Determination of Cation Exchange Capacity and Exchangeable Cations (Including Water Soluble Ions) in Soils, Related Materials and Sewage Sludge 1979

Methods for the Examination of Waters and Associated Materials

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Contents

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Warning to users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary. Local Safety Regulations must be observed. Laboratory procedures should be carried out only in properly equipped laboratories. Field operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried. Care should be taken against creating hazards. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specification. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Code of Practice for Chemical Laboratories' and 'Hazards in the Chemical Laboratory' issued by the Royal Society of Chemistry, London; 'Safety in Biological Laboratories' (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards; and 'The Prevention of Laboratory Acquired Infection' Public Health Laboratory Service Monograph 6, HMSO, London.

Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radio chemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting, and rescue equipment. If in doubt, it is safer to assume that the hazard may exist and take reasonable precautions, rather than to assume that no hazard exists until proved otherwise.

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About this series

This booklet is part of a series intended to provide recommended methods for the determination of water quality. In addition, the series contains short reviews of the more important analytical techniques of interest to the water and sewage industries. In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, has issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as individual methods, thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods being issued when necessary. The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users — the senior analytical chemist, biologist, bacteriologist etc, to decide which of these methods to use for the determination in hand. Whilst the attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is one of the joint technical committees of the Department of the Environment and the National Water Council. It has nine Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

1.0 General principles of sampling and accuracy of results
*2.0 Instrumentation and on-line analysis
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General nonmetallic substances
6.0 Organic impurities
7.0 Biological methods
*8.0 Sludge and other solids analysis
9.0 Radiochemical methods

The actual methods etc are produced by smaller panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee. The names of those associated with this method are listed inside the back cover.

Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No 5, and the current status of publication and revision will be given in the biennial reports of the Standing Committee of Analysts.

Whilst an effort is made to prevent errors from occurring in the published text, a few errors have been found in booklets in this series. Correction notes for booklets in this series are given in the Reports of The Standing Committee of Analysts, published by the Department of the Environment but sold by the National Water Council, 1 Queen Anne's Gate, London SW1H 9BT. Should an error be found affecting the operation of a method, the true sense not being obvious, or an error in the printed text be discovered prior to sale, a separate correction note will be issued for inclusion in the booklet.

* These two Working Groups are in process of being wound up. Their tasks are being redistributed among the other Working Groups.

T A DICK
Chairman

L R PITTWELL
Secretary

25 September 1981

Determination of Cation Exchange Capacity and Exchangeable Cations (Including Water-Soluble) in Soils, Related Materials and Sewage Sludge

Introduction

1. Cation exchange capacity, CEC, is extensively used in characterising soils for survey purposes and in assessing their ability to supply cationic nutrients to plants. Cation exchange is a consequence of the negative electric charges on the colloidal clay and humus particles in soils and is balanced by the adsorption of positively charged counter ions (mainly Ca^{2+} but also Mg^{2+}, K^{+}, Na^{+}, Al^{3+}, and H^{+}). Cation exchange capacity is a measure of the ability of a soil to adsorb cations in such a form that they can be readily desorbed by competing ions. It can be considered as equivalent to the negative charge of the soil, expressed in milliequivalents per unit mass (meq/kg soil).

Soils with higher CEC's have a greater ability to adsorb cationic heavy metals and the U.S. EPA has recommended that the CEC of soils be used in calculating the maximum amounts of heavy metals that can be applied to soils. It would be useful therefore to determine the soil CEC before sewage sludge is disposed to land as it will have an important bearing on the availability of cationic elements to plants.

2. Exchangeable cations are normally determined by leaching the soil with a netural salt solution eg. ammonium acetate. The determination of exchangeable cations is straightforward when the soil contains only very small amounts of water-soluble salts, which is normally the case for soils in Britain. Extracts of saline soils however can contain water soluble Ca, Mg, Na or K from salts deposited in the soils and allowance can be made for the amounts of these elements dissolved in the extraction process by carrying out a separate determination of water-soluble cations where necessary (see 2.1 below).

