium, magnesium and calcium. The extent of interference is strongly dependent on the flame stoichiometry. Optimisation of the stoichiometry or the use of the nitrous oxide-acetylene flame can eliminate the interference.

3.5.3 Copper - No interferences have been reported for copper in the air-acetylene flame, but some depression has been noted at high Zn/Cu ratios. This can be minimised by use of a lean air-acetylene flame or a nitrous oxide-acetylene flame.

3.5.4 Iron - Interference from citric acid has been reported to suppress the absorbance by up to 50% for a citric acid level of 200 mg/L. The effect is not overcome by adjustment of flame stoichiometry. The interference has been minimised by measuring the absorbance in the presence of phosphoric acid. It is necessary to select an optimum burner height to gain maximum freedom from interference. There is also some evidence that high sulphate concentrations have a slightly depressive effect on iron determination. The use of a nitrous oxide-acetylene flame has been found to remove all interference.

3.5.5 Manganese - In a reducing air-acetylene flame the absorbance is depressed in the presence of phosphate, perchlorate, iron, nickel, silicon and cobalt. In an oxidising air-acetylene flame or nitrous oxide-acetylene flame these interferences do not arise.

3.5.6 Nickel - At 232.0 nm, non-atomic species in the flame absorb strongly. Where the sample has a high concentration of dissolved solids it is necessary to correct for non-atomic absorption by using background correction. At 352.4 nm this effect is minimal even for high matrix solutions. In hydrochloric and perchloric acid solution a slight (5%) absorbance depression has been observed in the presence of iron, cobalt and chromium. In a more oxidising flame the effects are minimised and in the nitrous oxide-acetylene flame no interferences are observed.

3.5.7 Lead - No cationic interferences have been observed for the air-acetylene flame; however a number of anionic interferences have been reported. Phosphate, carbonate, iodide, fluoride and acetate suppress lead absorbance significantly at concentrations ten times greater than lead. These interferences can be largely

overcome by the addition of EDTA solution so that the samples are 0.1 M with respect to EDTA. At the 217.0 nm wavelength, non-atomic species in the flame absorb strongly. Where the sample has a high concentration of dissolved solids it is necessary to correct for non-atomic absorption by using background correction.

3.5.8 Zinc - No chemical interferences have been found for the air-acetylene flame. At the 213.9 nm wavelength, non-atomic species in the flame absorb strongly. Where the sample has a high concentration of dissolved solids it is necessary to correct for non-atomic absorption by using background correction.

4. PRINCIPLE

Soils are pre-digested overnight at room temperature with nitric acid in a digestion tube. Hydrogen peroxide is then added and the samples refluxed for four and a half hours at 120°C in a heated block. The cooled digest is made up with deionised water, mixed and any particulates allowed to settle overnight prior to analysis.

5. SAMPLE HANDLING AND PRESERVATION

5.1 Samples should be collected into plastic containers or plastic bags.

5.2 Solid samples require no preservation other than storage at 4 °C.

6. APPARATUS

6.1 Block digestor.

6.2 Glass tubes to fit the block.

6.3 Glass teardrop stoppers to allow refluxing.

7. REAGENTS

7.1 NITRIC ACID, HNO3. Concentrated (sp gr 1.41) Aristar grade.

7.2 HYDROGEN PEROXIDE, H2O2. 30%.

8. STANDARDS

8.1 STOCK METAL STANDARDS, 1000 mg/L. Use commercial solutions.

8.2 FLAME AAS MULTIPLE INTERMEDIATE STANDARD, 30 mg/L in 0.1 % HNO_3. Pipette 0.1 mL of nitric acid into a 100-mL flask then pipette in 3 mL of the 1000 mg/L stock solution of each element and make to volume with deionised water.

8.3 FLAME AAS WORKING STANDARDS. 0, 0.15, 0.30, 0.60, and 1.50 mg/L in **5 %** HNO_3. Pipette 2.5 mL of concentrated HNO_3 into 50-mL volumetric flasks. Pipette in 0, 0.25, 0.50, 1.00 and 2.50 mL of multiple intermediate stock. Make to volume with water.

9. QUALITY ASSURANCE

9.1 LABORATORY CONTROL SAMPLE

9.1.1 Digest a tube of a Laboratory Control Sample as the first sample. Refer to the LCS control charts - all analyte concentrations must fall within three standard deviations of the mean for the data to be accepted.

9.2 DUPLICATES

9.2.1 One sample in every ten should be digested in duplicate. The relative percent difference between duplicates must less than 25 %.

10. SAMPLE PREPARATION

10.1 Prepare soil samples by air drying at 30 °C then grinding by mortar and pestle to pass a 2-mm sieve. Sieve mesh should be nylon to avoid metal contamination.

10.2 If analysis of specific size fractions are required e.g. <63 μm, wet sieve the sample using plastic or nylon sieves and collect the desired fractions then air dry. The sample may need to be lightly broken up with a mortar and pestle when dry.

11. DIGESTION

11.1 Weigh a set of glass digestion tubes. (W_1)

11.2 Weigh about 1 g of dry sample into tubes and record the weight. (W_2)

11.3 Add 5 mL of concentrated HNO_3 (reagent 7.1.)

11.4 Allow tubes to stand overnight at room temperature.

11.5 Add 5 mL of hydrogen peroxide (reagent 7.2.) and replace the teardrop stoppers. These prevent contamination and encourage refluxing, but allow escape of acid vapours when pressure builds up.

11.6 Place tubes in digestor block. Allow tubes stand at room temperature for 30 minutes and then heat slowly to about 50 °C. Watch closely during this period for signs of foaming, and remove the tubes from the block if necessary to cool and allow the foam to subside.

11.7 After a brief holding period, and when all foaming has subsided, slowly increase

the temperature to 120 °C, where the samples will reflux gently for 4½ hours.

11.8 At the end of the heating period, allow to cool then add 40 mL of water by dispenser.

11.9 Vortex tubes to mix, then reweigh. (W_3)

11.10 Allow the digests to stand overnight for any suspended material to settle.

11.11 Carefully decant supernatant liquid into tubes suitable for the analysis technique to be used.

11.12 Analyse for all metals by flame AAS first to screen which samples and/or metals will require the more sensitive GFAAS technique. Copper, iron, manganese and zinc will almost invariably be at levels measurable by flame AAS, while cadmium, chromium, lead and nickel may require GFAAS.

12. CALCULATIONS

Metal (mg/kg) = $(a - b) \times (W_3-W_2) / (W_2-W_1) \times MF$

where:

a	=	metal in sample solution (mg/L)
b	=	metal in blank solution (mg/L)
W_1	=	weight of tube (g)
W_2	=	weight of tube + sample (g)
W_3	=	weight of tube + sample + extract (g)
MF	=	moisture factor

Report results to 3 significant figures, or as less than the detection limit if appropriate.

13. REFERENCES

Cook, J.M., Gardner, M.J., Griffiths, A.H., Jessep, M.A., Ravenscroft, J.E., and Yates, R. Marine Pollution Bulletin, Vol 34, No. 8, pp 637 – 644, 1997.

Kovacs, B., Prokisch, J., Gyori, Z., Kovacs, A.B., and Palencsar, A. Communications in Soil and Plant Analysis, Vol 31, Pt 3, pp 1949 – 1963, 2000.

USEPA SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods; Method 3050 Acid digestion of sediments, sludges and soils.

140 AVAILABLE BORON

1. INTRODUCTION

Hot water extraction has commonly been used to estimate the availability of boron in soils. The method was modified by Parker and Gardner (1981) to use hot 0.02 M $CaCl_2$ as the extractant. This modification minimises analytical problems caused by organic matter extraction and clay dispersion. However some soil extracts are still coloured by organic matter, which causes interference with the colorimetric method. Activated charcoal is added to adsorb the extracted organic matter, but because it can adsorb or release boron, it is added to the standards as well as the samples (H. Watts, pers comm).

The concentration of boron in the extracts is determined by Gaines and Mitchell's (1979) version of the azomethine-H method.

Boron is a ready contaminant in the laboratory and is also a constituent of laboratory borosilicate glassware so care must be taken to prevent sample contamination. In practice this means acid washing all glass and plastic ware prior to use, and using glassware for short-term storage only.

2. REAGENTS

2.1 CALCIUM CHLORIDE, 0.02 M. Dissolve 5.881 g $CaCl_2.2H_2O$ in water and make to 2 L.

2.2 BUFFER-MASKING REAGENT. Dissolve 280 g ammonium acetate, 20.0 g potassium acetate, 20.0 g tetrasodium salt of EDTA, and 8.0 g nitrilotriacetic acid in 400 mL water. Slowly add 125 mL acetic acid while stirring. Heat gently in a water bath if necessary to dissolve contents and filter through No. 1 Whatman filter paper to remove any undissolved residue.

2.3 AZOMETHINE-H REAGENT. Dissolve 0.90 g azomethine-H and 2.0 g ascorbic acid in water with gentle heating in a water bath, and dilute to 100 mL. If solution is turbid, reheat in water bath. Reagent will keep for 14 days if stored in a brown bottle under refrigeration.

2.4 WORKING SOLUTION. Add 20 mL azomethine-H reagent to 80 mL buffer-masking reagent. This is sufficient for 16 determinations. Prepare fresh on day of use.

2.5 ACTIVATED CHARCOAL POWDER. Acid wash with 1+1 HCl. Remove acid by washing several times with water using a Buchner funnel. Dry at 105EC.

3. STANDARDS

3.1 STOCK SOLUTION (100 mg/L B). Dissolve 0.5717 g boric acid in water and make to 1 L.

3.2 WORKING STANDARDS. Pipette 0, 1, 2, 3, 4 and 6 mL Stock solution into 200-mL volumetric flasks, and make to volume with 0.02 M calcium chloride. These standards contain 0, 0.5, 1.0, 1.5, 2.0, and 3.0 mg/L B respectively.

4. PROCEDURE

4.1 EXTRACTION

4.1.1 Weigh 10.00 g soil (air-dry, < 2 mm) (Take 5.00 g for loamy and 3.00 g for peaty soils) into a 100-mL conical flask.

4.1.2 Include six flasks for standards and two for blanks.

4.1.3 Add 0.2 g activated charcoal powder.

4.1.4 To the sample and blank flasks add 20 mL 0.02 M $CaCl_2$.

4.1.5 To each standard flask pipette 20 mL of the appropriate working standard.

4.1.6 Fit an air refluxing tube to the flask, and boil gently on a hotplate for five - six minutes.

4.1.7 Remove from heat and while still hot, filter through no. 42 Whatman filter paper into small plastic or glass tubes.

4.2 DETERMINATION

4.2.1 Pipette 4 mL aliquot of filtrate into a tube.

4.2.2 Add 5 mL azomethine-H working solution and mix.

4.2.3 Allow colour to develop for one hour.

4.2.4 Read absorbance on a spectrophotometer at 420 nm. The colour is stable for at least four hours after adding the colour reagent.

5. CALCULATION

Prepare a standard curve of mg/L B against absorbance.
Read off unknowns as mg/L B.

Available B mg/kg = (a - b) x 20/W x MF

where:
- a = B in sample solution (mg/L)
- b = B in blank solution (mg/L)
- 20 = Volume of extractant
- W = sample weight (g)
- MF = moisture factor.

Report results to one decimal place.

6. REFERENCES

Gaines, T.P.; Mitchell, G.A. 1979. Boron determination in plant tissue by the azomethine-H method. Communications in Soil Science and Plant Analysis 10: 1099-1108.

Parker, D.; Gardner, E.H. 1981. The determination of hot-water soluble boron in some acid Oregon soils using a modified azomethine-H procedure. Communications in Soil Science and Plant Analysis 12: 1311-1322.

142 PHOSPHATE-EXTRACTABLE SULPHATE

1. INTRODUCTION

The anion-exchange membrane method for determining phosphate-extractable sulphate in soil was developed by Searle (1988a), and was modified for use in laboratories without continuous flow analysers (Searle, 1988b). The method uses a phosphated anion-exchange membrane to extract sulphate from soil suspended in water. Extracted sulphate is eluted from the membrane strip by phosphoric acid and is determined turbidimetrically as barium sulphate.

2. REAGENTS

2.1 ANION-EXCHANGE MEMBRANE, BDH Cat. No. 55164. Cut membrane sheets into strips (40 x 4 mm). Place strips in a filter funnel with a No. 542 Whatman filter paper and wash with five successive 100 mL aliquots of 0.5 M H_3PO_4 to convert the membrane to the phosphate form. Store strips in 0.5 M H_3PO_4.

2.2 ELUTING SOLUTION, 0.5 M phosphoric acid. Carefully add 30 mL conc. H_3PO_4 (sp. gr. 1.75) to 800 mL water and make to 1 L.

2.3 BARIUM CHLORIDE, 10% in gelatine solution. Put 1.0 g gelatine sheet cut into small pieces into a 400-mL beaker. Add 50 mL water. Boil 100 mL water and pour over soaking gelatine, stirring until dissolved. Add 25 g $BaCl_2.2H_2O$ to the cold solution, dissolve, filter through No. 1 Whatman filter paper and make to 250 mL. Make fresh on day of use.

2.4 SULFATE SEED SOLUTION, 100 mg/L S. Carefully add 30 mL conc. H_3PO_4 to 800 mL water. Add 100 mL of 1,000 mg/L S stock solution (see 3.1 below) and make to 1 L.

3. STANDARDS

3.1 STOCK SOLUTION, (1,000 mg/L S). Dissolve 5.436 g K_2SO_4 (dried at 105°C) in water and make to 1 L.

3.2 WORKING STOCK SOLUTION, (100 mg/L S). Pipette 100 mL stock solution (1,000 mg/L S) into a 1-L volumetric flask and make to volume with water.

3.3 WORKING STANDARDS. Pipette 0, 2, 5, 10, 15 and 20 mL working stock solution into 200-mL volumetric flasks. Add 100 mL 1 M H_3PO_4 (60 mL conc. H_3PO_4 (sp. gr. 1.75) made to 1 L) and make to volume with water. These standards contain 0, 1, 2.5, 5, 7.5 and 10 mg/L S respectively.

Note: As the amount of SO_4 in phosphoric acid varies considerably, the eluting solution and standards should be made from the same bottle of conc. H_3PO_4 to avoid large positive or negative blanks.

4. PROCEDURE

4.1 EXTRACTION

4.1.1 Weigh 2.50 g soil (air-dry, < 2 mm) into a screw cap 50-mL polypropylene centrifuge tube.

4.1.2 Two reagent blanks should be included with each batch of samples.

4.1.3 Add 10 mL water.

4.1.4 Add one membrane strip (remove strip from the 0.5 M H_3PO_4, rinse with water, remove excess water with a filter paper).

4.1.5 Shake on an end-over-end shaker for 16 hours.

4.1.6 Remove membrane strip from centrifuge tube with tweezers, rinse with water and remove excess water with a filter paper.

4.1.7 Place strip into 25 mL of eluting solution in a stoppered test tube.

4.1.8 Leave strip in eluting solution for at least three hours, shaking every ½ hour.

4.1.9 Remove membrane strip with tweezers. The solutions are now ready for sulphate determination.

4.1.10 Wash membrane strips with two or three portions of 0.5 M H_3PO_4 and store in 0.5 M H_3PO_4 for re-use.

4.2 DETERMINATION

4.2.1 Place 25 mL of each working standard into a stoppered test tube.

4.2.2 Add 1 mL sulphate seed solution to each sample, blank and standard tube, mix.

4.2.3 Add 4 mL barium chloride reagent and shake well.

4.2.4 After at least 15 minutes, read absorbance on a spectrophotometer at 580 nm, shaking gently before measurement.

Note: For soils containing greater than 100 mg/kg SO_4-S (> 10 mg/L in solution), shake 0.5 g soil with 10 mL water and two membrane strips, elute in 50 mL 0.5 M H_3PO_4 and add 2 mL sulphate seed solution and 8 mL barium chloride reagent.

5. CALCULATION

Prepare a standard curve of mg/L S against absorbance.
Read off unknowns as mg/L S.

SO_4-S (mg/kg) = (a - b) x V/W x MF

where:
- a = SO_4-S in sample solution (mg/L)
- b = SO_4-S in blank solution (mg/L)
- V = volume of 0.5 M H_3PO_4 elutant (mL)
- W = sample weight (g)
- MF = moisture factor.

For a 1:10 soil:elutant ratio (2.5 g soil: 25 mL H_3PO_4)

SO_4-S (mg/kg) = (a - b) x 10 x MF

For a 1:100 soil:elutant ratio (0.5 g soil: 50 mL H_3PO_4)

SO_4-S (mg/kg) = (a - b) x 100 x MF

Report results to nearest whole number.

6. REFERENCES

Searle, P.L. 1988a. The determination of phosphate-extractable sulphate in soil with an anion-exchange membrane. Communications in Soil Science and Plant Analysis 19: 1477-1493.

Searle, P.L. 1988b. A simple manual method for the determination of phosphate-extractable (ion-exchange membrane) sulphate in soils. Fiji Agricultural Journal 50: 35-39.

144 PHOSPHATE RETENTION

1. INTRODUCTION

Phosphate retention is an empirical measure of the ability of a soil to remove phosphorus rapidly from solution. This process is considered to be a precursor to the much slower process of phosphorus fixation, which renders phosphorus unavailable to plants. In acid soils (pH < 6.5) compounds of iron and aluminium are involved in the retention process, particularly those of low-range order such as allophane and ferrihydrite. The solution phosphate concentration for the method was chosen to give a good differentiation between low and high phosphorus retaining soils and so soils with a wide range of allophane and ferrihydrite contents will give 98-100% retention. A retention solution of pH 4.6 is used, as maximum retention in most soils occurs close to this pH.

Samples are shaken for 16 hours with a 1,000 mg/L P solution, and after centrifuging, the phosphorus left in solution is determined by a vanado-molybdate colorimetric method.

The method was devised by Saunders (1965), and the analysis procedure is from Blakemore et al. (1987).

2. REAGENTS

2.1 PHOSPHATE-RETENTION SOLUTION, 1,000 mg/L P. Dissolve 8.80 g potassium dihydrogen phosphate (KH_2PO_4), and 32.8 g anhydrous sodium acetate (CH_3COONa) in about 500 mL water, add 23 mL glacial acetic acid and make to 2 L in a volumetric flask. The pH should be 4.6 ± 0.05.

2.2 NITRIC VANADOMOLYBDATE ACID REAGENT.

2.2.1 Dissolve 0.8 g ammonium vanadate (NH_4VO_3) in about 500 mL boiling water, cool, add 6 mL conc. HNO_3 and dilute to 1 L.

2.2.2 Dissolve 16 g ammonium molybdate ($(NH_4)_6Mo_7O_{24}.2H_2O$) in water at 50EC, cool and make to 1 L

2.2.3 Add 100 mL conc. HNO_3 to water and make to 1 L.

2.2.4 To the dilute nitric acid add first the vanadate solution and then the molybdate solution. Mix well.

3. STANDARDS

3.1 WORKING STANDARDS. Pipette 0, 10, 20, 30, 40 and 50-mL aliquots of the phosphate-retention solution (1,000 mg/L P) into 50-mL volumetric flasks and make to volume with water. These solutions contain 0, 200, 400, 600, 800 and 1,000 mg/L P and correspond to 100, 80, 60, 40, 20 and 0 percent retention respectively.

4. PROCEDURE

4.1 Weigh 5.00 g soil (air-dry, < 2 mm) into a screw cap 50-mL polypropylene centrifuge tube.

4.2 Add 25 mL phosphate retention solution.

4.3 Shake on an end-over-end shaker for 16 hours.

4.4 Centrifuge at 2,000 rpm for 15 minutes.

4.5 Dilute 1 mL sample and working standards with 19 mL nitric vanado-molybdate reagent. Mix well.

4.6 Read absorbance after at least 30 minutes on a spectrophotometer at 466 nm.

5. CALCULATION

Prepare a standard curve of percent phosphate retention against absorbance.

Read off unknowns directly as percent phosphate retention.

Report results to nearest whole number.

Because the method is empirical, a moisture factor is not used to correct results to an oven-dry basis.

6. REFERENCES

Blakemore, L.C.; Searle, P.L.; Daly, B.K. 1987. Methods for Chemical Analysis of Soils. New Zealand Soil Bureau Scientific Report 80. 103 p.

Saunders, W.M.H. 1965. Phosphate retention in New Zealand soils and its relationship to free sesquioxides, organic matter and other soil properties. New Zealand Journal of Agricultural Research 8: 30-57.

148 CALCIUM CARBONATE BY WEIGHT LOSS

1. INTRODUCTION

If the pH of a soil sample is more than 7.0, it should be analysed for carbonate, because the presence of calcium carbonate ($CaCO_3$) must be allowed for in determinations of exchangeable cations. Calcium carbonate occurs in soils from arid regions, soils derived from limestone, soils affected by lime-bearing ground waters, and heavily limed soils.

The weight loss method uses 1 + 1 HCl to evolve CO_2 from carbonate in the sample, the weight loss being recorded using an electronic top-pan balance. A correction for evaporation weight loss is applied to allow for the loss of water vapour and HCl. The HCl gas is lost from soil-catalysed decomposition of hydrochloric acid and therefore the weight-loss correction is obtained from the first sample and not from a beaker of acid.

Recoveries of approximately 98% are obtained from added $CaCO_3$. It is known that when appreciable quantities of magnesium carbonates are present, evolution of CO_2, is slow and approaches the evaporation constant.

The method is adapted from that described by Blakemore *et al* (1987).

2. REAGENTS

2.1 HYDROCHLORIC ACID, 1 + 1. Carefully add 250 mL of hydrochloric acid (HCl) to 250 mL water and mix.

3. STANDARD

3.1 CALCIUM CARBONATE. Dry approximately 1 g of A.R. grade calcium carbonate ($CaCO_3$) at 105 °C for 2 - 3 hours, then store in a dessicator until ready to use.

4. PROCEDURE

4.1 Weigh 5 g soil (< 2 mm, air-dry) into a 200-ml tall-form beaker. More or less sample can be taken if the expected result is very low or very high. Use 0.5 g of calcium carbonate (standard 3.1)

4.2 Place approximately 40 mL 1 + 1 HCl into a 100-mL beaker.

4.3 Place both beakers on a top-pan balance (readable to 3 decimal places) and set to zero with tare adjustment.

4.4 Pour the acid into the 200-mL beaker containing the sample and place empty acid beaker back on balance pan. Start stopwatch.

4.5 After about 30 seconds gently swirl beaker and place back on pan.

4.6 As the evolved CO_2 is heavier than air, waft a sheet of paper above the sample beaker at regular intervals to help disperse it from inside the beaker.

4.7 Record weight loss after 2 minutes, and at 1minute intervals following for up to 10 minutes. By this time the weight loss should be constant and due only to evaporation (about 0.003-0.008 g/min).

4.8 Record total weight loss and number of minutes.

Subsequent samples need be left on the balance only until their rate of weight loss drops to the rate of weight loss by evaporation (usually 4 or 5 minutes).

5. CALCULATIONS

$$\%CaCO_3 = a - (b \times c) \times 100 / 44 \times 100 / d \times MF$$

where:

a	=	total weight loss (g)
b	=	evaporative weight loss rate (g/minute)
c	=	total elapsed time (minutes)
100 / 44	=	weight of calcium carbonate over weight of carbon dioxide
100	=	factor to convert to g/100g (%).
d	=	sample weight (g)
MF	=	moisture factor

6. REFERENCES

Blakemore, L.C.; Searle, P.L.; Daly, B.K. 1987. Methods for Chemical Analysis of Soils. New Zealand Soil Bureau Scientific Report 80. 103 p.

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PLANT METHODS

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202 PLANT SAMPLE PREPARATION

1. INTRODUCTION

Plant samples collected for chemical analysis are dried to prevent spoilage by microbiological activity during storage and are ground so that representative sub-samples can be taken when small sample weights are used for analyses. Samples must be dried as soon as possible after sampling but they will generally last for several days if loosely packed in open plastic bags or paper bags, to allow air circulation, and stored in a refrigerator. If it is not possible to process the sample within this time it should be sealed into a plastic bag and frozen.

To remove contaminants such as dust, soil, fertilizer and sprays, samples may need to be washed before preparation. The washing must be carried out carefully to avoid damage to the foliage and the possible loss of ions such as potassium by leaching.

2. APPARATUS

2.1 FORCED AIR DRYING OVENS, controllable at 80°C.

2.2 KNIFE OR HAMMER MILL. (Coffee grinder is useful for small samples)

3. PROCEDURE

3.1 REGISTRATION

3.1.1 Sort samples into the order of field or client numbers.

3.1.2 Assign a laboratory number to each sample and record job number, laboratory number, clients number and analyses requested in the register.

3.2 WASHING (if required)

3.2.1 Wash each leaf quickly using tap water. Rub gently with fingers if necessary to remove adhering soil.

3.2.2 Rinse twice with distilled water.

3.2.3 Drain off excess water.

3.3 DRYING

3.3.1 Place sample into a paper bag, labelled with the laboratory number.

3.3.2 Put bag into forced-air oven set at 80°C and dry for 16 hours.

3.4 GRINDING AND SUB-SAMPLING

3.4.1 Label a sample container with the lab number.

3.4.2 Grind the sample to < 2 mm using a Wiley mill or similar.

3.4.3 Mix the ground sample thoroughly.

3.4.4 Carefully sub-sample and fill the sample container.

3.4.5 Store for analyses.

3.4.6 Brush out or use a vacuum cleaner to clean grinder between samples.

Note: As dried samples adsorb water readily they need to be briefly re-dried for half an hour at 105 °C or two hours at 80 °C before weighing out sample for analyses.

204 NITROGEN, PHOSPHORUS, POTASSIUM, CALCIUM & MAGNESIUM BY KJELDAHL DIGESTION

1. INTRODUCTION

Nitrogen, Phosphorus and Potassium are measured after a Kjeldahl digestion of the plant sample, using the sulphosalicylic acid method to include nitrate-nitrogen. The method is also used for protein determination in animal feeds, where the nitrogen content is multiplied by a factor (6.25) to estimate crude protein.

The digestion is carried out in 50-mL calibrated test tubes inserted in a drilled aluminium block on a hotplate. Nitrogen is determined in the digest by steam distillation followed by titration and phosphorus by a modified Murphy-Riley colorimetric procedure. Potassium, calcium and magnesium are determined by atomic absorption or flame emission spectrometry. The hotter nitrous oxide acetylene flame is necessary for Ca to prevent sulphate interference.

Phosphorus and potassium (and Ca & Mg) can also be brought into solution for analysis by a dry ashing technique, however their determination in the Kjeldahl digest has two advantages. Unless oxidation conditions are optimal during dry ashing, phosphorus may be lost as volatile oxides, and if only the three major nutrients (N, P & K) are required, they can be determined in the one digest.

The method is derived from those described by Blakemore et al. (1987) and Daly et al. (1984).

2. STANDARDS

2.1 STOCK SOLUTION, 50 mg/L P, 500 mg/L K, 200 mg/L Ca and 100 mg/L Mg). Dissolve 0.229 g disodium hydrogen orthophosphate, Na_2HPO_4 (dried at 105 °C), 0.953 g potassium chloride, KCl (dried at 105 °C) in water a 1 L flask. Add 20 mL 10,000 mg/L Ca solution (see method 206) and 100 mL 1,000 mg/L Mg solution (method 206). Make to 1 L with water and store in a refrigerator.

2.2 WORKING STANDARDS. Prepare six blank digests as described below (5.1 - 5.12), but add about 20 mL water instead of 50 mL (5.13). Pipette 0, 1, 2.5, 5, 7.5, and 10 mL stock solution into the blank digests, and make to 50 mL with water.

Standard	Volume of stock (mL per 50 mL)	Concentration working standards (mg/L)			
		P	K	Ca	Mg
0	0	0	0	0	0
1	1	1	10	4	2
2	2.5	2.5	25	10	5
3	5	5	50	20	10
4	7.5	7.5	75	30	15
5	10	10	100	40	20

DIGESTION

3. APPARATUS

3.1 DIGESTION TUBES, 50-mL calibrated glass test tubes.

3.2 ALUMINIUM HEATING BLOCK, 220 x 220 x 50 mm drilled with four rows of five holes (27 mm diameter, 35 mm depth).

3.3 HOT PLATE, domestic stove style single radiant element with a diameter of about 200 mm and an output of about 2 kW, mounted on a steel frame and fitted with a simmerstat.

4. REAGENTS

4.1 SULPHURIC ACID-SALICYLIC ACID MIXTURE. Dissolve 20 g salicylic acid in 600 mL conc. H_2SO_4.

4.2 SODIUM THIOSULPHATE, Crystals.

4.3 KJELDAHL COPPER CATALYST TABLETS, BDH Cat No. 33064. Each tablet contains 1 g sodium sulphate and 0.1 g copper sulphate.

5. PROCEDURE

5.1 Weigh 0.100 g plant material (oven-dry, < 2 mm) into a dry 50-mL calibrated test tube.

5.2 Two reagent blanks should be should be included with each batch of samples. If required, six blanks for preparing standard solutions should also be included.

5.3 Add 4 mL sulphuric acid-salicylic acid mixture.

5.4 Stand with occasional shaking for one hour.

5.5 Stopper tube and leave overnight.

5.6 Add about 0.25 g (a scoop is accurate enough) sodium thiosulphate carefully so that all of the crystals of salt reach the sample-acid mixture.

5.7 Heat gently on the hotplate for about five minutes, until white fumes are evolved.

5.8 Remove from heat, and when cool, add one Kjeldahl catalyst tablet.

5.9 Swirl gently to mix and place on the preheated aluminium block.

5.10 Boil the digestion mixture until it decolorises, and then carry on digestion for a further 20 - 30 minutes to ensure conversion of all nitrogen to ammonium sulphate.

5.11 Remove tube from block.

5.12 Before the digest is completely cooled (five - six minutes after removal from block), add carefully 10 - 15 mL water and swirl to dissolve digest.

5.13 When cool, make to 50 mL mark with water (only add 20 mL to standard blank solutions), stopper, and shake vigorously.

5.14 Keep solution for the determination of N, P, and K.

DETERMINATION OF NITROGEN

6. REAGENTS

6.1 SODIUM HYDROXIDE SOLUTION, approx. 10 M. Carefully dissolve 400 g NaOH pellets in 1 L water, stirring constantly.

6.2 BORIC ACID, 1%. Dissolve 5.00 g H_3BO_3 in water and make to 500 mL.

6.3 HYDROCHLORIC ACID, 1 M. Prepare from standard ampoule or add 87 mL conc. HCl (sp. gr. 1.18) to 500 mL water and make to 1 L.

6.4 HYDROCHLORIC ACID, 0.02 M. Pipette 20 mL 1 M HCl into a 1-L volumetric flask and make to volume with water.

6.5 BROMOCRESOL GREEN-METHYL RED MIXED INDICATOR. Mix 100 mL 0.1% bromocresol green (0.1 g bromocresol green dissolved in 100 mL 95% ethanol) with 20 mL 0.1% methyl red (0.1 g methyl red dissolved in 100 mL 95% ethanol).

7. PROCEDURE

7.1 Transfer a 20 mL aliquot to a steam distillation apparatus.

7.2 Add 10 mL 10 M sodium hydroxide.

7.3 Into a 100 mL conical flask add 10 mL 1% boric acid and five - six drops mixed indicator, and place flask under the delivery tube of the condenser so that the tip is under the surface of the liquid.

7.4 Start steam entry. The liquid will boil, and the indicator in the boric acid will change colour as the ammonia begins to distil over.

7.5 When about 50 mL of distillate has been collected remove 100 mL flask, rinsing the tip of the delivery tube into the flask.

7.6 Stop the entry of steam. The distillation flask will empty and then can be removed from the apparatus.

7.7 Titrate the distillate against 0.02 M HCl, to the neutral grey colour of the indicator. Record titres, T_1 for blanks and T_2 for samples.

8. CALCULATION

$$\text{Nitrogen \%} = (T_2 - T_1) \times M \times 0.014 \times 100/W \times 50/v$$

where:

T_1	=	blank titre (mL)
T_2	=	sample titre (mL)
M	=	molarity of HCl
0.014	=	weight of 1 milliequivalent nitrogen (g)
W	=	sample weight (g)
v	=	aliquot of digest solution (mL)

For 0.1 g sample, 0.02 M HCl and a 20 mL aliquot:

$$\text{Nitrogen \%} = (T_2 - T_1) \times 0.70$$

DETERMINATION OF PHOSPHORUS

9. REAGENTS

9.1 MURPHY AND RILEY REAGENT A, 1.2% ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, with 100 mg/L antimony in 2.5 M H_2SO_4. Dissolve 60 g ammonium molybdate in 1 L water. The rate of solution may be increased by heating, but do not heat above 60 °C. Cool. Dissolve 1.334 g antimony potassium tartrate in 250 mL water. Add both solutions to 2.5 L 5 M H_2SO_4. Mix well, make to 5 L with water and store in dark bottles.

9.2 MURPHY AND RILEY REAGENT B. Dissolve 1.06 g ascorbic acid in 100 mL of reagent A and mix. Prepare on day of use.

9.3 p-NITROPHENOL INDICATOR. Dissolve 0.5 g p-nitrophenol in 25 mL water.

9.4 AMMONIUM HYDROXIDE, 50% v/v. Mix 250 mL conc. NH_4OH with 250 mL water.

9.5 SULFURIC ACID, 0.5 M. Carefully add 14 mL conc. H_2SO_4 to water and make to 500 mL.

10. PROCEDURE

10.1 Pipette 5 mL sample digest and standard solutions (2.2) into 100-mL volumetric flasks.

10.2 Add about 60 mL water, and then adjust pH to about 5 as follows.

10.3 Add one drop p-nitrophenol indicator.

10.4 Add 50% NH_4OH drop-wise, mixing between additions, until the solution just turns yellow.

10.5 Add 0.5 M H_2SO_4 drop-wise, mixing between additions, until the solution just loses its yellow colour.

10.6 Add 8 mL Murphy and Riley reagent B, make to 100 mL, and mix well.

10.7 Maximum colour is produced in one hour and is stable for about 24 hours.

10.8 Read absorbance on a spectrophotometer at 880 nm. Another, less sensitive peak at 660 nm can also be used if the spectrophotometer cannot be used at 880 nm.

11. CALCULATION

Prepare a standard curve of mg/L P in standard solutions (0 - 10 mg/L P) against absorbance.

Read off unknowns as mg/L P in digest.

$$\text{Phosphorus (\%)} = (a - b) \times 50/W \times 10^{-4}$$

where:

	a	=	P in sample solution (mg/L)
	b	=	P in blank solution (mg/L)
	50	=	digest volume (mL)
	W	=	sample weight (g)
	10^{-4}	=	factor to convert mg/L to g/100g (%).

For 0.1 g sample:

$$\text{Phosphorus (\%)} = (a - b) \times 0.05$$

DETERMINATION OF POTASSIUM, CALCIUM & MAGNESIUM

12. PROCEDURE

12.1 Determine K, Ca or Mg concentration directly on sample digests by comparison with the standard solutions (from 2.2) using flame emission or atomic absorption spectrometry. For K use an air-acetylene flame at 766.2 and determine Mg by AAS at 285.2 nm. Ca is determined at 422.7 nm using a N_2O / C_2H_2 flame to prevent sulphate interference.

12.2 Use either standard no. 3 or 5 as the top standard, depending on levels in samples.

12.3 Rotate the burner to reduce sensitivity and improve linearity of calibration (about 90° for K and Mg and about 45° for Ca).

13. CALCULATION

$$\text{K or Ca or Mg (\%)} = (a - b) \times 50/W \times 10^{-4}$$

where:

	a	=	metal in sample solution (mg/L)
	b	=	metal in blank solution (mg/L)
	50	=	digest volume (mL)
	W	=	sample weight (g)
	10^{-4}	=	factor to convert mg/L to g/100g (%).

For 0.1 g sample:

$$\text{K or Ca or Mg (\%)} = (a - b) \times 0.05$$

14. REFERENCES

Blakemore, L.C.; Searle, P.L.; Daly, B.K. 1987. Methods for Chemical Analysis of Soils. New Zealand Soil Bureau Scientific Report 80. 103 p.

Daly, B.K.; Manu, V.T.; Halavatau, S.M. 1984. Soil and plant analysis methods for use at the Agricultural Research Station, Vaini, Tonga. New Zealand Soil Bureau Laboratory Report AN2.

206 Ca, Mg, Na, Fe, Mn, Zn & Cu by DRY ASHING

1. INTRODUCTION

This group of elements in plants is known as bases (calcium, magnesium and sodium) and traces (iron, manganese, zinc and copper). The method for their determination is based on that of Prasad and Spiers (1978), and involves dry ashing the sample at 475 °C, dissolving the ash in 2 M HCl and determining Ca, Mg, Na, Fe, Mn, Zn and/or Cu by atomic absorption spectrometry. Lanthanum is added to the diluted solution for the determination of bases to prevent chemical interferences in the measurement of Ca and Mg, and ionization interference in the measurement of Na.

2. REAGENTS

2.1 HYDROCHLORIC ACID, 2 M. Add 174 mL conc. HCl to approximately 500 mL water and make to 1 L.

2.2 HYDROCHLORIC ACID, 0.2 M. Transfer 100 mL 2 M HCl to a 1-L volumetric flask and make to volume.

2.3 LANTHANUM SOLUTION, (10,000 µg /mL). Dissolve 26.7 g lanthanum chloride ($LaCl_3.7H_2O$) in water and make to 1 L.

3. STANDARDS

3.1 CALCIUM STOCK, 10,000 mg/L. Use commercial solution or carefully dissolve 6.243 g calcium carbonate ($CaCO_3$), dried at 120 °C, in enough 1+1 (approx. 5 M) HCl to just dissolve it (about 20 mL), and make up to 250 mL with 0.2 M HCl.

3.2 MAGNESIUM STOCK, 1,000 mg/L. Use commercial solution or carefully dissolve 0.500 g magnesium ribbon (cleaned by dipping in dilute HCl, rinsed with water and dried) in 10 mL 1+1 HCl, and make to 500 mL with 0.2 M HCl.

3.3 SODIUM STOCK, 1,000 mg/L. Use commercial solution or dissolve 1.271 g NaCl (dried at 105 °C for 2 hours) in 0.2 M HCl and make to 500 mL with 0.2 M HCl.

3.4 BASES MULTIPLE WORKING STOCK SOLUTION, (250 mg/L Ca, 100 mg/L Mg & 50 mg/L Na). Pipette 5 mL Ca, 20 mL Mg, and 10 mL Na stock solutions into a 200-mL volumetric flask. Make to volume with 0.2 M HCl.

3.5 BASES WORKING STANDARDS. Pipette aliquots of the bases multiple working stock solution into 100-mL volumetric flasks according to the following table:

Bases Working Standard	Volume of bases multiple working stock (mL per 100 mL)	Concentration of bases working standards (mg/L)		
		Ca	Mg	Na
0	0.0	0.0	0.0	0.0
1	2.0	5.0	2.0	1.0
2	5.0	12.5	5.0	2.5
3	10.0	25.0	10.0	5.0

Add 10 mL lanthanum solution (10,000 mg/L) and make to 100 mL with water.

3.6 TRACE STOCK SOLUTIONS (1,000 mg /L Fe, Mn, Zn & Cu). Use commercial solutions or prepare from pure metal (0.500 g / 500 mL) dissolved in HCl.

3.7 TRACES MULTIPLE WORKING STOCK SOLUTION. (50 mg/L Fe & Zn, 100 mg/L Mn, and 20 mg/L Cu). Pipette 25 mL Fe, 25 mL Zn, 50 mL Mn and 10 mL Cu stock solutions into a 500-mL volumetric flask. Make to volume with 0.2 M HCl.

3.8 TRACES WORKING STANDARDS. Pipette aliquots of the traces multiple working stock solution into 100-mL volumetric flasks according to the following table:

Traces Working Standard	Volume of traces multiple working stock (mL per 100 mL)	Concentration of traces working standards (mg/L)			
		Fe	Mn	Zn	Cu
0	0.0	0.0	0.0	0.0	0.0
1	2.0	1.0	2.0	1.0	0.4
2	5.0	2.5	5.0	2.5	1.0
3	10.0	5.0	10.0	5.0	2.0
4	20.0	10.0	20.0	10.0	4.0

Make to 100 mL with 0.2 M HCl.

4. PROCEDURE

4.1 ASHING

4.1.1 Weigh 1.00 g plant material (oven-dry, < 2 mm) into a 30-mL tall-form porcelain crucible.

4.1.2 Include two reagent blanks.

4.1.3 Place in a cold muffle furnace and switch on. Heat slowly to 475 °C, and then ash for four hours.

4.1.4 Cool.

4.2 DISSOLUTION

4.2.1 Add 5 mL 2 M HCl.

4.2.2 Heat gently on a hotplate for 20 minutes.

4.2.3 Cool and transfer to a 50-mL volumetric flask, rinse crucible with water and make flask to volume with water.

4.2.4 Filter approximately 20 mL through a Whatman No. 42 filter paper into a tube.

4.2.5 Pipette 1 mL of filtrate into a 50-mL volumetric flask.

4.2.6 Add 5 mL 10,000 mg/L lanthanum solution and make to volume with water (50x dilution).

4.3 DETERMINATION

4.3.1 Determine Ca, Mg and Na concentrations in the dilutions by atomic absorption spectrometry (AAS) or flame emission spectrometry (FES). Use an air-acetylene flame and determine Ca by AAS at 422.7 nm, Mg by AAS at 285.2 nm, and Na by FES at 589.0 nm.