Ammonium acetate at pH 7.0 dissolves considerable amounts of calcium carbonate under the prolonged treatment during the extraction procedure and this solution cannot therefore be used for calcareous soils containing more than 0.4% calcium carbonate. An alternative replacing solution (containing lithium chloride – lithium acetate at pH 8.2) should be used in this instance to obtain a true exchangeable calcium value.

Exchangeable cations and CEC are closely related to soil properties and the methods for the determination of these are therefore described together. The extracts prepared during the saturation stage in CEC determinations contain the exchangeable cations, consisting mainly of Ca, Mg, K and Na, with sodium in larger amounts in saline soils and hydrogen and aluminium in addition from acid soils. Special alternative methods are normally used to measure exchangeable hydrogen and aluminium in acid soils but these extracts can be used directly for the determination of exchangeable cations. The method of "compulsive exchange" is suitable however for soils of widely differing textures and calcium carbonate and organic matter contents, is less time consuming than other methods and is therefore recommended for CEC determinations. The separate ammonium acetate leaching for the measurement of the exchangeable cations Ca, Mg, K and Na, which are important plant nutrients, is the most widely used procedure for this determination. For further information useful texts are:

Cation Exchange Capacity of Soils

1. Soil Conditions and Plant Growth.	E W Russell 10th Edition 1973 Longmans, London.
2 Chemistry of the Soil	F E Bear. Editor. 2nd Edition 1964, Reinhold, New York.

Exchangeable Cations

3. Soil and Plant Analysis.	C S Piper Hassell Press 1947, Adelaide, Australia.

2.1 The Water-soluble cations in saline soils can be determined by leaching with distilled or deionized water replacing the ammonium acetate leach liquid (A5.4) in method A.

Cation Exchange Capacity

Determination of Cation Exchange Capacity in Soils, Related Materials and Sewage Sludges

1 Performance Characteristics of the Method

<table>
<tr><td>1.1</td><td>Parameter determined.</td><td>Cation exchange capacity (CEC)</td></tr>
<tr><td>1.2</td><td>Type of sample.</td><td>Soils, sediments and related solids in a dry state (1) and also solid and liquid sewage sludges.</td></tr>
<tr><td>1.3</td><td>Basis of method.</td><td>Saturation of the cation exchange complex with barium followed by displacement of the exchanged barium (2,3) with magnesium from a standard solution (by "compulsive exchange", see section 2.2) and measurement of the non-absorbed magnesium.</td></tr>
<tr><td>1.4</td><td>Range of application.</td><td>Up to 500 meq/kg CEC.</td></tr>
<tr><td>1.5</td><td>Calibration function.</td><td>Linear.</td></tr>
<tr><td>1.6</td><td>Standard deviation.
(Titrimetric method)</td><td>Four different soils.
<table>
<tr><th>%$CaCO_3$</th><th>CEC meq/kg</th><th>Standard Deviation</th><th>Degrees of Freedom</th></tr>
<tr><td>0</td><td>37</td><td>0.67</td><td>10</td></tr>
<tr><td>4.5</td><td>50</td><td>0.96</td><td>10</td></tr>
<tr><td>27</td><td>50</td><td>0.82</td><td>10</td></tr>
<tr><td>37</td><td>30</td><td>0.58</td><td>10</td></tr>
<tr><td colspan="4">Liquid digested sludge.</td></tr>
<tr><td>–</td><td>670</td><td>25.2</td><td>11</td></tr>
</table></td></tr>
<tr><td>1.7</td><td>Limit of detection.</td><td>Not applicable.</td></tr>
<tr><td>1.8</td><td>Sensitivity.</td><td>Not known.</td></tr>
<tr><td>1.9</td><td>Bias.</td><td>None known.</td></tr>
<tr><td>1.10</td><td>Interferences.</td><td>Calcium salts. See section 3.1</td></tr>
<tr><td>1.11</td><td>Time required for analysis.</td><td>For 8 samples analytical time is 9 hours and operator time 6 hours (excluding standing overnight).</td></tr>
</table>

2 Principle

2.1 Cation exchange capacity may be considered as equivalent to the negative charge on the sample, expressed in milliequivalents per unit mass (meq/kg sample).