4.3.2 Determine Fe, Mn, Zn and Cu concentrations in the original filtrate by atomic absorption spectrometry. Use an air-acetylene flame and determine Fe at 248.3 nm, Mn at 279.5 nm, Zn at 213.9 nm, and Cu at 324.8 nm.

5. CALCULATIONS

5.1 BASES

$$\text{Ca, Mg or Na (\%)} = (a - b) \times V/W \times d \times 10^{-4}$$

where:

	a	=	concentration in sample solution (mg/L)
	b	=	concentration in blank solution (mg/L)
	V	=	final volume of digest solution (mL)
	W	=	sample weight (g)
	d	=	dilution ratio
	10^{-4}	=	factor to convert mg/L to g/100g (%).

For 1 g sample, 50 mL final digest volume and a 50x dilution:

$$\text{Ca, Mg or Na (\%)} = (a - b) \times 0.25$$

5.2 TRACES

Fe, Mn, Zn or Cu (mg/kg) = (a - b) x V/W

where: a = concentration in sample solution (mg/L)
b = concentration in blank solution (mg/L)
V = volume of digest solution (mL)
W = sample weight (g)

For 1 g sample and 50 mL final digest volume:

Fe, Mn, Zn or Cu (mg/kg) = (a - b) x 50

6. REFERENCE

Prasad, M.; Spiers, M. 1978. Comparative study of ashing techniques for the digestion of horticultural plant samples. Agricultural and Food Chemistry 26: 824-827.

207 K, Ca, Mg, Na, Fe, Mn, Zn & Cu by ACID DIGESTION

1. INTRODUCTION

Traditionally, plant sample preparation utilises dry ashing for the destruction of organic matter followed by dissolution of the ash in acid. However, losses of some components have been reported, varying with analyte, time and ashing temperature. Additionally, batch sizes are limited by the number of crucibles which can fit into the muffle furnace, whereas wet acid digestion using a block digestor enables much larger batch sizes to be processed. The method described here is that of Kovacs (1996) which uses nitric acid and hydrogen peroxide to digest plant samples, followed by flame atomic absorption determination of major nutrients and trace elements.

2. SCOPE

2.1 This method is applicable to plant tissue, including leaf, wood and seeds.

2.2 Digests prepared by this method can be analysed by flame atomic absorption spectrometry or graphite furnace atomic absorption spectrometry depending on the metal levels.

3. INTERFERENCES

3.1 In sample preparation, cleanliness is of prime concern. The work area, including bench top and fume hood should be regularly cleaned in order to eliminate environmental contamination.

3.2 Specific interferences in the atomic absorption determination step are discussed in the method for metals in soils by flame AAS (method 138).

3.3 All metals are not equally stable in the digest, particularly since hydrochloric acid is not used in this method. The digestate should therefore be analysed as soon as possible.

4. PRINCIPLE

Plants are pre-digested in a heated block for 30 minutes at 60°C with nitric acid in a digestion tube then left to stand overnight at room temperature. Hydrogen peroxide is then added and the samples refluxed for 90 minutes at 120 °C. The cooled digest is made to volume with deionised water, mixed and any particulates allowed to settle prior to analysis by flame atomic absorption spectrometry.

5. SAMPLE HANDLING AND PRESERVATION

5.3 Samples should be collected into paper bags.

5.4 Samples should be dried at 80 °C as soon as possible after collection to prevent degradation, although they may be stored refrigerated storage for several days prior to drying.

5.5 Dried samples should be ground in a mill to pass a 1-mm screen.

6. APPARATUS

6.1 Block digestor.

6.2 Glass tubes to fit the block.

6.3 Glass teardrop stoppers to allow refluxing.

7. REAGENTS

7.1 NITRIC ACID, HNO3. Concentrated (sp gr 1.41) Aristar grade.

7.2 HYDROGEN PEROXIDE, H_2O_2. 30%.

7.3 LANTHANUM SOLUTION, (10,000 mg / L). Dissolve 26.7 g lanthanum chloride ($LaCl_3.7H_2O$) in water and make to 1 L.

8. STANDARDS

8.1 POTASSIUM STOCK, 1,000 mg/L. Use commercial solution or carefully dissolve 0.953 g potassium chloride, KCl (dried at 105 °C) in water and make to volume in a 500 mL flask.

8.2 CALCIUM STOCK, 10,000 mg/L. Use commercial solution or carefully dissolve 6.243 g calcium carbonate ($CaCO_3$), dried at 120 °C, in enough 1+1 (approx. 5 M) HCl to just dissolve it (about 20 mL), and make up to 250 mL with deionised water.

8.2 MAGNESIUM STOCK, 1,000 mg/L. Use commercial solution or carefully dissolve 0.500 g magnesium ribbon (cleaned by dipping in dilute HCl, rinsed with water and dried) in 10 mL 1+1 HCl, and make to 500 mL with deionised water.

8.3 SODIUM STOCK, 1,000 mg/L. Use commercial solution or dissolve 1.271 g NaCl (dried at 105 °C for 2 hours) in water and make to 500 mL with deionised water.

8.4 BASES MULTIPLE WORKING STOCK SOLUTION, (250 mg/L K and Ca, 100 mg/L Mg & 50 mg/L Na). Pipette 50 mL K, 5 mL Ca, 20 mL Mg, and 10 mL Na stock solutions into a 200-mL volumetric flask. Make to volume with deionised water.

8.5 BASES WORKING STANDARDS. Pipette aliquots of the bases multiple working stock solution into 100-mL volumetric flasks according to the following table:

Bases Working Standard	Volume of bases multiple working stock (mL per 100 mL)	Concentration of bases working standards (mg/L)			
		K	Ca	Mg	Na
0	0.0	0.0	0.0	0.0	0.0
1	2.0	5.0	5.0	2.0	1.0
2	5.0	12.5	12.5	5.0	2.5
3	10.0	25.0	25.0	10.0	5.0

Add 10 mL lanthanum solution (10,000 mg/L), 5 mL HNO3 and make to 100 mL with deionised water.

8.6 TRACE STOCK SOLUTIONS (1,000 mg /L Fe, Mn, Zn & Cu). Use commercial solutions or prepare from pure metal (0.500 g / 500 mL) dissolved in HCl.

8.7 TRACES MULTIPLE WORKING STOCK SOLUTION. (50 mg/L Fe & Zn, 100 mg/L Mn, and 20 mg/L Cu). Pipette 25 mL Fe, 25 mL Zn, 50 mL Mn and 10 mL Cu stock solutions into a 500-mL volumetric flask. Pipette 0.5 mL of nitric acid into the flask and make to volume with deionised water

8.8 TRACES WORKING STANDARDS (in 5% HNO_3). Pipette aliquots of the traces multiple working stock solution into 100-mL volumetric flasks according to the following table:

Traces Working Standard	Volume of traces multiple working stock (mL per 100 mL)	Concentration of traces working standards (mg/L)			
		Fe	Mn	Zn	Cu
0	0.0	0.0	0.0	0.0	0.0
1	2.0	1.0	2.0	1.0	0.4
2	5.0	2.5	5.0	2.5	1.0
3	10.0	5.0	10.0	5.0	2.0
4	20.0	10.0	20.0	10.0	4.0

Pipette 5 mL of nitric acid into the flasks and make to volume with deionised water.

9 QUALITY ASSURANCE

9.1 LABORATORY CONTROL SAMPLE

9.1.1 Digest a tube of a Laboratory Control Sample as the first sample.

9.1.2 Refer to the LCS control charts - all analyte concentrations must fall within three standard deviations of the mean for the data to be accepted.

9.2 DUPLICATES

9.2.1 One sample in every twenty should be digested in duplicate where sample quantity permits. Calculate the relative percent difference (RPD) as follows:

$$\% \text{ Difference} = \frac{(Ca - Cb)}{(Ca + Cb)/2} * 100$$

where: Ca = concentration of original sample (mg/L)
Cb = concentration of duplicate sample (mg/L)

Typically the RPD should be less than 15%, but this can vary depending on the level of analyte. If the RPD is considered to be out of range then the batch must be redigested and analysed again.

10. DIGESTION

10.1 Plant material should be dried at 80 °C as soon as possible after collection, then ground to pass a 1.0 mm sieve.

10.2 Crisp samples at 80 °C for 1 hour prior to weighing out.

10.3 Weigh a set of glass digestion tubes ($W_{1)}$.

10.4 Weigh about 0.50 g of plant material into digestion tubes and record the weight (W_2).

10.5 Add 5 mL of concentrated HNO_3 (reagent 7.1) and cover the tubes with teardrop stoppers. These prevent contamination and encourage refluxing but allow escape of acid vapours when pressure builds up.

10.6 Place tubes into a block digestor in a fume cupboard and heat for 30 minutes at 60°C.

10.7 Leave tubes to stand in the block in the fume cupboard with the door pulled down overnight.

10.8 Add 1.5 mL of hydrogen peroxide (reagent 7.2.) and replace the teardrop stoppers.

10.9 Heat the tubes to about 40 °C, and holds for a short period. Watch closely during this period for signs of foaming, and remove the tubes from the block if necessary to cool and allow the foam to subside.

10.10 Slowly increase the temperature to 120°C where the samples will reflux gently for 90 minutes.

10.11 At the end of the heating period, allow to cool then add 45 mL of water by dispenser.

10.12 Vortex tubes for at least 10 seconds once the vortex is established to the bottom of the tube, then reweigh (W_3).

10.13 Allow the digests to stand, preferably overnight, for any suspended material to settle.

11. ANALYSIS

11.1 Carefully decant supernatant liquid into a 12 mL plastic tube.

11.2 Pipette 0.2 mL of each digest from the plastic tube to a second plastic tube. Add 1.0 mL of 10,000 mg / L La solution, 8.8 mL of water, cap and mix. This is a 50x dilution.

11.3 Determine Fe, Mn, Zn and Cu in the undiluted digest supernatant by atomic absorption spectrometry with a straight long-path burner.

11.4 Determine bases in the 50x dilutions of the digest supernatant by flame spectrometry. A slightly reducing air-acetylene flame is used; and the burner head is angled offset from the light path by about 15° to reduce sensitivity. Calcium is measured at 422.7 nm and magnesium at 285.2 nm both by atomic absorption. Potassium is measured at 766.5 nm and sodium at 589.0nm, both by flame emission.

12 CALCULATIONS

12.1 BASES

K, Ca, Mg or Na (%) = $(a - b) \times (W_3-W_2) / (W_2-W_1) \times 50 \times 10^{-4}$

where:

a	=	concentration in sample solution (mg/L)
b	=	concentration in blank solution (mg/L)
W_1	=	weight of tube (g)
W_2	=	weight of tube + sample (g)
W_3	=	weight of tube + sample + extract (g)
50	=	dilution factor
10^{-4}	=	factor to convert mg/L to g/100g (%).

For 0.5 g sample, 50 mL final digest volume and 0.2mL digest diluted to 10 mL:

Ca, Mg or Na (%) = $(a - b) \times 0.5$

However if the first formula is used exact weights and volumes are not necessary for the digestion.

12.2 TRACES

Fe, Mn, Cu, Zn (mg/kg) = $(a - b) \times (a - b) \times (W_3-W_2) / (W_2-W_1)$

where:	a	=	concentration in sample solution (mg/L)
	b	=	concentration in blank solution (mg/L)
	W_1	=	weight of tube (g)
	W_2	=	weight of tube + sample (g)
	W_3	=	weight of tube + sample + extract (g)

For 0.5 g sample and 50 mL final digest volume:

Fe, Mn, Zn Cu (mg/kg) = (a - b) x 100

Report results to 3 significant figures, or as less than the detection limit if appropriate.

13 REFERENCES

Kovacs, B., Gyori, Z., Prokisch, J., Loch, J. and Daniel, P. Communications in Soil and Plant Analysis, Vol 27 (5-8), pp 1177 – 1198, 1996.

208 BORON

1. INTRODUCTION

This method is based on that of Gaines and Mitchell (1979), in which the concentration of boron in an acid extract of plant tissue ash is determined by the azomethine-H method.

Boron is a ready contaminant in the laboratory and is a constituent of laboratory glassware so care must be taken to prevent sample contamination. In practice this means acid washing all glass and plastic ware prior to use, and only using glassware for short-term storage.

2. REAGENTS

2.1 SULFURIC ACID, 0.18 M. Carefully add 10 mL conc H_2SO_4 to water and dilute to 1 L.

2.2 BUFFER-MASKING REAGENT. Dissolve 280 g ammonium acetate, 20.0 g potassium acetate, 20.0 g tetrasodium salt of EDTA, and 8.0 g nitrilotriacetic acid in 400 mL water. Slowly add 125 mL acetic acid while stirring. Heat gently in a water bath if necessary to dissolve contents and filter through No. 1 Whatman filter paper to remove any undissolved residue.

2.3 AZOMETHINE-H REAGENT. Dissolve 0.90 g azomethine-H and 2.0 g ascorbic acid in water, with gentle heating in a water bath, and dilute to 100 mL. If solution is turbid reheat in water bath. Reagent will keep for 14 days if stored in a brown bottle under refrigeration.

2.4 WORKING SOLUTION. Add 20 mL azomethine-H reagent to 80 mL buffer-masking reagent. This is sufficient for 16 determinations. Prepare fresh on day of use.

3. STANDARDS

3.1 STOCK SOLUTION (100 mg/L B). Dissolve 0.5717 g boric acid and make to 1 L.

3.2 WORKING STANDARDS. Pipette 0, 2, 4, 6, 8 and 10 mL Stock Solution into 200 mL volumetric flasks, and make to volume with 0.18 M H_2S_O4. These standards contain 0, 1.0, 2.0, 3.0, 4.0 and 5.0 mg/L B respectively.

4. PROCEDURE

4.1 SAMPLE PREPARATION

4.1.1 Weigh 1.00 g plant material (oven-dry, < 2 mm) into a 30 mL tall-form porcelain crucible.

4.1.2 Include two reagent blanks with each batch of samples.

4.1.3 Ash for one hour in a muffle furnace at 600 °C.

4.1.4 Cool.

4.1.5 Wet the ash with five drops water.

4.1.6 Add 10 mL 0.18 M H_2SO_4.

4.1.7 Let stand for one hour with occasional swirling.

4.1.8 Filter through No. 1 Whatman filter paper into small plastic or glass vials or tubes.

4.2 DETERMINATION

4.2.1 Pipette 4 mL aliquot of filtrate or standard solution into a tube.

4.2.2 Add 5 mL azomethine-H working solution and mix.

4.2.3 Allow colour to develop for one hour. The colour is stable for at least four hours after adding the colour reagent.

4.2.4 Read the absorbance on a spectrophotometer at 420 nm.

5. CALCULATION

Prepare a standard curve of mg/L B in standard solutions against absorbance.

Read off unknowns as mg/L B.

Boron (mg/kg) = (a - b) x V/W

where:
- a = boron in sample solution (mg/L)
- b = boron in blank solution (mg/L)
- V = digest volume (mL)
- W = sample weight (g).

For 1 g sample and 10 mL digest volume:

Boron (mg/kg) = (a - b) x 10

6. REFERENCE

Gaines, T.P.; Mitchell, G.A. 1979. Boron determination in plant tissue by the azomethine-H method. Communications in Soil Science and Plant Analysis 10: 1099-1108.

210 CHLORIDE

1. INTRODUCTION

This method is adapted from those of Metson (1972) and Blakemore et al. (1987) and involves extraction of chloride with boiling water and determination by titration with mercuric nitrate. Chloride ions combine with mercuric ions to form the very slightly dissociated salt mercuric chloride.

$$Hg^{2+} + 2Cl^{-} \; 6 \; HgCl_2$$

The indicator diphenylcarbazone is used to detect the end point as it forms a deep violet-blue complex with excess mercuric ions in slightly acid solution with pH of 2.3 to 2.8.

Activated charcoal is used as a decolourising agent because of the difficulty in obtaining a clear extract to permit detection of the end point.

2. REAGENTS

2.1 NITRIC ACID, 2 M. Carefully add 126 mL of conc HNO_3 to water and make to 1 L.

2.2 MERCURIC NITRATE SOLUTION, about 0.02 N. Add 20 mL of 2 M HNO_3 to about 500 mL water, dissolve about 3.4 g $Hg(NO_3)_2.H_2O$, and make to 1 L.

2.3 CHLORIDE STANDARD SOLUTION, 0.02 N. Dissolve 1.169 g of NaCl (dried at 105EC for two hours) in water and make to 1 L.

2.4 DIPHENYLCARBAZONE INDICATOR, 0.1% in ethanol. Dissolve 0.1 g s-diphenylcarbazone in 100 mL of 95 % ethanol and store in a refrigerator. Reagent will keep for one - two months.

2.5 ACTIVATED CHARCOAL.

3. PROCEDURE

3.1 EXTRACTION

3.1.1 Weigh 0.50 g sample (freshly oven dried at 105EC for one hour) into a 150-mL beaker.

3.1.2 Include two reagent blanks with each batch of samples.

3.1.3 Add 100 mL water.

3.1.4 Place on a pre-heated hot plate and boil gently for 10 minutes. Avoid as far as possible the deposition of plant material on the walls of the beaker and excessive evaporation of the water.

3.1.5 Remove from hot plate and add 0.5 g activated charcoal (use scoop).

3.1.6 Filter through No. 41 or 54 filter paper into a 200-mL volumetric flask.

3.1.7 Wash with two or three portions of water.

3.1.8 When cool make to 200 mL.

3.2 STANDARDIZATION OF MERCURIC NITRATE SOLUTION

3.2.1 Pipette 10 mL of 0.02 N NaCL into a 50-mL conical flask and add 10 drops of diphenylcarbazone indicator solution.

3.2.2 While stirring, add mercuric nitrate solution drop-wise until a faint blue-violet colour appears. This indicates the end point of titration. Further addition of mercuric nitrate will intensify the colour.

3.2.3 Make three or four repeat titrations to ensure constant results. Record titre to two decimal places (T_1).

3.3 SAMPLE TITRATION

3.3.1 Transfer 40 mL aliquot to a 100-mL conical flask.

3.3.2 Add 10 drops diphenylcarbazone indicator solution.

3.3.3 Titrate with mercuric nitrate solution to a pale blue-violet end point.

3.3.4 Record titre to two decimal places (T_2 for blanks and T_3 for samples).

4. CALCULATIONS

$$N = 0.2 / T_1 \quad \textbf{(1)}$$

$$Cl\ (\%) = (T_3 - T_2) \times N \times V/v \times 100/W \times 35.5/1000 \quad \textbf{(2)}$$

Where:
- T_1 = titre for NaCl standardisation (mL)
- T_2 = titre for blank (mL)
- T_3 = titre for sample (mL)
- N = normality of $Hg(NO_3)_2$ from **(1)**.
- V = final volume of extract (mL)
- v = aliquot of extract (mL)
- W = weight of sample (g)
- 35.5 = atomic weight of Cl.

For 0.5 g sample, 200 mL final extract volume, 40 mL aliquot

$$Cl\ (\%) = (T_3 - T_2) \times 7.1/T_1 \quad \textbf{(3)}$$

5. REFERENCES

Blakemore, L.C.; Searle, P.L.; Daly, B.K. 1987. Methods for Chemical Analysis of Soils. New Zealand Soil Bureau Scientific Report 80. 103 p.

Metson, A.J. 1972. in Soil Bureau Laboratory Methods. New Zealand Soil Bureau Scientific report 10B.

WATER METHODS

300 COLLECTION AND PRESERVATION OF WATER SAMPLES

1 INTRODUCTION

The most important objectives in water sampling are to obtain a representative sample and to prevent deterioration and contamination of the sample before analysis. According to the USEPA, "95% of total error in environmental measurements is due to sample collection and handling, with only 5% due to mistakes in the laboratory analyses". Sampling costs (travel, equipment and personnel) can be the largest component of a research budget, and subsequent costs incurred in analysis and data interpretation can be wasted as well if the sampling was not performed correctly. This procedure covers the minimum requirements to ensure quality and consistency of the field aspects of water sample collection.

2 PREPARATION

The choice of measurement parameters will depend on the the objectives of the study. Once these have been decided, talk to the laboratory that will be performing the measurements and ask the following questions:

- Can the laboratory perform these tests?
- Are the detection limits adequate?
- Does the laboratory hold formal accreditation for these tests?
- How much do the tests cost?
- What sort of sample containers should be used?
- How should the sample containers be prepared?
- How should the samples be collected?
- How much sample is required?
- Should the samples be field filtered?
- What sort of preservation is necessary?
- What sort of Quality Control samples should be collected?
- How and when should the samples be transported?
- How long before results are available?