2.2 The sample is saturated with barium by treatment with 0.5M barium chloride solution and washed with water. A wide sample: solution ratio (1:40) is used. The adsorbed barium is then displaced by addition of a fixed aliquot of 0.025M magnesium sulphate solution and the excess (i.e. non-adsorbed) magnesium is determined and related to the cation exchange capacity. The efficiency of displacement of barium by magnesium in the magnesium sulphate treatment is increased by the precipitation of barium as barium sulphate so achieving a "compulsive exchange".

3 Interferences

3.1 For samples with a high calcium salt content, a pH value of not less than 8.1 ± 0.05 during the saturation stage is essential to reduce the solubility of the calcium salts. For this reason the 0.5M barium chloride solution used is buffered at pH value 8.1 ± 0.05 with triethanolamine.

4 Reagents

Normally Analytical Grade reagent chemicals are suitable.

4.1 **Water**

Distilled or deionised water is suitable.

4.2 **Triethanolamine solution**

Dilute 90 ± 1 ml triethanolamine with water to 1 litre and adjust to pH value 8.1 ± 0.05 by adding 145 ± 5 ml 2M hydrochloric acid. Dilute this solution to 2 litres with water, mix and protect from carbon dioxide during storage.

4.3 **Barium chloride solution,** approx 1M

Dissolve 244 ± 2 g barium chloride dihydrate in water and make up to 1 litre.

4.4 **Buffered barium chloride solution**

Mix equal volumes of the solutions described in sections 4.2 and 4.3.

4.5 **Magnesium sulphate solution,** 0.025M

Dissolve 6.2 ± 0.05 g magnesium sulphate heptahydrate in water and make up to 1 litre, (i.e. 608 mg Mg per litre) in a volumetric flask.

4.6 **Ammonia solution,** approx 2M

Dilute 140 ± 2 ml of 30% w/w ammonia solution (d_{20} 0.89) with water to 1 litre.

4.7 **Standard disodium ethylene diaminetetraacetic acid (EDTA)** 0.01M

Dissolve 3.723 ± 0.005 g of the disodium salt of EDTA in water and dilute to 1 litre in a volumetric flask.

4.8 **0.1% M/V Catechol violet indicator solution**

Dissolve 0.1 ± 0.005 g Catechol Violet in water and make up to 100 ± 2 ml. This solution must be freshly prepared on the day of use.

5 Apparatus

5.1 **A laboratory centrifuge** (capable of attaining an RCF of at least 500) fitted with 250 ml polyethylene or polypropylene centrifuge bottles.

5.2 **An atomic absorption spectrophotometer and magnesium hollow cathode lamp** may be used for the final determination of magnesium (i.e. as an alternative to EDTA titration). (See Reference 5).

6 Sample Preparation

The determination is normally carried out in soils, sediments and related solids which have been dried and sieved (1 and 11). Sewage sludges may also be dried but the determination can be carried out on liquid sludges if necessary.

7 Analytical Procedure

Step	Procedure	Notes
	Cation Exchange	
7.1	**Sample**	
7.1.1	*Dried Samples* Weigh 5.0 ± 0.05 g (W) of the prepared sample (see note a) into a 250 ml polyethylene centrifuge bottle fitted with a tight stopper. Weigh the bottle plus sample to within ± 0.1 g (M). Some samples may require pretreatment (see note b).	(a) Reference (1). (b) Some samples, e.g. clay soils and organic materials are sometimes difficult to wet and disperse and may require an initial dispersion in 20 ± 2 ml water to be effective.
7.1.2	*Liquid sludges* Weigh an empty 250 ml polyethylene centrifuge bottle to within ± 0.1 g (M_b). Measure out the volume of liquid sludge which contains 2.5 ± 0.025 g (W) dry solids and transfer to the weighed centrifuge bottle. Add water to make up the volume to 200 ± 2 ml and centrifuge at RCF 415 for 15 ± 1 min. Collect the supernatant and determine its dry solids content to within ±0.025 g (M_s). Weight of bottle plus sample $M_l=M_b+W_l$, where $W_l=W-M_s$	
7.2	**Saturation procedure** Add 100 ± 5 ml buffered barium chloride solution to the suspension prepared in steps 7.1.1 or 7.1.2 and leave to stand for 1 hour with occasional shaking. Centrifuge at RCF 415 for 15 ± 1 min. and discard the supernatant (note c). Break up the sample cake. Add a further 200 ± 5 ml buffered barium chloride solution and stand overnight. Centrifuge as above and discard the supernatant (note c).	(c) With organic samples some particles may float after centrifugation making it difficult to decant cleanly, in which case the liquid may be drawn off with a sintered filter stick (4).
7.4	**Washing procedure** Add 200 ± 5 ml distilled water and shake for 2 to 3 min. to break up the sample cake. Centrifuge at RCF 415 for 15 ± 1 min. and discard the supernatant liquid. Repeat this washing procedure for a second time (see note d). Weigh the bottle and contents to within 0.1 g (M_2).	(d) This second wash can be omitted when working with dried samples.
7.4	**Displacement procedure** Pipette into the bottle 100 ± 0.1 ml 0.025M magnesium sulphate solution and shake the stoppered bottle at intervals over a period of 2 h. Centrifuge at RCF 415 for 15 ± 1 min. and transfer the clear supernatant liquid immediately to a stoppered flask.	