Before going into the field, ensure that you have sufficient sample containers bearing in mind that, depending on the tests to be performed, more than one bottle of sample may need to be collected at each site. A single 125 mL bottle for each preservation type (e.g. glass, unfiltered, filtered, acid-preserved) is usually sufficient. For solids, a separate 1 L bottle is necessary. Take a sheet of pre-printed labels and affix once the sample is collected. Secure the label by taping around the bottle with sellotape. The label only needs to show a unique sample ID, and preservation status. Other details such as matrix type, project ID, date and time of collection, sampler ID etc are not required by the laboratory and can simply be recorded in a field notebook.

Plastic bottles must be cleaned before use as follows:

1. Clean in the dishwasher using phosphate-free detergent and RO water rinse cycles.
2. Soak overnight in a solution of 5 % hydrochloric acid.
3. Rinse by using the dishwasher with no detergent and RO water rinse cycles.

4. Allow to dry and cap.

    - If bottles are to be used for ultra-low level metals, repeat steps 2 and 3 using 10 % HNO_3 before drying.
    - Do not use detergent to clean glass bottles for carbon samples. When dry, bake at 450 °C for 2 hours.

Table 1 below summarises the sample container, initial preservation and maximum holding time recommendations for water samples.

Table1. Summary of sample requirements

Parameter	Container	Filtration	Preservation	Maximum Storage
Total carbon	Amber glass	None	Refrigerate	1 week
Dissolved carbon	Amber glass	0.45 µm	Refrigerate	1 week
Br^-, Cl^-, F^-	Plastic	None	Refrigerate	1 month
Conductivity	Plastic	None	Refrigerate	48 hours
Metals - dissolved	Plastic	0.45 µm	0.2 % HNO_3	6 months
Metals – total or total recoverable	Plastic	None	0.2 % HNO_3	6 months
NH_3-N	Plastic	0.45 µm	Freeze	1 month
NO_3-N	Plastic	0.45 µm	Freeze	1 month
NO_2-N	Plastic	0.45 µm	Freeze	48 hours
pH	Plastic	None	Refrigerate	48 hours
Dissolved reactive phosphorus	Plastic	0.45 µm	Freeze	1 month
Solids (suspended & dissolved)	Plastic	None	Refrigerate	1 week
Sulphate	Plastic	None	Refrigerate	1 month
Total nitrogen & phosphorus	Plastic	None	Freeze	1 month

3 SAMPLE COLLECTION

Water samples are best collected before any other work is done at the site. If other work (i.e., sediment sample collection, flow measurement or biological/habitat sample collection or assessment) is done prior to the collection of water samples, it might be difficult to collect representative samples for water chemistry from the disturbed stream. Care must be taken, though, to not disturb sediment collection sites when taking water samples.

Sample collectors should keep their hands clean and refrain from eating or smoking. Gloves are not necessary except where ultra-trace metals are being determined. Petroleum products (gasoline, oil, exhaust fumes) are prime sources of contamination. Spills or drippings (which are apt to occur in boats) must be removed immediately. Exhaust fumes can contaminate samples with lead while cigarette smoke contains measurable ammonia and cyanide.

Samples for routine chemistry should not be collected during periods of abnormally high turbidity if at all possible, as it is difficult to collect a representative grab sample. Samples with high turbidity are also particularly unstable in terms of soluble metals.

Field measurements should always be made using a separate subsample that is then discarded once the measurements have been made. They should never be made on a water sample that is returned to the laboratory for further chemical analyses.

Samples should be collected from mid-stream to reduce the possibilities of contamination (i.e., shore effects - back eddies, seepage from near shore soils, atmospheric components such as pollen concentrating in slow moving water, etc.) Preferably samples will be collected from a boat. On arrival at a site the motor is shut down while the boat still has forward momentum, allowing the boat to drift clear of possible contamination from the motor or propeller. The sample should be collected from the front of the boat, upcurrent of any disturbances.

When boat access is not possible, the options in order of desirability are:

1. Wade out into the main flow and sample upstream so that the sample is unaffected by the sediment disturbance caused by wading.
2. Sampling midstream from bridges or causeways
3. Off jetties or climbing out on overhanging branches using a bucket.
4. If none of these are possible, use a telescopic pole with a beaker attached to the end so as to reach as far out from the bank as possible.

Water samples are often obtained by filling a container held just beneath the surface of the water, commonly referred to as a grab sample. In most streams, near-surface water is representative of the water mass. Through the use of special depth samplers (such as a Van Dorn bottle), grab samples can also be obtained from deep waters. This is especially important in lakes where distinct thermal and chemical differences can occur throughout the water column. Composite samples are obtained by mixing equal volumes of discrete grab samples (collected at one point at regular time intervals or, collected from multiple points such as varying depths). A composite sample provides an estimate of average water quality conditions.

Wherever possible, collect samples directly into bottles as follows:

1. Remove the lid and hold it aside without touching the inner surface.
2. With your other hand, grasp the bottle well below the neck. Plunge it beneath the surface in front of you to about 20 cm depth with the opening facing directly down, then immediately orient the bottle into the current. Avoid collecting surface scum and film.
3. Once the bottle is full, remove it from the water by forcing it forward (into the current) and upwards.
4. Cap and shake vigorously.

5. Rinse by emptying the bottle over the cap three times. Do not rinse however when a sample is to be analysed for suspended sediments as suspended particles are retained on the interior surface of each bottle with each rinsing.
6. Fill the bottle, leaving a 2 cm headspace to allow for thermal expansion when the sample is frozen for preservation. The exception is where pH and/or carbon is to be determined – fill these to the brim to prevent changes occurring due to dissolved gases.

If it is not possible to sample directly into the bottle use a bucket that is reserved for water sampling only – label it as such. Clean the bucket before use with a non-phosphate detergent such as Decon, rinse thoroughly, then rinse with dilute (5%) hydrochloric acid. Triple rinse with deionised water again and keep covered with a snug-fitting lid until use. Lower it over the upstream side of the bridge, being careful not to disturb bridge surfaces with the rope or bucket. This avoids contamination of the sample from the bridge itself or substances falling into the water or into the bucket from the bridge. Allow the bucket to submerge then haul up.

4 SAMPLE FILTRATION

Samples for dissolved metals and nutrients (ammonia, NO_x, dissolved reactive P) should be field filtered as follows using 50 mL Terumo luer-lock syringes and Sartorius 0.45 µm Minisart filters:

1. Collect a grab sample in a bucket as described above.
2. Prepare the syringe by drawing up sample to past the 60 mL mark and then squirting to waste three times. Ensure that the hands do not touch the part of the syringe barrel that enters the water.
3. Fill the syringe again.
4. Attach the Minisart filter.
5. Filter approximately 10 mL of sample into the sample bottle.
6. Cap, shake vigorously, and then discard the rinse water.
7. Filter the remaining contents of the syringe into the bottle.

Syringes may be used for multiple samples if rinsed well between samples with deionised water then with sample as in step 2. Discard after using for samples suspected of having high nutrient levels. A fresh Minisart should be used for each sample. For samples particularly high in particulates, a prefilter may be screwed onto the syringe ahead of the 0.45 µm filter.

5 SAMPLE PRESERVATION

The shorter the elapsed time between collection and analysis, the more reliable the analytical results. Ideally samples should be analysed within 24 hours of collection; in practice most samples need to be preserved and held for longer periods of time. Refer to Table 1 above for an indication of maximum holding times.

Absorption and desorption, precipitation and flocculation, and chemical reactions, particularly redox, are the main causes of change in the levels of metals in solution. Preservation by acidification has found to be an effective means of preventing these events. Immediately after collection add sufficient acid to reduce the pH below 2. Typically 0.2 mL

of HNO_3 per 100mL of sample is adequate for most samples. If dissolved metals are to be determined the sample must be filtered before acidifying.

For the common anions (bromide, chloride, fluoride, sulphate) refrigeration at 4 °C provides adequate preservation by reducing reaction rates to about a quarter of their value at room temperature, hence the rate of chemical and biological changes is greatly reduced. Immediately after collection place the containers in ice in a chilly bin.

Most problems with the stability of nutrients ((ammonia, NO_x, dissolved reactive P)) relate to the presence of biological material, so preservation for these is aimed at reducing the activity of micro-organisms present by filtration followed by chilling in the field. Subsequent freezing back in the lab reduces reaction rates and keeps reactants apart. Samples for total N & P should be frozen also, but not filtered.

6 QUALITY CONTROL

A series of quality-control samples (field blanks and replicates) is obtained in water-quality investigations because the quality of the data collected and the validity of any interpretation cannot be evaluated without quality-control data. Field quality control requires the submission of blank samples to test: 1) the purity of chemical preservatives; 2) to check for contamination of sample containers, filtering equipment or any other equipment that is used in sample collection, handling or transportation; and 3) to detect other systematic and random errors occurring from the time of the sampling to the time of analysis. Replicate samples must also be collected to check that the sample is reproducible. Replicate samples allow the precision of the sampling and measurement process to be estimated, and are an additional check on sample contamination.

6.1 FIELD BLANKS

Blanks are samples that do not contain the variable to be analysed and are used to assess and control sample contamination. Field blanks are carried through the entire sample collection and handling process so that the blank is exposed to the same potential sources of contamination as actual samples. They are exposed to the sampling environment at the sample site and mimic the extra sampling and preservative process but do not come in contact with ambient water. Consequently, they provide information on contamination resulting from the handling technique and through exposure to the atmosphere. They are processed in the same manner as the samples (i.e., they are exposed to all the same potential sources of contamination as the sample). This includes handling and, in some cases, filtration and/or preservation. Prepare the blanks as the first samples as follows:

1. Pour deionised water into the sample collection bucket (if used) or bottle. This simulates sample collection.
2. Filter the blank if the associated sample requires filtration.
3. Add preservative if the associated sample requires preservation

Collect a minimum of one blank for each bottle/preservation type per trip and submit for analysis in the same manner as samples.

6.2 REPLICATES

Sample replicates are designed to provide information needed to estimate the precision of concentration values determined from the combined sample-processing and analytical scheme. They are independent samples collected as close as possible to the same point in space and time and are intended to be identical. These samples are essential in documenting the precision of the entire sampling and analytical (laboratory) process. Replicates should be collected at a rate of 5% or, if less than 20 samples are collected, one set of duplicates per trip.

7 TRANSPORT

Samples should be securely packed in a solid-walled chilly bin. Ice packs should be used as opposed to loose ice or bagged ice. When loose ice melts, the contents of the cooler are free to shift, potentially allowing contamination of samples with melted ice water and/or breakage of glass bottles. Pack the samples upright in the chilly bin with plenty of ice packs. Ensure that the samples that are most likely to deteriorate (i.e., those that are not chemically preserved) are closest to the ice packs. Ensure that the glass bottles are separated from each other by ice packs, plastic bottles, or clean packing material to prevent them from breaking, or preferably wrap them in bubble-wrap.

Enclose a set of instructions for the laboratory including client name and contact details, list of samples and their preservation details, and the analyses required. Place these in a plastic bag so they remain dry. Seal the chillybin with packing tape to reduce the possibility of it accidentally opening and to prevent tampering with the samples. Arrange for transport to the laboratory by courier, never at the end of a week or the samples may deteriorate in transit over the weekend. Notify the laboratory by email that the samples are on the way together with a spreadsheet copy of the sample details.

8 REFERENCES

Standard Methods for the Analysis of Water and Wastewater. 20th Edition. (1998) American Public Health Association, Washington DC. Method 4500-H+ B. pH Value / Electrometric Method.

302 pH

1. INTRODUCTION

pH is the most widely made measurement on natural waters. Values for pH usually range between 4 and 9, with most waters being slightly alkaline due to the presence bicarbonates and carbonates of calcium, magnesium and sodium. (Standard Methods for the Analysis of Water and Wastewater)

The basic principle of pH measurement is the determination of the activity of the hydrogen ions by potentiometric measurement using a glass electrode and a reference electrode, which are usually combined into a single probe. The pH meter is calibrated against reference buffers.

Measurement of pH of water samples should be made as soon as possible after sampling, before microbiological-induced changes occur.

2. REAGENTS

2.1 pH 7 BUFFER. Use commercially available buffer. Because prepared buffers have a limited life (a month or two at most) it is preferable to use the sachet form that can be prepared when needed.

2.2 pH 4 BUFFER, 0.05 M potassium hydrogen phthalate. Dissolve 1.021 g $COOH.C_6H_4.COOK$ in water in a 100-mL volumetric flask and make up to 100 mL.

2.3 pH 9.23 BUFFER, 0.01 M sodium borate. Dissolve 0.380 g $Na_2B_4O_7.10H_2O$ in freshly boiled (CO_2-free) water and make to 100 mL.

3. PROCEDURE

3.1 Calibrate pH meter with the pH 7 buffer, following the meter standard operating procedure.

3.2 Make preliminary reading of sample.

3.3 If pH is > 7 set slope or sensitivity with the pH 9.2 buffer. If pH is < 7 set slope with the pH 4 buffer.

3.4 Read and record pH of samples. Report results to one decimal place.

4. REFERENCES

Standard Methods for the Analysis of Water and Wastewater. 20th Edition. (1998) American Public Health Association, Washington DC. Method 4500-H+ B. pH Value / Electrometric Method.

304 ELECTRICAL CONDUCTIVITY

1. INTRODUCTION

This method describes the measurement of electrical conductivity (EC) in water which results from ions in solution from dissolved salts. Measurement of conductivity gives an estimate of the concentration of these dissolved salts (salinity). In natural waters the salts may be derived from seawater, geologic or pedogenic processes, or excess fertiliser. High salt levels in irrigation waters can cause damage to plants. Water with EC below 250 µS/cm is rated as low salinity, and EC values greater than 750 indicate high salinity (Richards, 1969).

Total dissolved solids may be estimated by multiplying the conductivity by an empirical factor, usually 0.55 for natural waters. (Standard Methods for the Analysis of Water and Wastewater) Waters with high dissolved solids are of inferior palatability, with a limit of 1000 mg /L desirable for drinking water. (Drinking Water Standards for New Zealand)

It is important to measure conductivity as soon as possible after sampling, as microbiological activity can change the ionic concentration.

2. APPARATUS

2.1 CONDUCTIVITY METER. Preferably with automatic temperature compensation.

3. STANDARDS

3.1 STANDARD POTASSIUM CHLORIDE SOLUTION, 0.01 M KCl. Dissolve 0.7456 g of KCl, dried at 105 °C for 2 hours, in water in a 1 L volumetric flask and make to 1L. This standard reference solution at 25°C has a conductivity of 1412 µS/cm.

4. PROCEDURE

4.1 Ensue the temperature compensation of the meter is set to 0.02 C^{-1}.

4.2 Check meter using the 0.01 M KCl solution. Adjust the reading to 1412 µS/cm. This automatically adjusts the cell constant internal to the meter.

4.3 Immerse the probe in the sample. If the probe has an air hole, this must be beneath the water surface.

4.4 Stir the sample vigorously using the probe for about 30 seconds then read and record conductivity as µS/cm.

4.5 Rinse the probe with deionised water between samples.

5. CALCULATIONS

For meters with automatic temperature compensation, the meter reading is the conductivity result with no further calculations necessary. If meter is not temperature compensated and temperature of solutions is not 25°C apply temperature corrections according to the instrument manual.

Conductivity results are quoted directly as µS/cm.

(Note: mS/cm = 1 m mho/cm = 1000 µS/cm)

Report EC results as a whole number.

An approximate total dissolved solids (TDS) value can be derived using the relationship:

TDS (mg/L) (approx.) = µS/cm x 0.55

Report TDS results to nearest 5 or 10.

6. REFERENCES

Drinking Water Standards for New Zealand 2000. Ministry of Health. Wellington. Procedures Manual.

Richards, L.A. (Ed) 1969. Diagnosis and Improvement of Saline and Alkali Soils. US Department of Agriculture Regional Salinity Laboratory, Riverside, California. 140p.

Standard Methods for the Analysis of Water and Wastewater. 20th Edition. (1998) American Public Health Association, Washington DC. Method 2510 Conductivity.

306 TOTAL SUSPENDED SOLIDS

1. INTRODUCTION

Solids refer to matter suspended or dissolved in water. "Total solids" is the term applied to the material left after evaporation of a sample. Total solids includes "total suspended solids", the portion retained by a filter, and "total dissolved solids", the portion that passes through the filter. (Standard Methods for the Analysis of Water and Wastewater)

Suspended solids measurements are usually made on river water samples to enable total sediment load to be calculated. Waters high in suspended solids may be aesthetically unsuitable for purposes such as bathing. (Drinking Water Standards for New Zealand)

If only suspended solids are required, use this procedure. If both dissolved and suspended solids are required then use Procedure 306 – Total Dissolved Solids and Total Suspended Solids. It is important that the sample taken from the bulk sample for filtration contains a representative portion of the sediment, so care must be taken to ensure re-suspension of the particles prior to subsampling.

2. APPARATUS

2.1 Vacuum filtering apparatus such as Millipore glass filter holders that hold 7 cm GFC (or equivalent) glass fibre filters.

3. PROCEDURE

Make all weighings to four decimal places. The aim is to collect between 2.5 – 200 mg of dried residue. If a sample filters through very rapidly, use as much volume of sample as can be spared. If complete filtration takes longer than 15 minutes, discard the filter and repeat with a smaller volume of sample, down to a minimum of 50 mL, and analyse in duplicate.

3.1 Dry a 7 cm GFC filter at 105°C for one hour and weigh (W_1).

3.2 Place filter in vacuum filtering apparatus and turn the vacuum on.

3.3 Vigorously mix sample and pouring quickly, approximately half fill a 100-mL or 200-mL measuring cylinder. (Use the smaller size for samples with high suspended solids). Remix sample and, again pouring quickly, approximately fill measuring cylinder. Record volume of sample (V_1).

3.4 Wet the paper with a small squirt of deionised water from a wash bottle to seal it.

3.5 Pour the sample onto the filter, leaving about 50 mL in the measuring cylinder.

3.6 When filtering is complete, swirl the last 50 mL in the measuring cylinder and pour on to the filter.

3.7 Wash the sides of the measuring cylinder with a small squirt of deionised water from a wash bottle, swirl and pour on to the filter.

3.8 Use the wash bottle to quickly rinse the sides of the filter housing.

3.9 When all liquid has been pulled through the filter, release the vacuum and lift the filter housing off the flask.

3.10 Carefully lift the filter paper off using tweezers and dry at 105°C for two hours.

3.11 Replace the housing on the flask and put under vacuum again.

3.12 Rinse the flask and filter housing with deionised water before going on to the next sample.

3.13 Weigh the dry filter (W_2).

4. CALCULATIONS

Suspended solids (mg/L) = $(W_2 - W_1) \times 10^6/V_1$

where: W_1 = weight of glass fibre filter (g)
W2 = weight of filter + sediment (g)
V1 = sample volume (mL).

Express results to nearest whole number.

5. REFERENCE

Standard Methods for the Analysis of Water and Wastewater. 20th Edition. (1998) American Public Health Association, Washington DC. Method 2540 D. Total Suspended Solids Dried at 103 - 105 °C.

308 TOTAL DISSOLVED SOLIDS & TOTAL SUPENDED SOLIDS

1. INTRODUCTION

Solids refer to matter suspended or dissolved in water. "Total solids" are comprised of "total suspended solids", the portion retained by a filter, and "total dissolved solids", the portion that passes through the filter. (Standard Methods for the Analysis of Water and Wastewater.) Waters with high dissolved solids are of inferior palatability, with a limit of 1000 mg /L desirable for drinking water. (Drinking Water Standards for New Zealand)

This procedure is essentially Procedure 305 - Total Suspended Solids, with additional steps necessary to collect the filtrate quantitatively in order to measure the dissolved solids as well. Total dissolved solids may be also estimated by multiplying the conductivity by an empirical factor (see Procedure 304 - Electrical Conductivity).

It is important that the sample taken from the bulk sample for filtration contains a representative portion of the sediment, so care must be taken to ensure re-suspension of the particles prior to subsampling.

2. APPARATUS

2.1 Vacuum filtering apparatus such as Millipore glass filter holders that hold 7 cm GFC (or equivalent) glass fibre filters.

2.2 Set of numbered 250-mL glass beakers.

3. PROCEDURE

Make all weighings to four decimal places. The aim is to collect between 2.5 – 200 mg of dried residue. If a sample filters through very rapidly, use as much volume of sample as can be spared. If complete filtration takes longer than 15 minutes, discard the filter and repeat with a smaller volume of sample, down to a minimum of 50 mL, and analyse in duplicate.

3.1 Dry a 7 cm GFC filter at 105°C for one hour and weigh (W_1).

3.2 Dry a set of numbered 250-mL beaker at 105°C for one hour and weigh (W_2).

3.3 Place filter in vacuum filtering apparatus.

3.4 Vigorously mix sample and pouring quickly, approximately half fill a 100-mL or 200-mL measuring cylinder. (Use the smaller size for samples with high suspended solids). Remix sample and, again pouring quickly, approximately fill measuring cylinder. Record volume of sample (V_1).

3.5 Wet the paper with a small squirt of deionised water from a wash bottle to seal it, then pour about 10mL of sample through glass fibre filter.

3.6 Release the vacuum and lift the filter housing off the flask.

3.7 Swirl the filtrate to rinse the flask then discard.

3.8 Replace the housing on the flask and put under vacuum again.

3.9 Pour the remainder of the sample onto the filter.

3.10 When filtering is complete, release the vacuum and lift the filter housing off the flask.

3.11 Pour the filtrate into a clean measuring cylinder and record the volume (V_2)

3.12 Carefully transfer the filtrate to the appropriate numbered weighed 250-mL beaker.

3.13 Dry the beakers of filtrate overnight at 105°C.

3.14 Weigh the dry beakers to four decimal places and record weight (W_3).

3.15 Replace the housing on the flask and put under vacuum again.

3.16 Rinse the measuring cylinder used on the original sample with about 10 mL of water, swirl and transfer rinsing onto the filter.

3.17 When filtering is complete, remove filter and dry at 105°C for two hours.

3.18 Weigh the dry filter (W_4).

3.19 Rinse the flask and filter housing with water before going on to the next sample.

4. CALCULATIONS

Suspended solids (mg/L) = $(W_4 - W_1) \times 10^6/V_1$

where: W_1 = weight of glass fibre filter (g)
W_4 = weight of filter + sediment (g)
V_1 = sample volume (mL).

Express results to nearest whole number.

Dissolved solids (mg/L) = $(W_3 – W_2) \times 10^6/V_2$

where: W_2 = weight of beaker (g)
W_3 = weight of beaker + dried filtrate (g)
V_2 = filtrate volume (mL).

Express results to nearest whole number.

5. REFERENCE

Standard Methods for the Analysis of Water and Wastewater. 20th Edition. (1998) American Public Health Association, Washington DC. Method 2540 D. Total Suspended Solids Dried at 103 - 105 °C. and Method 2540 C. Total Dissolved Solids Dried at 180 °C.

310 CALCIUM, MAGNESIUM, SODIUM & POTASSIUM

1. INTRODUCTION

The presence of calcium and magnesium in water results from passage over deposits of limestone, dolomite, gypsum and shale. Small concentrations of their carbonates can combat corrosion of pipes by laying down a protective layer, however excess can cause scale. Because of the potential damage to boilers and heating elements the levels of calcium and magnesium are often controlled by water softening processes.

Total hardness can be calculated from the calcium and magnesium concentrations and is often used as a measure of potable water quality. (Standard Methods for the Analysis of Water and Wastewater) A maximum level of 200 mg/l is the guideline for drinking water. (Drinking Water Standards)

Sodium and potassium are commonly associated with aluminosilicate minerals. Sodium typically remains in solution, whereas potassium is readily assimilated by plants and is incorporated into clay mineral structures. These elements are measured in natural waters to determine the suitability of the water for irrigation. High salt levels in irrigation waters cause damage to plants, while high sodium levels or high sodium relative to calcium and magnesium, causes problems with the soil by raising the exchangeable sodium. A maximum level of 200 mg/l is the guideline for drinking water. (Drinking Water Standards)

Caesium is added to eliminate ionisation interference in the determination of potassium and sodium, and strontium is added to prevent chemical interference in the determination of calcium and magnesium.

2. REAGENTS

2.1 STRONTIUM - CAESIUM SOLUTION, 7500 mg/L Sr & 25000 mg/L Cs. Dissolve 23 g $SrCl_2.6H_2O$ and 31.8 g CsCl in water and make to 1 L.

2.2 1+3 DILUENT SOLUTION. Carefully add 27 mL conc. HCl to about 200 mL water, add 107 mL Sr/Cs solution and make to 1 L.

2.3 HYDROCHLORIC ACID, 0.2 M. Carefully add 17.5 mL conc. HCl to water and make to 1 L.

3. STANDARDS

3.1 CALCIUM STOCK, 5,000 mg/L. Use commercial solution or carefully dissolve 6.243 g calcium carbonate ($CaCO_3$), dried at 105°C, in enough 1+1 HCl (approx. 5 M) to just dissolve it (about 20 mL), and make up to 500 mL with 0.2 M HCl.

3.2 MAGNESIUM STOCK, 1,000 mg/L. Use commercial solution or carefully dissolve 0.500 g magnesium ribbon (cleaned by dipping in dilute HCl, rinsed with water and dried) in 10 mL 1+1 HCl, and make to 500 mL with 0.2 M HCl.

3.3 POTASSIUM STOCK, 1,000 mg/L. Use commercial solution or dissolve 0.953 g KCl (dried at 105°C for 2 hours) in 0.2 M HCl and make to 500 mL with 0.2 M HCl.

3.4 SODIUM STOCK, 1,000 mg/L. Use commercial solution or dissolve 1.271 g NaCl (dried at 105°C for 2 hours) in 0.2 M HCl and make to 500 mL with 0.2 M HCl.

3.5 MULTIPLE WORKING STOCK SOLUTION, 500 mg/L Ca, 50 mg/L Mg, 50 mg/L K and Na. Pipette 50 mL Ca stock (5,000 mg/L), 25 mL Mg stock (1,000 mg/L), 25 mL K stock (1,000 mg/L) and 25 mL Na stock (1,000 mg/L) into a 500-mL volumetric flask, and make to volume with water. Store in an inert plastic bottle (preferably teflon).

3.6 WORKING STANDARDS. Pipette aliquots of the multiple working stock solution into 200-mL volumetric flasks according to the following table:

Working Standard	Volume of multiple working stock (mL per 200 mL)	Concentration of working standards (mg/L)			
		Ca	Mg	K	Na
0	0.0	0	0	0	0
1	1.0	2.50	0.25	0.25	0.25
2	2.0	5.00	0.50	0.50	0.50
3	5.0	12.50	1.25	1.25	1.25
4	10.0	25.00	2.50	2.50	2.50

To each flask add 4 mL conc. HCl and 16 mL Sr/Cs solution. Make to 200 mL with water and mix well. Store in plastic bottles.

4. PROCEDURE

4.1 Pipette 3 mL sample and 9 mL of the 1+3 bases diluent solution into tubes. Stopper and shake to mix.

4.2 Determine bases by flame spectroscopy using the working standards.

Note: An air-acetylene flame is used for all elements. Mg is determined by atomic absorption spectrophotometry (AAS) at 285.2 nm, Ca by AAS at 422.7 nm, K by FES at 766.5 nm and Na by FES at 589.0 nm.

5. CALCULATIONS

Ca, Mg, K or Na (mg/L) = a x 4

where: a = concentration of sample solution (mg/L)
4 = factor for a 1+3 dilution

Report results to two decimal places.

Hardness by calculation:

Hardness (Equivalent to mg $CaCO_3$ /L) = (2.497 x a) + (4.118 x b)

where: a = concentration of calcium (mg/L)
b = concentration of magnesium (mg/L)

6. REFERENCES

Standard Methods for the Analysis of Water and Wastewater. 20th Edition. (1998) American Public Health Association, Washington DC. Method 2340 B. Hardness by Calculation. Method 3111 B. Atomic Absorption Spectrometry / Direct Air-Acetylene Flame Method.

312 OTHER METALS BY FLAME ATOMIC ABSORPTION SPECTROSCOPY

1. INTRODUCTION

Metals in solution may be readily determined by flame atomic absorption spectrophotometry. The method is simple, rapid and applicable to a large number of sample types such as waters, effluents, soils and sediments. Analysis for dissolved metals does not require prior digestion of sample.

Metal ions are dissolved in surface and groundwater when the water comes into contact with rock or soils containing the metal salts. Metals can also enter with discharges from sewage treatment plants and industrial plants. The toxicity of metals is dependent on their solubility and this in turn depends heavily on the pH, hardness, and presence of other anions and cations.

Cadmium occurs in sulphide minerals and is generally associated with zinc at a ratio of about 1 part Cd to 500 parts Zn. The metal is used in electroplating, batteries, paint pigments and in alloys. Cadmium is not essential for plants or animals. It is extremely toxic and accumulates in the kidneys and liver.

Chromium is found chiefly in chrome-iron ore. It is used in alloys, in electroplating and in pigments. Chromate compounds are added to cooling water for corrosion control. Chromium exists in both the trivalent and hexavalent states. The trivalent state forms strong complexes with amines, and is adsorbed by clay minerals. It rarely occurs in potable water. Hexavalent chromium compounds have been shown to be carcinogenic by inhalation and are corrosive to tissue. The atomic absorption technique determines total chromium only i.e. tri- and hexavalent.

Copper occurs in its native state and also in many minerals as sulphides, oxides and carbonates. It is widely used in electrical wiring, roofing, alloys, pigments, cooking utensils, piping and in the chemical industry. Copper salts are used in water supply systems to control biological growths in reservoirs, and in fungicides. Corrosion of copper-containing alloys in pipe fittings may introduce measurable amounts of copper into water. Copper is an essential trace element for plants and animals; however some compounds are toxic by inhalation or ingestion.

Iron occurs in the minerals hematite, magnetite and pyrite. It is widely used in steel and other alloys. The solubility of ferrous iron is controlled by the carbonate concentration. Because groundwater is often anoxic, any soluble iron is usually in the ferrous state. On exposure to air ferrous iron is oxidised to ferric iron and may hydrolyse to form red insoluble hydrated ferric oxide. Ferric iron is not significantly soluble unless the pH is very low. Elevated iron levels in water can cause stains in plumbing, laundry and cooking utensils, and can impart objectionable tastes and colours to food.

Manganese is associated with iron minerals and occurs in nodules in ocean and freshwaters and in soils. It is used in steel alloys, batteries and food additives. The aqueous chemistry of manganese is similar to that of iron. Since groundwater is often anoxic, any soluble

manganese in water is in the reduced state, Mn^{2+}. Upon exposure to air groundwater containing Mn^{2+} will precipitate black MnO_2. Manganese is considered an essential trace element for plants and animals.

Nickel is obtained chiefly from pyrrhotite and garnierite. It is used in alloys, magnets, protective coatings, catalysts and batteries. The common aqueous species is Ni^{2+}. In reducing conditions insoluble sulphides can form, while in aerobic conditions complexes with hydroxide, carbonates and organic ligands can form. It is suspected to be an essential trace element for some plants and animals.

Lead is obtained chiefly from galena, PbS. It is used in batteries, ammunition, solder, piping, pigments, insecticides, and alloys. It was also used for many years as an anti-knock additive in petrol. The common aqueous species are Pb^{2+} and hydroxide and carbonate complexes. Lead in water supplies may come from industrial, mine or smelter discharges or from corrosion of plumbing. Lead is nonessential for plants and animals, is toxic by ingestion and is a cumulative poison.

The solubility of zinc is controlled by adsorption on mineral surfaces, carbonate equilibrium and organic complexes. Zinc is used in alloys such as brass and bronze, and in batteries, fungicides and pigments. Zinc is an essential growth element for plants and animals but at elevated levels is toxic to some aquatic life. Concentrations above 5 mg/L can cause a bitter astringent taste and opalescence in alkaline waters. Zinc most commonly enters the domestic water supply from the deterioration of galvanised iron.

2 SCOPE

2.3 This method is applicable to groundwaters, surface waters, drinking waters and wastewaters. Saline waters must be diluted to avoid clogging the nebuliser.

2.4 It covers the determination of dissolved metals, which are defined as those metals in an unacidifed sample that pass through a 0.45 μm membrane filter.

2.5 Total metals may also be determined using this method after vigorous acid digestion of an unfiltered sample (see method 316) and using matrix-matched standards.

2.6 Colourless, transparent, non-turbid samples may be analysed directly without digestion and reported as total metals.

The working standards cover the range 0.15 – 1.5 mg/L. This may be extended upward by dilution. Lower detection limits are achieved by using graphite furnace atomic absorption spectrometry (GFAAS).

3 INTERFERENCES

3.1 CADMIUM

No major interferences have been reported in the air-acetylene flame.

3.2 CHROMIUM

Cobalt, iron and nickel have been found to cause depression of chromium absorbance. This can be overcome by use of an oxidising air-acetylene flame or preferably a nitrous oxide-acetylene flame. Interference has also been found in the air-acetylene flame from copper, barium, aluminium, magnesium and calcium. The extent of interference is strongly dependent on the flame stoichiometry. Optimisation of the stoichiometry or the use of the nitrous oxide-acetylene flame can eliminate the interference.

3.3 COPPER

No interferences have been reported for copper in the air-acetylene flame, but some depression has been noted at high Zn/Cu ratios. This can be minimised by use of a lean air-acetylene flame or a nitrous oxide-acetylene flame.

3.4 IRON

Interference from citric acid has been reported to suppress the absorbance by up to 50% for a citric acid level of 200µg/mL. The effect is not overcome by adjustment of flame stoichiometry. The interference has been minimised by measuring the absorbance in the presence of phosphoric acid. It is necessary to select an optimum burner height to gain maximum freedom from interference. There is also some evidence that high sulphate concentrations have a slightly depressive effect on iron determination. The use of a nitrous oxide-acetylene flame has been found to remove all interference.

3.5 MANGANESE

In a reducing air-acetylene flame the absorbance is depressed in the presence of phosphate, perchlorate, iron, nickel, silicon and cobalt. In an oxidising air-acetylene flame or nitrous oxide-acetylene flame these interferences do not arise.

3.6 NICKEL

At 232.0 nm, non-atomic species in the flame absorb strongly. Where the sample has a high concentration of dissolved solids it is necessary to correct for non-atomic absorption by using background correction. At 352.4 nm this effect is minimal even for high matrix solutions. In hydrochloric and perchloric acid solution a slight (5%) absorbance depression has been observed in the presence of iron, cobalt and chromium. In a more oxidising flame the effects are minimised and in the nitrous oxide-acetylene flame no interferences are observed.

3.7 LEAD

No cationic interferences have been observed for the air-acetylene flame; however a number of anionic interferences have been reported. Phosphate, carbonate, iodide, fluoride and acetate suppress lead absorbance significantly at concentrations ten times greater than lead. These interferences can be largely overcome by the addition of EDTA solution so that the samples are 0.1 M with respect to EDTA. At the 217.0 nm wavelength, non-atomic species in the flame absorb strongly. Where the sample has a high concentration of dissolved solids it is necessary to correct for non-atomic absorption by using background correction.

3.8 ZINC

No chemical interferences have been found for the air-acetylene flame. At the 213.9 nm wavelength, non-atomic species in the flame absorb strongly. Where the sample has a high concentration of dissolved solids it is necessary to correct for non-atomic absorption by using background correction.

4 PRINCIPLE

In flame atomic absorption spectrometry, a sample is aspirated into a flame and atomised. A light beam is directed through the flame into a monochromator and on to a detector that measures the amount of light absorbed by the atomised element. Because each metal has its own characteristic absorption wavelength the source lamp is composed of that element. The amount of energy at the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the flame.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Samples should be collected into plastic bottles.

5.2 Bottles should be cleaned and acid washed before use.

5.3 Samples should be preserved immediately after sampling by addition of sufficient concentrated nitric acid to take the pH to below 2. With most waters, an acid level of 0.1 % (0.25 mL acid to 250 mL sample) is sufficient.

5.4 If dissolved metals are being determined, filter through a 0.45 µm filter **before** acidifying.

5.5 After acidifying, store samples refrigerated at 4 °C to prevent volume changes due to evaporation. Under theses conditions, samples should be stable for up to 6 months.

6 APPARATUS

6.1 Flame atomic absorption spectrophotometer.

6.2 Appropriate hollow cathode lamps.

7 STANDARDS

Use Aristar grade nitric acid for all standard preparation.

7.1 STOCK SOLUTIONS, 1,000 mg/L. Use commercial solutions for all elements.

7.2 MULTIPLE INTERMEDIATE STOCK, 30 mg/L in 0.1 % HNO3. Pipette 0.1 mL of nitric acid into a 100-mL flask then pipette in 3 mL of the 1000 mg/L stock solution of each element and make to volume with deionised water. Store in a Teflon bottle and prepare fresh 6-monthly.

7.3 WORKING STANDARDS. 0, 0.15, 0.30, 0.60 and 1.50 mg/L. If analysing dissolved or undigested samples, pipette 0.1 mL of nitric acid into 100-mL flasks

to make the standards in 0.1 % HNO_3. (If analysing digested samples, pipette 5 mL of nitric acid instead to make the standards in 5 % HNO_3.) Pipette 0, 0.50, 1.00, 2.00 and 5.00 mL of multiple intermediate stock into each and make to volume with deionised water. Store in plastic vials and prepare weekly.

7.4 QC STOCK STANDARD, 1000 mg/L. Use a commercial mixed element ICP standard.

7.5 QC INTERMEDIATE STANDARD, 10 mg/L. Pipette 0.05 mL of nitric acid and 0.5 mL of QC stock standard (standard 7.4 above) into a 50-mL flask and make to volume with deionised water. Store in a Teflon bottle and prepare fresh 6-monthly.

7.6 QC WORKING STANDARD, 1 mg/L. Pipette 0.1 mL of QC stock standard (standard 7.4 above) and 9.9 mL of water into a plastic tube. If analysing digested samples, pipette 0.1 mL of QC stock standard (standard 7.4 above), 0.5 mL of nitric acid and 9.4 mL of water into a plastic tube. Cap and mix.

8 QUALITY ASSURANCE

8.1 QC SAMPLE

8.1.1 Analyse a tube of the QC standard (standard 7.5) as the first sample immediately after calibration, and as the last sample in the batch.

8.1.2 Both values must be within 10% of the theoretical value.

8.2 DUPLICATES

8.2.1 One sample in every ten should be analysed in duplicate where sample volume permits.

8.2.2 The relative percent difference between duplicates must be less than 15 % for concentrations above 1 mg/L and less than 25 % for concentrations below 1 mg/L.

9 PROCEDURE

9.1 Pour samples into 12-mL plastic tubes up to the 10 mL mark.

9.2 Drop a small aliquot of sample onto pH indicator paper to check whether or not samples have been acidified to below pH 2. If not, add 10 µL of nitric acid, cap and shake to mix. The volume change introduced is negligible and can be ignored.

9.2 Determine metals by flame spectroscopy using the standards prepared in section 7 above and following the instrument operating procedure.

10 CALCULATIONS

10.1 All metal concentrations are given in mg/L. No further calculations are necessary unless samples were diluted prior to analysis.

10.2 Report results to 3 significant figures, or as less than the detection limit given in Table 1 below if appropriate:

Table 1. Flame AAS detection limits

Element	LOD (mg/L)	Element	LOD (mg/L)
Cd	0.005	Mn	0.005
Cr	0.008	Ni	0.02
Cu	0.005	Pb	0.03
Fe	0.01	Zn	0.005

11 REFERENCE

Standard Methods for the Examination of Water and Wastewater. 21st Edition. (2005) American Public Health Association, Washington DC. Method 3111 B. Atomic Absorption Spectrometry / Direct Air-Acetylene Flame Method.

313 DISSOLVED METALS BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY

1. INTRODUCTION

Graphite furnace atomic absorption spectroscopy (GFAAS) permits detection of most metals with detection limits from 20 to 1000 times better than those of conventional flame techniques. This increase in sensitivity is due to an increase in atom density within the confines of the furnace tube as compared to in a flame. An additional advantage of GFAAS is that only microlitre amounts of sample are required. The disadvantages though are that it is subject to more interferences than the flame procedure, it requires increased analysis time and, because of the high sensitivity, it is extremely susceptible to contamination.

2 SCOPE

2.7 This method is applicable to groundwaters, surface waters, drinking waters and wastewaters.

2.8 It covers the determination of dissolved metals, which are defined as those metals in an unacidifed sample that pass through a 0.45 μm membrane filter.

2.9 Total metals may also be determined using this method after vigorous acid digestion of an unfiltered sample and using matrix-matched standards.

2.10 Colourless, transparent, non-turbid samples may be analysed directly without digestion and reported as total metals.

2.11 The working standards vary depending on the metal, but are typically in the μg/L or parts per billion (ppb) range.

3 INTERFERENCES

3.1 PHYSICAL

3.1.1 SURFACE TENSION

If the sample solution matrix consists of organic solutions, high acid concentrations or detergents, sample spreading may cause reduced sensitivity and poor reproducibility. This is due to variations in atomic distribution at the atomisation stage. These effects may be overcome by:

- Reducing the sample volume
- Lengthening the drying programme
- Flash volatilising the sample (hot injection)
- Ridges in the graphite tube confining sample to the central part of the tube

3.1.2 VISCOSITY

At the other end of the scale, if a sample is highly viscous, the auto sampler can retain traces on the outside of the capillary. This amount can carry over from one injection to another, giving poor reproducibility. This can be overcome by diluting the sample with a low viscosity solvent or detergent. Addition of a small amount of nitric acid (to 0.01 % by volume) to the rinse solution helps prevent drops from adhering to the outside of the capillary.