Step | Procedure | Notes

Determination of non-absorbed magnesium

7.5 **Titration method**

To a 5 ± 0.01 ml aliquot of the supernatant add 6 drops 2M ammonia solution and two drops freshly prepared indicator giving a clear blue colour. Titrate with standard 0.01M EDTA solution (titre A ml). The colour changes from blue to reddish purple at the end point but with liquid sludges the change may be to violet blue. Similarly titrate a 5 ± 0.01 ml aliquot of 0.025M magnesium sulphate (titre B ml) (see note e.)

(e) This titration need only be carried out once with each daily batch of determinations.

7.6 **Calculation of results**

The sample titre (A ml) must be corrected for the effect of the volume of liquid retained by the centrifuged sample after the water wash thus:
Corrected titre (T) = $A(100 + M_2 - M_1)/100$ ml

then

CEC of sample = $\frac{400}{W}(B-T)$meq/kg (see note f)

If the CEC exceeds 500 meq/kg (1000 meq/kg for liquid sludges) the determination should be repeated using less sample and the calculation adjusted accordingly.

(f) W_1 replaces W where it is required that CEC for liquid sludges needs to be expressed on a suspended solids basis.

(g) for further details see reference 5 in Section 8.

7.7 **Alternative atomic absorption method**
(see note g)

Set up the instrument according to the manufacturers instructions, using an air/acetylene flame. The wavelength required is 285.2 nm. Nebulize pure water and adjust the zero. Nebulize an appropriate magnesium calibration standard solution and adjust the instrument to give a suitable response. Nebulize pure water and readjust zero if necessary. Nebulize alternately the calibration standard solutions and pure water.
Nebulize alternately suitably diluted sample solutions and pure water. To check the instrument calibration nebulize a suitable standard after every eighth sample. Calculate the magnesium concentration in the sample solutions from step 7.4 in mg/l.

7.8 **Calculation of results**

Let the concentration of magnesium in the residual solution from step 7.4 be x mg/l. Then CEC of the sample equals

$$\left[\frac{608 - \frac{x(100+M_2-M_1)}{100}}{121.6}\right] \text{ x } \left[\frac{1000}{W}\right] \text{meq/kg (note f)}$$

Exchangable Cations Two Methods

A

Determination of Exchangable Cations (Including Water Soluble) in Soils, Related Materials and Sewage Sludges

A1 Performance Characteristics of the Method

A1.1	Parameter determined	Principal exchangeable cations including calcium, magnesium, potassium and sodium.
A1.2	Type of sample	Soils, related materials and sewage sludges containing less than 0.4% calcium carbonate. For materials containing more than 0.4% calcium carbonate method B should be used for the leaching of calcium only.
A1.3	Basis of method	Saturation of the cation exchange complex with the ammonium ion by leaching with an ammonium acetate solution. (1) The leachate obtained is analysed for the exchangeable cations.
A1.4	Range of application(a)	Calcium 0–7500 mg/kg, Potassium 0–500 mg/kg, Magnesium 0–1250 mg/kg, Sodium 0–250 mg/kg.
A1.5	Calibration function (a)	Linear
A1.6	Standard deviation (a)	See Table 1
A1.7	Limit of detection (a)	(Calcium 0.5, magnesium 0.05, potassium 0.2 and sodium 0.1 mg/l
A1.8	Sensitivity (a)	(10 mg/l Ca gives an absorbance of approximately 0.05. 1.0 mg/l Mg gives an absorbance of approximately 0.045. 1.0 mg/l K gives approximately 10% full scale deflection. 1.0 mg/l Na gives approximately 6% full scale deflection.
A1.9	Bias	None known
A1.10	Interferences	Calcium carbonate in excess of 0.4% in the original sample enhances the calcium value.
A1.11	Time required for analysis	For extraction of 16 samples, the analytical and operator times are the same at 5.5 hrs (excluding the overnight period). The analytical and operator times for the determination of four elements in the extracts is a further 3 hrs.

(a) These data were obtained at the Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen.

Table 1 **Determination of exchangeable cations (including water soluble) in soils, related materials and sewage sludges – Method A**

Results expressed as mg/kg in <2 mm fine soil

	Day 1	Day 2	Day 3	Day 4	Day 5	RMSD	Day 1	Day 2	Day 3	Day 4	Day 5	RMSD
			Calcium						Magnesium			
Soil 1	2100 2100	1970 2010	1940 1840	1880 1860	1800 1780	±110	84 84	90 85	94 88	84 82	86 88	±3.4
Soil 2	2050 2060	2200 2120	2100 2140	1960 1880	1880 1940	±104	72 70	75 74	81 74	71 74	75 76	±2.9
Soil 3	2020 1920	1800 1850	1800 1860	1680 1740	1580 1600	±114	96 94	96 101	102 107	90 94	100 102	±4.9
Soil 4	1120 1090	1080 1090	1070 1130	1010 1020	1070 1040	± 38	15 15	15 15	15 16	15 15	15 15	±0.3
Soil 5	2340 2260	2230 2100	2140 2240	2060 2180	2000 1970	±114	88 87	94 92	98 99	92 86	94 97	±4.4
Soil 6	2540 2670	2530 2470	2650 2530	2340 2600	2420 2440	±101	56 55	57 57	61 61	57 55	58 60	±2.2
			Potassium						Sodium			
Soil 1	56 56	62 62	66 48	45 43	52 54	±7.2	26 24	30 25	34 27	30 27	24 25	±3.1
Soil 2	208 203	214 214	193 188	179 184	194 189	±11.8	19 20	22 33	23 21	24 24	19 22	±3.9
Soil 3	96 94	93 96	92 83	80 80	86 90	±6.0	46 47	41 44	51 47	47 50	45 44	±2.6
Soil 4	90 90	86 83	78 74	72 69	81 78	±6.9	23 24	23 19	22 24	26 26	22 22	±2.0
Soil 5	150 146	136 132	128 128	116 116	132 135	±10.4	45 45	41 38	44 46	44 43	42 43	±2.2
Soil 6	80 80	74 74	66 69	66 64	72 84	±6.5	44 44	38 37	41 44	46 40	39 45	±3.2

Analyses carried out at the Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen

A2 Principle

2.1 Cation exchange is a reversible reaction and complete replacement can only be effected if the replaced ions are removed from the sphere of action.

Equilibrium between the exchange complex and displacing solution is rapidly established and removal of the cations is only quantitative when a leaching procedure is adopted.

2.2 The sample is successively leached with aliquots of ammonium acetate at pH value 7.0. The combined leachate is examined for exchangable cations using the appropriate methods of analysis; the result is expressed as mg/kg.

A3 Interferences

A3.1 Ammonium acetate at pH value 7.0 dissolves appreciable quantities of calcium carbonate; the calcium content of such leachates will represent both exchangeable and dissolved calcium. The method is therefore only applicable to samples containing less than 0.4% calcium carbonate. An alternative replacing solution (containing lithium chloride – lithium acetate) should be used in this instance to obtain a true exchangeable calcium value (Method B).

A4 Hazards

The exhaust fumes from the flame photometer and the atomic absorption spectrophotometer are toxic and must be ducted away to the outside atmosphere.