3.1.3 SPATTERING

If drying is too rapid, particularly for samples containing mixtures of solvents or with a high salt content, spattering may occur causing sample to be ejected from the furnace. Ramp drying permits a controlled increase of temperature. In method development, visual inspection of the drying stage with a mirror allows checking as to whether spattering is occurring.

3.1.4 BACKGROUND ABSORPTION

Absorption of the hollow cathode lamp output by molecular species or by scatter from particles is a major interference in graphite furnace AAS. Carbon particles can be released from the tube at atomisation, organic matter still present after ashing can be pyrolysed to give smoke, and molecular absorption may occur when matrix components volatilize during atomization causing broadband absorption. The Zeeman effect is the phenomenon observed when an atomic spectral line is split into a number of components under the influence of a strong magnetic field. The effect is used in AAS to modify the atomic absorption wavelength profile so that the background absorbance at the analyte wavelength can be measured separately from the total background plus sample absorbance. Background correction should be used when analyzing samples containing high concentrations of acid e.g. digests, or high dissolved solids, and when using wavelengths below 350 nm.

While Zeeman is generally considered superior to deuterium lamp correction for GFAAS in terms of ability to cope with structured backgrounds and spectral interferences, there are also some limitations which the analyst must be aware of. Firstly, Zeeman background correction suffers from a loss in sensitivity due to the incomplete splitting of the absorption profile in the magnetic field. This loss of sensitivity is expressed as the magnetic sensitivity ratio, or MSR. For most elements however the MSR is greater than 80% and not a major problem. Additionally, due to the dependence of the efficiency of splitting on the concentration of the analyte, Zeeman background correction suffers from a loss of dynamic range and increased calibration curvature to the point of reflex curvature, or rollover. In practice this means that above a certain absorbance marking the reflex point, two different concentrations can give the same absorbance. The Varian 240Z system monitors peak absorbance and indicates an error when the maximum permissible absorbance (MAX ABS), slightly below the reflex point, is exceeded.

3.1.5 INCANDESCENCE

If the emission from the furnace is strong enough to flood the photomultiplier tube with DC emission, a spurious absorption can be obtained. This is because the amplification circuit cannot separate the modulated signal from the emission. This incandescence is only a problem for metals that require high temperatures and have wavelengths between 400 – 600 nm such as Ca and Ba. This interference may be minimised by:

- Proper furnace alignment
- Increased lamp current to reduce the photomultiplier gain
- Reduced slit heights
- Reduced atomisation temperatures.

3.1.6 MEMORY EFFECTS

Memory effects occur when the analyte is not totally volatilized during atomization. It depends on factors such as volatility of the analyte and its chemical form, the rate of atomization, and furnace design. The presence of memory effects is determined through blank burns, where no sample is injected. To prevent memory effects, the tube should be cleaned at regular intervals by operating the furnace at full power for short intervals. Persistent memory effects are an indication that the pyrolytic coating is wearing off and tube replacement is needed.

3.2 CHEMICAL

3.2.1 Stable compound formation can occur if the analyte reacts with carbon or nitrogen yet the temperature is not high enough to dissociate these compounds during atomisation. This can be avoided by using pyrolytically coated tubes and argon as the inert gas.

3.2.2 Volatile compound formation causes premature loss of the element during the ashing stage. Most metal chlorides show this behaviour. Matrix modification should be used to convert the metal into another compound that remains stable at higher temperatures. Specific modifiers may be used for each analyte as described in section 3.3 below, or alternatively palladium together with Ar/H_2 purge gas (commonly referred to as “forming gas”) may be used as a common matrix modifier for all analytes.

3.2.3 Acid selection is important, as some acids will cause severe depression while some will enhance the response, depending on the metal. The use of nitric acid is preferred in order to minimize vapour state chemical interferences. Hydrochloric acid should be avoided as it can cause the volatile compound formation described in 3.2.2 above.

3.3 ELEMENT SPECIFIC INTERFERENCES

3.3.1 CADMIUM

Cadmium analyses can suffer from severe non-specific absorption and light scattering by matrix components during atomisation. Background correction is required to compensate. Ammonium phosphate is the preferred modifier.

3.3.2 CHROMIUM

Nitrogen should not be used as the purge gas because of a possible CN band interference. Generally chromium does not require the use of a modifier; however if method development indicates possible interferences, palladium in forming gas should be tested.

3.3.3 COPPER

Generally copper does not require the use of a modifier; however if method development indicates possible interferences, palladium in forming gas should be tested.

3.3.4 IRON

Generally iron does not require the use of a modifier; however if method development indicates possible interferences, palladium in forming gas should be tested.

3.3.5 MANGANESE

Generally manganese does not require the use of a modifier; however if method development indicates possible interferences, palladium in forming gas should be tested. Manganese analyses can suffer from severe non-specific absorption and light scattering by matrix components during atomisation. Background correction is recommended to compensate.

3.3.6 NICKEL

Generally nickel does not require the use of a modifier; however if method development indicates possible interferences, palladium in forming gas should be tested. Nickel analyses can suffer from severe non-specific absorption and light scattering by matrix components during atomisation. Background correction is recommended to compensate.

3.3.7 LEAD

Lead recoveries may be improved by the use of a matrix modifier such as ammonium phosphate which allows use of a higher ashing temperature.

3.3.8 ZINC

Generally zinc does not require the use of a modifier; however if method development indicates possible interferences, palladium in forming gas should be tested. Zinc analyses can suffer from severe non-specific absorption and light scattering by matrix components during atomisation. Background correction is required to compensate.

3.3.9 HALIDE MATRIX MODIFICATION

When working with a halide matrix is unavoidable, e.g. with aqua regia digests or saline samples, the use of palladium combined with a reducing agent as a common matrix modifier should be considered. The reducing agent can be an organic acid such as citric acid, or alternatively use commercially available “forming gas”, consisting of 5% hydrogen in argon, as the inert gas during the atomisation stage. Palladium corrects for general chemical interferences as well as allowing higher char and atomisation temperatures without premature liberation of the analyte.

3.4 CONTAMINATION

Cleanliness is vital in furnace analysis. Dust can high levels of iron, copper, potassium and calcium, and one dust particle falling on the furnace tube during a run can drastically change results. Benches and surfaces should be cleaned regularly to prevent build-up of particulates.

3.5 LABWARE

Labware used in furnace analysis should be cleaned meticulously to prevent contamination. The following procedure is recommended:

- Clean in the dishwasher using phosphate-free detergent and RO water rinse cycles.
- Soak overnight in a solution of 5 % hydrochloric acid.
- Rinse by using the dishwasher with no detergent and RO water rinse cycles.
- Soak overnight in a solution of 10 % nitric acid.
- Rinse by using the dishwasher with no detergent and RO water rinse cycles.

Pre-cleaned glassware open to the environment can collect airborne particulates so store either capped or filled with 10 % HNO_3, and rinse immediately before use.

Check pipette tips carefully before choosing a brand - yellow pipette tips have been known to contain cadmium for example. If necessary, clean tips before use by soaking in 10 % HNO_3. Rinse and dry, and store in a sealed plastic bag. Autoanalyser cups for the autosampler should be similarly pre-cleaned and stored.

Standards made up in volumetric flasks should be transferred to plastic containers for storage to avoid either a loss of metal by adsorption or conversely gain of metal by leaching from the glass.

3.6 SOLUTION PURITY

Water should be used direct from the deionising unit just prior to use rather than from bench-top storage containers. Aristar grade acid should be used for standard preparation and in digestions, and AnalaR grade chemicals for modifiers.

4 PRINCIPLE

Electrothermal AAS is based on the same principle as flame AAS but with an electrically heated graphite furnace replacing the burner head. A discrete sample volume is dispensed into the furnace tube. Typically, determinations are made by heating the sample in three stages. First, a low current heats the tube to dry the sample. The second (ashing or char) stage destroys organic matter and volatilises other matrix components at an intermediate temperature. Finally, a high current heats the tube to incandescence and, in an inert atmosphere, atomises the element being determined. Additional stages can be added to aid drying and charring and clean and cool the tube between samples.

A light beam is directed through the furnace into a monochromator and on to a detector that measures the amount of light absorbed by the atomised element. Because each metal has its own characteristic absorption wavelength the source lamp is composed of that element. The

amount of energy at the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the furnace tube.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Samples should be collected into plastic containers. Clean bottles before use as described in section 3.5 above.

5.2 Samples should be preserved immediately after sampling by addition of sufficient concentrated nitric acid to take the pH to below 2. With most waters, an acid level of 0.1 % (0.25 mL acid to 250 mL sample) is sufficient.

5.3 If dissolved metals are being determined, filter through a 0.45 µm filter **before** acidifying.

5.4 After acidifying, store samples refrigerated at 4 °C to prevent volume changes due to evaporation. Under theses conditions, samples should be stable for up to 6 months.

6 APPARATUS

6.1 Varian 240Z atomic absorption spectrophotometer with GTA graphite tube atomiser and PSD programmable sample dispenser autosampler.

6.2 Appropriate hollow cathode lamps.

7 MATRIX MODIFIERS

Determine the need for a modifier with each new sample matrix by checking the spike recovery (section 9.2 below) Recovery close to 100% indicates that the sample matrix does not affect the analysis and no matrix modification is necessary. The use of chemical modifiers can lead to sample contamination from impurities in the modifier solution, heavy modifier use can shorten the life of the graphite tube, and modifiers can be expensive. The working modifiers described here are for a 5µL modifier co-addition to 10 µL of sample. Where matrix modification is needed, use the ammonium dihydrogen phosphate modifier for the determination of cadmium and lead, and the palladium modifier for the other metals.

7.1 AMMONIUM PHOSPHATE SOLUTION, 5 mg/mL. Dissolve 0.25 g of AnalaR grade NH4H2PO4 in 50 mL of water.

7.2 STOCK PALLADIUM SOLUTION, 10 g/L. Use commercial solution.

7.3 WORKING PALLADIUM SOLUTION, 500 mg/L. Pipette 1.25 mL of palladium stock (reagent 7.1.2 above) into a 25 mL volumetric flask and make to volume with water. Store in a plastic vial when not in use.

7 STANDARDS

Note: Use Aristar grade nitric acid for all standard preparation.

7.1 INDIVIDUAL STOCK SOLUTIONS, 1,000 mg/L. Use commercial solutions for all elements. Make sure these are nitrate salts rather than halides.

7.2 INTERMEDIATE STANDARDS. Prepare single element intermediate standards using the volumes described in Table 1 below. Pipette the appropriate volume of the 1000 mg/L stock solution of the required analyte into a 100-mL volumetric flask containing 0.1 mL of Aristar HNO_3, and make to volume with deionised water.

Table 1. Preparation of GFAAS intermediate standards

Analyte	mL of 1000 mg/L stock solution	Final concentration mg/L	Final concentration µg/L
Aluminium	0.5	5	5000
Arsenic	0.5	5	5000
Cadmium	0.1	1	1000
Chromium	0.1	1	1000
Copper	0.5	5	5000
Iron	0.1	1	1000
Manganese	0.1	1	1000
Nickel	0.5	5	5000
Lead	0.5	5	5000
Vanadium	0.5	5	5000
Zinc	0.1	1	1000

7.3 WORKING STANDARDS, in 0.1 % HNO_3. Prepare single element working standards using the volumes described in Table 2 below. Pipette the appropriate volume of intermediate standard of the required element into a 100-mL volumetric flask containing 0.1 mL of Aristar HNO_3, and make to volume with deionised water. Prepare these fresh each use.

Table 2. Preparation of GFAAS working standards

Analyte	Concentration of intermediate standard µg/L	mL of intermediate standard	Final concentration of working standard µg/L
Aluminium	5000	0.48	24
Arsenic	5000	1.00	50
Cadmium	1000	0.10	1.0
Chromium	1000	0.80	8
Copper	5000	0.60	30
Iron	1000	0.60	6
Manganese	1000	0.30	3
Nickel	5000	0.50	25
Lead	5000	0.60	30
Vanadium	5000	2.00	100
Zinc	1000	0.07	0.7

7.4 QC WORKING STANDARD, in 0.1 % HNO_3. Use the report from the most recent Water Test ILPP round to select a Water Test sample to use as a check standard.

9 QUALITY ASSURANCE

9.1 QC SAMPLE

9.1.1 Analyse a tube of the QC standard (standard 8.4) as the first sample immediately after calibration, and as the last sample in the batch.

9.1.2 Both values must be within 10% of the theoretical value.

9.2 DUPLICATES

9.2.1 All standards and samples are analysed in duplicate when using GFAAS. For samples containing less than 10 µg/L, the difference between duplicates should be less than 2 µg/L. For samples containing greater than 10 µg/L, the difference between duplicates should be less than 5 µg/L.

10 PROCEDURE

10.1 Pour samples into 2-mL autoanalyser cups which have been pre-cleaned by soaking in 10% HNO_3.

10.2 Analyse by graphite furnace AAS following the instrument operating procedure and template methods.

11 CALCULATIONS

11.1 All element concentrations are calculated directly by the instrument in µg/L. No further calculations are necessary unless samples were diluted prior to analysis.

11.2 Report results to 1 or 2 significant figures or as less than the detection limit given in Table 4 below as appropriate:

Table 4. GFAAS detection limits

Element	LOD (µg/L)	Element	LOD (µg/L)
As	1	Mn	0.2
Cd	0.1	Ni	2
Cr	2	Pb	1
Cu	0.5	V	3
Fe	1	Zn	1

12 REFERENCES

Analytical methods for Graphite Tube Atomisers. September 1988. Publication No.85-100848-00. Varian Australia Pty Ltd.

Standard Methods for the Examination of Water and Wastewater. 21st Edition. (2005) American Public Health Association, Washington DC. Method 3113 B. Electrothermal Atomic Absorption Spectrometry.

USEPA Method 7010 Graphite Furnace Atomic Absorption Spectrophotometry. (1998)

314 ALUMINIUM AND SILICA

1. INTRODUCTION

The occurrence of aluminium in natural waters is largely due to finely suspended mineral particles. It is not an essential element and has been implicated in the aetiology of Alzheimer's disease. A guideline maximum value of 0.15 mg/L in drinking water has been recommended to avoid depositions and discolouration. (Drinking Water Standards for New Zealand)

Silicon does not occur freely in nature but as silica (SiO_2) from clay minerals and quartz. It is an essential trace element for animals but not plants. In the presence of magnesium it can form scale deposits.

2. STANDARDS

2.1 ALUMINIUM STOCK, 1,000 mg/L. Use commercial solution or dissolve 0.1000 g of aluminium metal in a mixture of 4 mL 1+1 HCl and 1 mL of conc HNO_3. Warm gently, add 10 mL 1+1 HCl and dilute to 1000 mL with water.

2.2 SILICA STOCK, 1,000 mg SiO_2/L. Use commercial solution or dissolve 0.0.4730 g of $Na_2SiO_3.9H_2O$ in water. Add 10 mL of conc HNO_3 and dilute to 1000 mL with water. Store in plastic.

2.3 MULTIPLE INTERMEDIATE STOCK, 50 mg Al/L and 50 mg SiO_2/L. Pipette 5 mL of the 1000 mg/L stock solution of each element into a 100-mL flask and make to volume with deionised water.

2.4 WORKING STANDARDS. 0, 0.50, 1.00, 2.50, 5.00 and 10.00 mg Al/L and mg SiO_2/L in 1% HNO_3. Pipette 0.5 mL of nitric acid into 50-mL flasks, then pipette 0, 0.50, 1.00, 2.50, 5.00 and 10.00 mL of multiple intermediate stock into each.

3. PROCEDURE

3.1 Pour samples into tubes.

3.2 Determine metals by flame atomic absorption spectrometry (AAS) using the standards prepared in section 2 above, following the instrument-operating manual.

A nitrous oxide-acetylene flame is used. Table 1 lists the recommended wavelengths and gives an indication of the typical instrument detection limits. Background correction should be used for Al.

Table 1. Recommended wavelengths for AAS.

Analyte	Wavelength nm	Instrument Detection Limit mg/L
Al	309.3	0.1
Si	251.6	0.3

4. CALCULATIONS

All element concentrations are read directly from the instrument printout. Method detection limits (MDLs) should be determined by analysing replicate aliquots of reagent water fortified to a concentration about a fifth the value of the lowest standard. If a concentration is below the method detection limit (MDL), quote the result as < "the MDL value."

5. REFERENCES

Drinking Water Standards for New Zealand 2000. Ministry of Health. Wellington.

Standard Methods for the Analysis of Water and Wastewater. 20th Edition. (1998) American Public Health Association, Washington DC. Method 3111 D. Atomic Absorption Spectrometry / Direct Nitrous Oxide-Acetylene Flame Method.

316 NITRIC ACID DIGESTION FOR TOTAL METALS

1 INTRODUCTION

Acid digestion reduces interference by organic matter and converts metals associated with particulates to a form that can determined by atomic absorption spectrometry (AAS.) Strictly speaking, only hydrofluoric acid treatment is capable of total dissolution of silicates to release metals into solution; however HF is a very hazardous chemical to work with. Other acids that are safer to handle can dissolve almost all elements that could become environmentally available. The term "total metal" can be used when using other acids but the operational digestion procedure must be specified.

Nitric acid will digest most samples adequately, and produces a matrix suitable for both flame and graphite furnace AAS. The method described here is based on APHA 3030E. Nitric Acid Digestion (Standard Methods for the Examination of Water and Wastewater). It is very similar to USEPA Method 3020A Acid Digestion of Aqueous Samples for Total Metals By GFAAS. Digests are typically analysed for cadmium, chromium, copper, iron, manganese, nickel, lead and zinc.

2 SCOPE

2.12 This method is applicable to groundwaters, surface waters, drinking waters and wastewaters.

2.13 Samples prepared by this method can be analysed by flame atomic absorption spectrometry or graphite furnace atomic absorption spectrometry depending on the metal levels.

3 INTERFERENCES

3.1 In sample preparation, cleanliness is of prime concern. The work area, including bench top and fume hood should be regularly cleaned in order to eliminate environmental contamination.

3.2 This digestion procedure may not be vigorous enough to destroy some metal complexes, particularly those bound in silicate phases.

3.3 Samples that have not been filtered but are colourless, transparent and non-turbid may be analysed directly without prior digestion and reported as total metals.

3.4 All metals are not equally stable in the digestate. The digest should be analysed as soon as possible.

4 PRINCIPLE

An aliquot of sample is gently heated, without boiling, with nitric acid in a digestion tube. The cooled digest is mixed and any particulates allowed to settle overnight prior to analysis.

5 SAMPLE HANDLING AND PRESERVATION

5.2 Samples should be collected into plastic bottles.

5.3 Bottles should be cleaned and acid washed before use.

5.4 Samples should **not** be filtered.

5.5 Samples should be preserved immediately after sampling by addition of sufficient concentrated nitric acid to take the pH to below 2. With most waters, an acid level of 0.1 % (0.25 mL acid to 250 mL sample) is sufficient.

5.6 After acidifying, store samples refrigerated at 4 °C to prevent volume changes due to evaporation. Under theses conditions, samples should be stable for up to 6 months.

6 APPARATUS

6.1 Block digestor.

6.2 Glass tubes to fit the block.

6.3 Glass teardrop stoppers to allow refluxing.

7 REAGENTS

7.1 NITRIC ACID, HNO_3. Concentrated (sp gr 1.41) Aristar grade.

8 QUALITY ASSURANCE

8.1 DUPLICATES

8.1.1 One sample in every ten should be digested in duplicate where sample volume permits.

8.1.2 For flame AAS, the relative percent difference between duplicates must be less than 15 % for concentrations above 1 mg/L and less than 25 % for concentrations below 1 mg/L. For GFAAS, the difference between duplicates should be less than 2 µg/L for samples containing less than10 µg/L and less than 5 µg/L for samples containing greater than 10 µg/L.

9 DIGESTION

9.1 Mix sample well then quickly pipette 20 mL into a digestion tube. Include two tubes of deionised water as digest blanks.

9.2 Add 1mL of concentrated HNO_3 (reagent 7.1.)

9.3 Place a tear drop stopper in each tube.

9.4 Place the rack of tubes into the block digester in a fume cupboard.

9.5 Using the digester control unit heat the solution in the tubes to 95 °C and holds it there for 2 hours. The samples should not boil.

9.6 Complete digestion is indicated by a clear light-coloured solution. If necessary add a further 0.5 mL of concentrated HNO_3 (reagent 7.1) heat the solution in the tubes back to 95 °C and hold it there for 30 minutes. Repeat this step as necessary until a clear light coloured solution is obtained.

9.7 Allow the samples to cool.

9.8 Vortex tubes for 10 seconds to mix.

9.9 Allow the digests to stand overnight for any suspended material to settle.

9.10 Carefully decant supernatant liquid into tubes or cups suitable for the analysis technique.

9.11 Analyse for metals by either flame or graphite furnace atomic absorption spectrometry depending on expected metal levels. Standards should be prepared in 5% HNO_3.

10 CALCULATIONS

Metal concentrations are on the instrument printout in mg/L (flame AAS) or µg/L (GFAAS).

10.1 Metal (mg/L or µg/L) = $(a - b) \times V_f / V_i$

where:
- a = metal in sample solution (mg/L or µg/L)
- b = metal in blank solution (mg/L or µg/L)
- V_f = volume sample + acid (mL)
- V_i = volume sample (mL)

10.2 Validation work has shown there is a negligible volume change during digestion, therefore:

Metal (mg/L or µg/L) = $(a - b) \times 21/20$

= $(a - b) \times 1.05$

10.3 Report results to 3 significant figures, or as less than the detection limit given in the table below if appropriate.

Metal	Detection Limit	
	Flame AAS mg/L	Furnace AAS µg/L
ım	0.005	0.1
Chromium	0.008	2
Copper	0.005	1
Iron	0.01	1
Manganese	0.005	0.2
Nickel	0.02	1
Lead	0.03	1
Zinc	0.005	0.1

13 REFERENCES

Standard Methods for the Analysis of Water and Wastewater. 21st Edition. (2005) American Public Health Association, Washington DC. Method 3030E. Nitric Acid Digestion

USEPA SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods; Method 3020A Acid digestion of aqueous samples and extracts for total metals for analysis by GFAA spectroscopy.

318 CHLORIDE BY FERRICYANIDE COLORIMETRY

1. INTRODUCTION

Chloride is one of the major anions present in water. A guideline maximum level of 250 mg/L is recommended for drinking water to avoid taste problems and corrosion of reticulation systems (Drinking Water Standards for New Zealand.)

Chloride ions react with mercuric thiocyanate to produce mercuric chloride and liberate thiocyanate ions. In the presence of ferric salts, these thiocyanate ions produce a characteristic orange colour, the intensity of which is proportional to the chloride ion concentration. (Methods for Determination of Inorganic Substances in Water and Fluvial Sediments.)

2. APPARATUS

2.1 SPECTROPHOTOMETER, for use at 457 nm.

3. REAGENTS

3.1 FERRIC AMMONIUM SULPHATE SOLUTION. Dissolve 20.7 g of ferric ammonium sulphate ($FeNH_4(SO_4)_2.12H_2O$) in 285 mL of concentrated nitric acid and dilute to 500 mL with water. Filter.

3.2 MERCURIC THIOCYANATE SOLUTION. Dissolve 1.5 g of mercuric thiocyanate ($Hg(SCN)_2$) in 500 mL of 95% ethanol. Stir for 1 hour to saturate the solvent, allow any undissolved thiocyanate to settle then filter.

4. STANDARDS

4.1 STOCK SOLUTION, 1,000 mg/L Cl^-. Dissolve 0.824 g sodium chloride (NaCl), dried at 105°C, in water and make to 500 mL in a volumetric flask.

4.2 HIGH RANGE WORKING STANDARDS, 100, 50, 25, 10, 0 mg/L Cl^-. Dilute 10, 5, 2.5, 1.0 and 0 mL of 1,000 mg/L stock solution to 100 mL with water.

4.3 LOW RANGE WORKING STANDARDS, 10, 8, 6, 4, 2, 0 mg/L Cl^-. Prepare working standards fresh for each run by pipetting aliquots of 10 mg/L working standard (as prepared in 3.3 above) and water into 15 mL plastic tubes according to the following table:

Tube Number	Volume of 10 mg/L Chloride working stock (mL)	Volume of water (mL)	Final Chloride Concentration (mg/L)
1	0	10.0	0
2	2.0	8.0	2.0
3	4.0	6.0	4.0
4	6.0	4.0	6.0
5	8.0	2.0	8.0
6	10.0	0	10.0

5. PROCEDURE

5.1 Pipette 2.5 mL of each of the high range standards, and of each water sample, into 15 mL tubes.

5.2 Pipette 1 mL of ferric ammonium sulphate solution into each tube.

5.3 Pipette 1 mL of mercuric thiocyanate solution into each tube then cap and shake.

5.4 Wait 30 minutes for the colour to develop then read the absorbance at 457 nm.

5.5 If the absorbance of any of the unknowns is higher than that of the top standard then the sample will have to be analysed again in dilution.

5.6 If any of the samples contains less than 10 mg/L Cl^- then the assay should be repeated using 10 mL of each of the low range standards prepared in 3.3, 10 mL of sample, and following steps 4.2 to 4.4.

6. CALCULATIONS

6.1 Prepare a calibration curve using the absorbances of the standards. The curve should be linear and pass through the origin.

6.2 Use the curve to determine the concentration in mg/L of chloride in the samples.

7. REFERENCES

Drinking Water Standards for New Zealand 2000. Ministry of Health. Wellington.

Skougstad, M.W., Fishman, M.J., Friedman, L.C., Erdmann, D.E. and Duncan, S.S. (1979). Methods for determination of inorganic substances in water and fluvial sediments. Techniques of Water-Resources Investigations of the United States Geological Survey, Book 5, Chapter A1, 331-332.

320 CHLORIDE BY MERCURIC NITRATE TITRATION

1. INTRODUCTION

Chloride is one of the major anions present in water. A guideline maximum level of 250 mg/L is recommended for drinking water to avoid taste problems along with corrosion of reticulation systems (Drinking Water Standards for New Zealand.)

Chloride can be titrated with mercuric nitrate because of the formation of soluble, slightly dissociated mercuric chloride. In the pH range 2.3 to 2.8, diphenylcarbazone indicates the titration endpoint by formation of a purple complex with the excess mercuric ions.

2. APPARATUS

2.1 BURETTE, readable to 0.05 mL.

3. REAGENTS

3.1 NITRIC ACID, 2 M. Carefully add 126 mL of concentrated HNO_3 to water and make to 1 L.

3.2 MERCURIC NITRATE SOLUTION, about 0.02 N. Add 20 mL of 2 M HNO_3 to approximately 700 mL water and then about 3.0 g $Hg(NO_3)_2$. Stir to dissolve and make to 1 L.

3.3 CHLORIDE STANDARD SOLUTION, 0.02 N. Dissolve 1.169 g of NaCl (dried at 105°C for two hours) in water and make to 1 L.

3.4 DIPHENYLCARBAZONE INDICATOR, 0.1% in ethanol. Dissolve 0.1 g s-diphenylcarbazone in 100 mL of 95 % ethanol and store in a refrigerator. Prepare fresh monthly.

4. PROCEDURE

4.1 STANDARDIZATION OF MERCURIC NITRATE SOLUTION

4.1.1 Pipette 10 mL of 0.02 N NaCl into a 50-mL conical flask and add 10 drops of diphenylcarbazone indicator.

4.1.2 While stirring, add mercuric nitrate solution drop-wise until a faint blue-violet colour appears. This indicates the end point of titration. Further addition of mercuric nitrate will intensify the colour.

4.1.3 Make three or four titrations to ensure consistent results. Record titre (T_1).

4.2 SAMPLE TITRATION

4.2.1 Transfer 20 mL aliquot of clear sample (filter if necessary) to a 100-mL conical flask. Titrate two 20 mL aliquots distilled water as blanks.

4.3.2 Add 10 drops diphenylcarbazone indicator.

4.3.3 Titrate with mercuric nitrate solution to a pale blue-violet end point.

4.3.4 Record titre to two decimal places (T_2 for blanks and T_3 for samples).

5. CALCULATIONS

Standardisation of mercuric nitrate:

$$N = 0.2 / T_1 \quad \textbf{(1)}$$

Sample titration:

$$Cl\ (mg/L) = (T_3 - T_2) \times N \times 1000/v \times 35.5 \quad \textbf{(2)}$$

Where:
- T_1 = titre for NaCl standardisation (mL)
- T_2 = titre for blank (mL)
- T_3 = titre for sample (mL)
- N = normality of $Hg(NO_3)_2$ from **(1)**.
- v = aliquot of sample (mL)
- 35.5 = atomic weight of Cl.

For a 20 mL aliquot

$$Cl\ (mg/L) = (T_3 - T_2) \times 355/T_1 \quad \textbf{(3)}$$

6. REFERENCES

Blakemore, L.C.; Searle, P.L.; Daly, B.K. 1987. Methods for Chemical Analysis of Soils. New Zealand Soil Bureau Scientific Report 80. 103 p.

Metson, A.J. 1972. in Soil Bureau Laboratory Methods. New Zealand Soil Bureau Scientific report 10B.

322 AMMONIUM-NITROGEN

1. INTRODUCTION

Ammonia in natural waters is produced largely by decomposition of organic nitrogen compounds. Its concentration is generally low as it adsorbs to soil particles and is not readily leached. A guideline value of 0.15 mg/L is suggested to avoid taste and odour problems with drinking water. (Drinking Water Standards)

Ammonium-nitrogen is determined by releasing the ammonia from alkaline solution by steam distillation, collection in dilute boric acid followed by titration with hydrochloric acid.

2. APPARATUS

2.1 STEAM DISTILLATION ASSEMBLY, glass system such as Parnas-Wagner or Markham, or semi-automated system such as Bucchi.

2.2 BURETTE, readable to 0.05 mL.

3. REAGENTS

3.1 SODIUM HYDROXIDE SOLUTION, approx. 10 M. Carefully dissolve 400 g NaOH pellets in 1 L water, stirring constantly.

3.2 BORIC ACID, 1%. Dissolve 5.00 g H_3BO_3 in water and make to 500 mL.

3.3 HYDROCHLORIC ACID, 1 M. Prepare from standard ampoule **OR** carefully add 87 mL conc. HCl (sp gr. 1.18) to 500 mL water and make to 1 L.

3.4 HYDROCHLORIC ACID, 0.02 M. Pipette 20 mL 1 M HCl into a 1-L volumetric flask and make to volume with water.

3.5 BROMOCRESOL GREEN-METHYL RED MIXED INDICATOR. Mix 100 mL 0.1% bromocresol green (0.1 g bromocresol green dissolved in 100 mL 95% ethanol) with 20 mL 0.1% methyl red (0.1 g methyl red dissolved in 100 mL 95% ethanol).

4. PROCEDURE

4.1 Before analysing samples wash distillation apparatus by carrying out a distillation using water only.

4.2 Transfer a 20 mL sample aliquot to the steam distillation apparatus.

4.3 Add 2 mL 10 M sodium hydroxide.

4.4 Into a 100-mL conical flask add 10 mL 1% boric acid and 5-6 drops mixed indicator and place flask under the delivery tube of the condenser so that the tip is under the surface of the liquid.

4.5 Steam distil sample solution. The indicator in the boric acid will change colour as the ammonia begins to distil over.

4.6 When about 30 - 40 mL of distillate has been collected remove 100-mL flask from apparatus, rinsing the tip of the delivery tube with water into the flask.

4.7 Stop the entry of steam. The distilling flask will empty and then can be removed.

4.8 Titrate the distillate against 0.02 M HCl, to the neutral grey colour of the indicator. Record titres, T_1 for blanks and T_2 for samples.

5. CALCULATION OF RESULTS

$$\text{Nitrogen (mg/L)} = (T_2 - T_1) \times M \times 14 \times 1000/V$$

where:

	T_2	=	sample titre (mL)
	T_1	=	blank titre (mL)
	M	=	molarity of HCl
	V	=	sample volume for distillation (mL)
	14	=	weight of 1 mM nitrogen (mg)

For 0.02 M HCl titrant and 20 mL sample aliquot:

$$\text{Nitrogen (mg/L)} = (T_2 - T_1) \times 14$$

Report results to one decimal place.

6. REFERENCE

Blakemore, L.C.; Searle, P.L.; Daly, B.K. 1987. Methods for Chemical Analysis of Soils. New Zealand Soil Bureau Scientific Report 80. 103 p.

324 NITRATE-NITROGEN BY UV SCREENING

1. INTRODUCTION

Nitrate can reach high levels in some groundwaters to due agricultural practices. It contributes to an illness known as methaemoglobinemia in infants; therefore a limit of 10 mg/L nitrate-N is imposed on drinking water. (Standard Methods for the Analysis of Water and Wastewater)

The uv-screening method is a very simple technique that can be used for screening samples that have low organic matter contents, i.e. uncontaminated natural waters and potable water supplies. Measurement of uv absorption at 220 nm enables rapid determination of NO_3-N. Because dissolved organic matter also may absorb at 220 nm and NO_3 does not absorb at 275 nm, a second measurement made at 275 nm may be used to correct the NO_3 value. The nitrate calibration curve follows Beer's Law up to 11 mg N/L. The extent of this empirical correction is related to the nature and concentration of organic matter and may vary from one water to another.

2. APPARATUS

2.1 SPECTROPHOTOMETER, for use at 220 nm and 275 nm.

3. REAGENTS

3.1 HYDROCHLORIC ACID, 1 M. Carefully add 87 mL conc. HCl (sp gr. 1.18) to 500 mL water and make to 1 L.

4. STANDARDS

4.1 NITRATE STOCK 1,000 mg/L NO_3-N. Carefully dissolve 7.218 g potassium nitrate (KNO_3), dried at 105°C for 1 hour, in water in a 1-litre volumetric flask and make to the mark.

4.2 NITRATE INTERMEDIATE STANDARD, 100 mg/L NO_3-N. Dilute 10 mL of nitrate standard (1000 mg/L NO_3-N) to 100 mL with water.

4.3 NITRATE WORKING SOLUTIONS; 10, 5, 2, 1, 0.5, 0 mg NO_3-N/L. Dilute 5, 2.5, 1, 0.5, and 0.25 mL of nitrate intermediate standard (100 mg/L NO_3-N) to 50 mL with water.

5. PROCEDURE

5.1 Filter turbid samples through a 0.45 µm filter.

5.2 Add 0.2 mL of 1M HCl and mix thoroughly.

5.3 Use distilled water to zero the spectrophotometer at 220nm.

5.4 Read the absorbance of the standard or sample at 220 nm.

5.5 Use distilled water to zero the spectrophotometer at 275 nm.

5.6 Read the absorbance of the standard or sample at 2750 nm.

6. CALCULATIONS

6.1 For both standards ands samples, subtract two times the absorbance reading at 275 nm from the reading at 220 nm to obtain absorbance due to NO_3.

6.2 Prepare a calibration curve of absorbance due to NO_3 against the concentration in mg/L of NO_3-N of the standards. The curve should be linear and pass through the origin.

6.3 Using sample absorbances corrected as in step 6.1, use the curve to determine the concentration in mg/L of NO_3-N in the samples.

Note: If the correction value is more than 10% of the reading at 220 nm, do not use this method.

7. REFERENCE

Standard Methods for the Analysis of Water and Wastewater. 20th Edition. (1998) American Public Health Association, Washington DC. Method 4500-$NO3^-$ B. Ultraviolet spectrophotometric screening method.

326 NITRATE-NITROGEN BY CADMIUM REDUCTION

1. INTRODUCTION

Nitrate can reach high levels in some groundwater to due agricultural practices. It contributes to an illness known as methaemoglobinemia in infants; therefore a limit of 10 mg/L nitrate-N is imposed on drinking water. (Standard Methods for the Analysis of Water and Wastewater)

Nitrate is reduced almost quantitatively to nitrite in the presence of cadmium. This method uses copperised cadmium granules packed in a glass column to perform the reduction step. The nitrite is then determined by diazotising with sulphanilamide and coupling with N-(1-naphthyl)-ethylene diamine dihydrochloride to form a highly coloured azo dye that is measured on a spectrophotometer. A correction is made for any nitrite originally present in the sample by analysing without the reduction step.

Nitrite may also be determined with this method by starting at step 5.2.5 i.e. direct colour formation without the cadmium reduction step.

2. APPARATUS

2.1 SPECTROPHOTOMETER for use at 543 nm.

2.2 REDUCTION COLUMN. Use commercial columns or construct from a 100-mL pipette as shown in Figure 1.

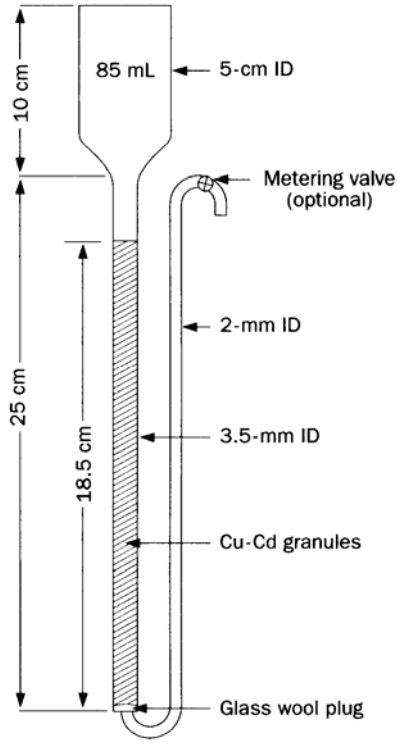

Figure 1. Cadmium reduction column

3. REAGENTS

HEALTH AND SAFETY WARNING: Cadmium is a hazardous chemical and a known carcinogen. A material safety data sheet should be obtained, read and understood before commencing work. It should be noted however that the material is always used here in a wet, granular form where it poses far less risk than when dry. Nevertheless it should be handled with care and gloves should be worn at all times.

3.1 ACETONE. Drum grade.

3.2 AMMONIUM CHLORIDE BUFFER. In a fumehood, add 500 mL water, 105 mL concentrated hydrochloric acid (HCl), 95 mL of ammonia solution (sp gr 0.91) and 1.0 g of disodium EDTA to a plastic 1-litre bottle. Stir magnetically till dissolved and make to the 1-litre mark with water. Adjust the pH to 8.5 with 10% HCl or 15 N NaOH.

3.3 2% COPPER SULPHATE SOLUTION. Dissolve 50 g of copper sulphate ($CuSO_4.5H_2O$) in 500 mL of water.

3.4 HYDROCHLORIC ACID, 10 %. Carefully add 100 mL of concentrated hydrochloric acid (HCl) to 900 mL of water and shake to mix.

3.5 NEDD COLOUR REAGENT. To 800 mL of water add 100 mL 85% phosphoric acid and 10 g of sulphanilamide and stir till dissolved. Add 1 g of N-(1-naphthyl)-ethylene diamine dihydrochloride (NEDD) and mix to dissolve. Make to 1 litre with water. This is stable for 1 month when stored in a brown bottle in the refrigerator.

4. STANDARDS

4.1 NITRATE STOCK 1,000 mg/L NO_3-N. Carefully dissolve 7.218 g potassium nitrate (KNO_3), dried at 105°C for 1 hour, in water in a 1-litre volumetric flask and make to the mark.

4.2 NITRATE INTERMEDIATE STANDARD, 20 mg/L NO_3-N. Dilute 2 mL of nitrate standard (1000 mg/L NO_3-N) to 100 mL with water.

4.3 NITRATE WORKING SOLUTIONS; 1.00, 0.50, 0.20, 0.10, 0.05, 0 mg NO_3-N/L. Dilute 5, 2.5, 1, 0.5, 0.25 and 0 mL of nitrate intermediate standard (20 mg/L NO_3-N) to 100 mL with water.

4.4 COLUMN CONDITIONING STANDARD, 0.25 mg/L NO_3-N in buffer. Add 25 mL of 1.0 mg/L NO_3-N standard to 75 mL of buffer and mix well.

5. PROCEDURE

5.1 PREPARATION OF REDUCTION COLUMN

5.1.1 Place about 25 g of new or used cadmium granules (20- to 100-mesh) into a 250 mL beaker.

5.1.2 Add 100 mL of acetone, swirl and decant. This removes any organic coating that may have accumulated on the granules.

5.1.3 Add 100 mL of deionised water, swirl and decant.

5.1.4 Repeat with a second 100 mL portion of deionised water.

5.1.5 Add 50 mL of 10% HCl, swirl and decant. This removes any oxide layer. Swirl for only 10 seconds though or the metal itself will begin to dissolve.

5.1.6 Repeat with a second 50 mL portion of 10% HCl.

5.1.7 Add 100 mL of deionised water, swirl and decant.

5.1.8 Repeat with a second 100 mL portion of deionised water.

5.1.9 Add 100 mL of 2% copper sulphate solution to the beaker, swirl for about a minute and decant.

5.1.10 Wash by swirling with a 25 mL portion of buffer and decanting.

5.1.11 Repeat 5.1.9 - 5.1.10 until a weak pale blue colour remains in the copper solution (typically about 5 washes.) At this stage the granules should be dark grey or black in colour. They may be slightly brown which indicates a degree of copperisation, but this is ok.

5.1.12 Wash the granules with at least five 25 mL portions of buffer to remove any fluffy colloidal copper, decanting between each wash.

5.1.13 Insert a glass wool plug into the bottom of the column.

5.1.14 Fill the column with buffer (reagent 3.2.)

5.1.15 Add sufficient copperised cadmium granules to produce a column 18.5 cm long. Store any excess granules in buffer solution.

5.1.16 Wash column with 200 mL of buffer solution. Always maintain the liquid level above the granules to prevent air entrapment.

5.1.17 Condition the column by passing through it at 10mL per minute, 100 mL of column conditioning standard (standard 4.4.)

5.2 TREATMENT OF SAMPLE

5.2.1 Pipette 25 mL of sample into a 100-mL volumetric flask, make to the mark with buffer (reagent 3.2) and mix.

5.2.2 Place a 25-mL measuring cylinder under the column outlet.

5.2.3 Pour the sample onto the column and adjust the flow to about 10 mL per minute.

5.2.4 Discard the first 25 mL, and collect the remainder in the original sample flask. There is no need to wash the column between samples as each first 25 mL discard volume flushes it.

5.2.5 As soon as possible, and not more than 15 minutes after reduction, pipette 50 mL into a glass tube.

5.2.6 Add 2.0 mL of colour reagent (reagent 3.5) and mix.

5.2.7 Between 10 minutes and 2 hours afterward, measure the absorbance at 543 nm.

5.2.8 If the nitrate concentration exceeds the standard range use the remainder of the reduced sample to make an appropriate dilution and analyse again.

5.2.9 Carry out reduction and colour formation treatment of the standards in the same manner.

5.2.10 Compare a 1 mg/L NO_2^--N standard against a reduced 1 mg/L NO_3^-N standard to calculate the efficiency of the cadmium column. Regenerate the cadmium when the efficiency falls below 75%.

5.2.11 At the end of the run pour 50 mL of buffer (reagent 3.2) onto the column and let it pass through.

6. CALCULATION

6.1 Prepare a calibration curve of absorbance against the concentration in mg/L of NO_3-N of the standards. The curve should be linear and pass through the origin.

6.2 Using sample absorbances use the curve to determine the concentration in mg/L of NO_3-N in the samples.

6.3 If the determined value is less than 0.5 mg/L report as mg/L NO_x-N. If the value exceeds 0.5 mg/L, then the sample must be re-analysed for nitrite alone using the nitrite standards so that the separate concentrations of both NO_2-N and NO_3-N can be reported.

7. REFERENCE

Standard Methods for the Analysis of Water and Wastewater. 20th Edition. (1998) American Public Health Association, Washington DC. Method 4500-NO3- E. Cadmium reduction method.

328 PHOSPHATE

1. INTRODUCTION

Phosphorus can arise from a number of sources such as water treatment chemicals, laundering agents, agricultural fertilisers and sewage. It is essential for the growth of organisms and can be a nutrient limiting primary productivity. It can also stimulate the growth of aquatic organisms to nuisance levels. (Standard Methods for the Analysis of Water and Wastewater)

Phosphorus occurs in natural waters and wastewaters almost solely as phosphates - orthophosphates, condensed or polyphosphates, and organically bound phosphates. The method described here measures orthophosphate only; to determine total phosphorus the sample must first be digested to oxidise organic matter and convert other forms to orthophosphate. In this method, known as the ascorbic acid reduction or Murphy-Riley method, ammonium molybdate and potassium antimonyl tartrate react in acid medium to form phosphomolybdic acid that is then reduced to intensely coloured molybdenum blue by ascorbic acid.

Analysis of an unfiltered sample gives total reactive orthophosphate; analysis of a 0.45µm filtered sample gives dissolved reactive orthophosphate.

2. APPARATUS

2.1 SPECTROPHOTOMETER, for use at 880 nm.

3. REAGENTS

3.1 SULPHURIC ACID, 5N. Carefully add 70 mL conc. H_2SO_4 to 300 mL water and make to 500 mL.

3.2 POTASSIUM ANTIMONYL TARTRATE SOLUTION. Dissolve 1.3715 g of potassium antimonyl tartrate, $K(SbO)C_4H_4O_6.½H2O$, in 500 mL of water.

3.3 AMMONIUM MOLYBDATE SOLUTION. Dissolve 20 g of ammonium molybdate ($(NH_4)_6Mo_7O_{24}.4H_2O$) in 500 mL of water.

3.4 ASCORBIC ACID, 0.1 M. Dissolve 1.76 g of ascorbic acid in 100 mL of water. This solution is stable for 1 week if stored in the refrigerator.

3.5 COMBINED REAGENT. Let all reagents come to room temperature, and mix in the order given: 50 mL 5N H_2SO_4, 5 mL potassium antimonyl tartrate solution, 15 mL ammonium molybdate solution and 30 mL ascorbic acid solution. This reagent is stable for 4 hours.

4. STANDARDS

4.1 PHOSPHATE STOCK 50 mg/L PO_4^{3-}-P. Carefully dissolve 0.2195 g of anhydrous KH_2PO_4 in water in a 1-litre volumetric flask and make to the mark.

4.2 PHOSPHATE WORKING SOLUTIONS; 2.0, 1.0, 0.50, 0.20, 0.10, 0 mg PO_4^{3-}-P /L. Dilute 4.0, 2.0 1.0, 0.40, 0.20 and 0 mL of phosphate stock standard (50 mg/L PO_4^{3-}-P) to 100 mL with water.

5. PROCEDURE

5.1 Pipette 50 mL of standard or sample into a tube.

5.2 Add 8 mL of combined reagent (reagent 3.6 above) and mix well.

5.3 After at least 10 minutes, but no longer than 30 minutes, read the absorbance at 880nm.

Natural colour of water does not usually interfere at the wavelength used. For highly coloured or turbid samples, prepare a blank by adding all reagents except ascorbic acid and potassium antimonyl tartrate to the sample. Subtract the blank absorbance from the absorbance of the sample.

6. CALCULATIONS

6.1 Prepare a calibration curve of absorbance against the concentration in mg/L of PO_4^{3-}-P of the standards. The curve should be linear and pass through the origin.

6.2 Using sample absorbances, use the curve to determine the concentration in mg/L of NO_3-N in the samples.

7. REFERENCE

Standard Methods for the Analysis of Water and Wastewater. 20th Edition. (1998) American Public Health Association, Washington DC. Method 4500-P. Ascorbic acid method.

330 SULPHATE – TURBIDIMETRIC METHOD

1. INTRODUCTION

Sulphate is widely distributed in nature and may range be present in natural waters in concentrations ranging from a few to several thousand milligrams per litre. Mine drainage waste may contribute large amounts of sulphate through pyrite oxidation. (Standard Methods for the Analysis of Water and Wastewater)

A guideline maximum level of 250 mg/L is recommended for drinking water to avoid taste problems and corrosion of reticulation systems (Drinking Water Standards for New Zealand.) High levels of sodium and magnesium can have cathartic effects.

In the turbidimetric method sulphate ions are precipitated in an acetic acid medium with barium chloride so as to form barium sulphate crystals of uniform size. Light absorbance of the $BaSO_4$ suspension is measured with a spectrophotometer. It is suitable for the range 1 to 40 mg/L.

2. APPARATUS

2.1 SPECTROPHOTOMETER, for use at 420 nm, preferably with a 2.5 to 10 cm light path.

2.2 MAGNETIC STIRRER. Use fleas of identical shape and size, and use a constant speed without splashing.

2.3 MEASURING SPOON, capacity 0.2 – 0.3 mL.

2.4 TIMER.

3. REAGENTS

3.1 BUFFER SOLUTION A. Dissolve 30 g of magnesium chloride, $MgCl_2.6H_2O$, 5 g sodium acetate, $CH_3COONa.3H_2O$, 1.0 g potassium nitrate, KNO_3 and 20 mL acetic acid (99%) in 500 mL water and make up to 1 L.

3.2 BUFFER SOLUTION B. Required when the sample sulphate concentration is less than 10 mg/L. Dissolve 30 g of magnesium chloride, $MgCl_2.6H_2O$, 5 g sodium acetate, $CH_3COONa.3H_2O$, 1.0 g potassium nitrate, KNO_3 0.111g sodium sulphate, Na_2SO_4 and 20 mL acetic acid (99%) in 500 mL water and make up to 1 L.

3.3 BARIUM CHLORIDE, $BaCl_2$ crystals, 20 to 30 mesh.

4. STANDARDS

4.1 STOCK SOLUTION, (100 mg/L SO_4^{2-}). Dissolve 0.1479 g anhydrous Na_2SO_4 (dried at 105°C) in water and make to 1 L.

4.2 WORKING STANDARDS. 40, 20, 10, 5, 2.5, and 0 mg SO_4^{2-} /L. Dilute 40.0, 20.0 10.0, 5.0, 20 and 0 mL of sulphate stock standard (100 mg/L SO_4^{2}) to 100 mL with water.

5. PROCEDURE

5.1 Measure 100 mL of standard or sample into a 250-mL flask.

5.2 Add 20 mL buffer solution and mix on a magnetic stirrer.

5.3 While stirring, add a spoonful of BaCl2 crystals and begin timing.

5.4 Stir for 60 seconds at constant speed.

5.5 After stirring period is complete, pour solution into spectrophotometer cell and measure absorbance at 420 nm after 5 minutes.

Correct for sample colour and turbidity if necessary by running blanks without added $BaCl_2$.

6. CALCULATION

6.1 Prepare a calibration curve of absorbance against the concentration in mg/L of SO_4^{2-} of the standards. The curve should be linear and pass through the origin.

6.2 Using sample absorbances, use the curve to determine the concentration in mg/L of SO_4^{2-} in the samples.

7. REFERENCES

Drinking Water Standards for New Zealand 2000. Ministry of Health. Wellington.

Standard Methods for the Analysis of Water and Wastewater. 20th Edition. (1998) American Public Health Association, Washington DC. Method 4500-SO_4^{2-} E. Turbidimetric Method.

332 ALKALINITY

1. INTRODUCTION

Alkalinity of water is its acid-neutralising capability. Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate and hydroxide content, it is taken as an indication of these constituents. The measured value may also include contributions from borates, phosphates, silicates or other bases if these are present.

Alkalinity is very susceptible to change between time of collection and analysis, with changes occurring rapidly once the bottle is opened. For these reasons, collect a sample for alkalinity with no headspace, and analyse as soon as possible after collection.

In this method, alkalinity is determined by titrating the water sample with a standard solution of strong acid. The end point of the titration is selected as pH 4.5. This is an arbitrary end-point, and corresponds to the true equivalence point only under ideal conditions.

2. APPARATUS

2.1 BURETTE. 50 mL capacity.

2.2 pH METER.

2.3 MAGNETIC STIRRER.

3. REAGENTS

3.1 SODIUM CARBONATE SOLUTION, approximately 0.05N. Dry 3 g of Na_2CO_3 at 250°C for 2 hours. Weigh 2.5 +/- 0.2 g and record the weight to the nearest milligram (W1). Transfer to a 1-L volumetric flask, dissolve in water then make to the mark. Do not keep longer than 1 week.

3.2 SULPHURIC ACID, 0.1N. Add 2.8 mL of concentrated H_2SO_4 (sp gr 1.834 – 1.836) to 500 mL of water in a 1-L volumetric flask, mix, and make to the mark with water.

3.3 SULPHURIC ACID, 0.02N. Dilute 200 mL of 0.1 N H_2SO_4 (reagent 3.2 above) to 1L with water in a volumetric flask. This reagent is only needed if measuring samples with low alkalinity.

4. PROCEDURE

4.1 STANDARDISATION OF ACID

4.1.1 Pipette 40 mL (V1) of 0.05N Na_2CO_3 (reagent 3.1) into a beaker.

4.1.2 Add about 60 mL water.

4.1.3 Titrate potentiometrically to pH 4.5 and record titre (V2)

4.1.4 Standardise 15 mL of the 0.02N H_2SO_4 in similar fashion.

4.2 TITRATION OF SAMPLE

4.2.1 From a settled, unfiltered sample, pipette 40 mL (V4) of sample into a suitable beaker.

4.2.2 Titrate to pH 4.5.

4.2.3 As the endpoint is approached, make smaller additions of acid and make sure that pH equilibrium is reached before adding more titrant.

4.2.4 Record the final titre volume. (V3)

4.3 TITRATION OF LOW ALKALINITY

For alkalinities less than 20 mg/L titrate a 100 to 200 mL volume of sample (V_5) as in 4.2 above, but using a 10 mL micro-burette and 0.02N standard acid solution. Stop the titration in the range 4.3 to 4.7 and record volume (V_6) and exact pH. Carefully add additional titrant to reduce the pH exactly 0.3 pH unit and again record volume (V_7).

5. CALCULATIONS

Normality of standard sulphuric acid:

Normality, N = (W1 x V1) / (53.00 x V2)

where: W_1 = weight of Na_2CO_3 used to prepare Na_2CO_3 solution (g)
V_1 = volume Na_2CO_3 solution taken for titration (mL)
V_2 = volume of acid used (mL)

Alkalinity, mg$CaCO_3$/L = $(V_3 \times N \times 50000) / V_4$

where: V_3 = volume of acid used (mL)
V_4 = volume sample taken for titration (mL)
N = normality of standard acid

For low alkalinity sample titrated with 0.02 N standard acid:

Alkalinity, mg$CaCO_3$/L = $(2(V_6 - V_7) \times N \times 50000) / V_5$

where: V_5 = volume sample taken for titration (mL)
V_6 = volume of acid used to first recorded pH (mL)
V_7 = volume of acid used to reach pH 0.3 unit lower (mL)
N = normality of standard acid

Report pH of end-point used.

6. REFERENCES

Standard Methods for the Analysis of Water and Wastewater. 20th Edition. (1998) American Public Health Association, Washington DC. Method 2320 B. Alkalinity - Titration Method.

334 HARDNESS BY EDTA TITRATION

1. INTRODUCTION

Originally, hardness was viewed as a measure of the capacity of water to precipitate soap; this mainly being caused by the calcium and magnesium ions present. Currently, total hardness is defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate, in mg/L.

Hardness by calculation involves a computation from the separate determinations of calcium and magnesium (usually by flame atomic absorption.) It is the preferred method as it yields higher accuracy. Refer to Procedure 310 Calcium, Magnesium, Sodium & Potassium for details.

The titration method described here provides a rapid screening, but it is subject to interferences, particularly with acidic or polluted waters that contain high amounts of heavy metals. Disodium EDTA forms a slightly ionised, colourless stable complex with alkaline earth ions. The indicator Eriochrome Black T is bright blue in the absence of alkaline earths but with them forms a deep red complex that has a higher ionisation constant than that of the disodium EDTA complex. Therefore, with Eriochrome Black T as an indicator, the alkaline earths can be titrated with disodium EDTA. . (Standard Methods for the Analysis of Water and Wastewater)

2. APPARATUS

2.1 BURETTE. 25 mL capacity

3. REAGENTS

3.1 BUFFER SOLUTION. Dissolve 16.9 g ammonium chloride (NH_4Cl) in 143 mL of conc ammonium hydroxide (NH_4OH). Add 1.25 g of magnesium salt of EDTA and dilute to 250 mL with water. Store in a tightly stoppered glass container for no longer than 1 month. Discard buffer when 1 or 2 mL added to the sample fails to produce a pH of 10.0 +/- 0.1 at the titration end point.

3.2 COMPLEXING AGENTS. For most waters no complexing agents are needed. Occasionally water containing interfering ions requires an appropriate complexing agent to give a clear sharp change in colour at the end point. If the end point colour change is not sharp a complexing agent is needed. The following are satisfactory:

3.2.1 INHIBITOR 1. Adjust acid samples to pH 6.0 or higher with buffer. Add 250 mg of sodium cyanide (NaCN) in powder form. Add sufficient buffer to adjust pH to 10.0 +/- 0.1. *Caution: NaCN is extremely poisonous. Take extra precautions in its use. Dispose of solutions containing this inhibitor carefully; preferably flush down a fumehood drain with large quantities of water after ensuring no acid is present to liberate volatile poisonous hydrogen cyanide.*

3.2.2 INHIBITOR II. Dissolve 5.0 g sodium sulphide nonahydrate ($Na_2S.9H_2O$) or 3.7 g $Na_2S.5H_2O$ in 100 mL water. Exclude air with a tighly-fitting stopper. Use 1 mL when necessary.

3.2.3 MgCDTA. Add 250 mg per 100 mL of sample of the magnesium salt of 1,2-cyclohexanediamine-tetraacetic acid, and dissolve completely before adding buffer. Use this complexing agent to avoid using toxic (inhibitor I) or malodorous (inhibitor 2) inhibitors when interfering substances are present in lower concentrations.

3.3 INDICATORS. If inhibitors do not sharpen the end point then the indicator is at fault.

3.3.1 ERIOCHROME BLACK T. Sodium salt of 1-(1-hydroxy-2-naphthylazo)-5-nitro-2-naphthol-4-sulphonic acid. Dissolve 0.5 g of dye in 100g triethanolamine. Add 2 drops per 50 mL solution to be titrated. OR:

3.3.2 CALMAGITE. 1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulphonic acid. This is stable in aqueous solution and produces the same colour change as Eriochrome Black T with a sharper end point. Dissolve 0.10 g of Calmagite in 100 mL water. Use 1 mL per 50 mL of solution to be titrated.

3.4 STANDARD EDTA, 0.01 M. Weigh 3.723 g of disodium EDTA in water and make to 1 L. Store in a plastic bottle.

3.5 STANDARD CALCIUM SOLUTION, 1 mL = 1.00 mg $CaCO_3$. Weigh 1.000g anhydrous calcium carbonate powder ($CaCO_3$) into a 500-mL Erlenmeyer flask. Place a funnel in the flask neck and add, a little at a time, 1+1 HCl until all $CaCO_3$ has dissolved. Add 200 mL water and boil for a few minutes to expel CO_2. Cool, add a few drops of methyl red indicator and adjust to the intermediate orange colour by adding 3N NH_4OH (200 mL of conc (sp gr 0.90) to 1 L) or 1+1 HCl as required. Transfer quantitatively to a 1-L volumetric flask and make to the mark with water.

3.6 SODIUM HYDROXIDE, 0.1 M. Dissolve 4 g of NaOH in water and make to 1L.

4. PROCEDURE

4.1 STANDARDISATION OF EDTA

4.1.1 Dilute 25 mL of standard calcium solution (reagent 3.5) to about 50 mL in a beaker.

4.1.2 Add 1 to 2 mL buffer solution. Usually 1 mL will be enough to give a pH of 10.0 – 10.1.

4.1.3 Add 1 to 2 drops of indicator solution.

4.1.4 Add EDTA titrant slowly from the burette with continuous stirring until the last reddish tinge disappears.

4.1.5 Add the last few drops at 3 to 5 second intervals. At end point the solution is normally blue. Daylight is recommended because ordinary incandescent light tends to produce a reddish tinge in the blue at the end point.

4.2 SAMPLE TITRATION.

4.2.1 Select a sample volume that requires less than 15 mL EDTA titrant.

4.2.2 Dilute 25 mL of sample to about 50 mL in a beaker.

4.2.3 Add 1 to 2 mL buffer solution. Usually 1 mL will be enough to give a pH of 10.0 – 10.1.

4.2.4 Add 1 to 2 drops of indicator solution.

4.2.5 Add EDTA titrant slowly from the burette with continuous stirring until the last reddish tinge disappears.

4.2.6 Add the last few drops at 3 to 5 second intervals. At end point the solution is normally blue. Daylight is recommended because ordinary incandescent light tends to produce a reddish tinge in the blue at the end point.

For low hardness samples (<5 mg/L), take a large sample, 100 – 1000mL, for titration and add proportionately more buffer, inhibitor and indicator. Add standard EDTA slowly from a micro-burette, and run an EDTA blank. Subtract the volume of EDTA used for the blank from the volume of EDTA used for the sample.

5. CALCULATION

Hardness (EDTA) as mg $CaCO_3$/L = (V1 x W x 1000) / V_2

Where: V_1 = mL EDTA titrant
W = mg $CaCO_3$ equiv. to 1.00 mL EDTA titrant
V_2 = mL sample titrated

Report values less than 10 mg/L as whole numbers, otherwise two significant figures.

6. REFERENCE

Standard Methods for the Analysis of Water and Wastewater. 20th Edition. (1998) American Public Health Association, Washington DC. Method 2340 B. Hardness - EDTA titration.