A5 Reagents

Normally Analytical grade reagent chemicals are suitable.

A5.1 Distilled or de-ionized water is suitable.

A5.2 **Acetic acid, 4M**

Dilute 465 ± 5 ml acetic acid, glacial (d_{20} 1.05) to 2 litres. Determine the molarity by titrating with M sodium hydroxide, using phenolphthalein as indicator, and adjust to 4M.

A5.3 **Ammonia solution, 4M**

In a fume cupboard dilute 445 ± 5 ml ammonia solution (d_{20} 0.880) NH_3, to 2 litres. Determine the molarity by titrating with M hydrocholoric acid, using methyl red as indicator, and adjust to 4M.

A5.4 **Ammonium Acetate solution, M**

In a fume cupboard mix with caution, one volume 4M acetic acid, one volume 4M ammonia solution and 2 volumes of water. Check that the pH value is 7.00 ± 0.05 adjusting, if necessary, with M acetic acid or M ammonia solution.

A5.5 **Standard sodium solutions**

A5.5.1 *Solution A* 1 ml contains 1 mg sodium.

Dissolve 2.542 ± 0.005 g of sodium chloride (dried for at least 1 hour at 140 ± 10°C) in water and dilute with water to 1 litre. This solution is stable for several months.

A5.5.2 *Solution B* 1 ml contains 100 μg sodium.

Dilute 10.00 ± 0.02 ml of standard solution A with water to 100 ml in a calibrated flask. This solution should be freshly prepared when required.

A5.6 **Standard potassium solutions**

A5.6.1 *Solution A* 1 ml contains 1 mg potassium

Dissolve 1.907 ± 0.005 g potassium chloride (dried for at least 1 hour at 140 ± 10°C) in water and dilute with water to 1 litre. This solution is stable for several months.

A5.6.2 *Solution B* 1 ml contains 100 μg potassium.

Dilute 10.00 ± 0.02 ml of standard potassium solution A with water to 100 ml in a calibrated flask. This solution should be freshly prepared when required.

A5.7 **6 M Hydrochloric acid** (approximately)

Dilute 535 ± 5 ml of hydrochloric acid (d_{20} 1.18) with water to 1 litre in a measuring cylinder. Alternatively constant boiling hydrochloric acid, redistilled from diluted analar acid may be used.

A5.8 **Standard calcium solution**

Solution A 1 ml contains 1 mg calcium

Dissolve 2.5 ± 0.01 g of oven-dried (120 ± 10°C) calcium carbonate in approximately 20 ml of 6 M hydrochloric acid in a 1 litre calibrated flask and dilute with water to the mark. This solution should be freshly prepared when required.

A5.9 **Standard magnesium solution**

Solution A 1 ml contains 100 μg magnesium

Dissolve 0.166 ± 0.001 g of oven-dried (120 ± 10°C) magnesium oxide in approximately 20 ml of 6 M hydrochloric acid in a 1 litre calibrated flask and dilute with water to the mark. This solution should be freshly prepared when required.

A5.10 **10% V/V Nitric Acid**

Dilute 100 ± 1 ml of nitric acid (d_{20} 1.42) with water to 1 litre.

A5.11 **1.0% m/V Strontium chloride solution**

Dissolve 30.43 ± 0.05 g of strontium chloride ($SrCl_2\ 6H_20$) in water. Add 10 ± 0.1 mls 6 M hydrochloric acid. Transfer to a 1-litre calibrated flask and dilute with water to the mark.

A5.12 **Strontium chloride solution** 2500 mg/l Sr.

Transfer 250 mls 1.0% Strontium chloride solution (A5.11) into a 1-litre calibrated flask, add 10 ± 0.1 ml 6 M hydrochloric acid and dilute with water to the mark.

A5.13 **Acetic acid glacial 99.7% CH_3COOH d_{20} 1.048 to 1.050**

A6 Apparatus

A6.1 All glassware should be of borosilicate glass. All glass and polyethylene ware should be cleaned by filling with or soaking in 10% V/V nitric acid followed by thorough rinsing with water.

A6.2 Sodium, potassium, calcium and magnesium are ubiquitous elements and precautions should be taken to guard the apparatus against contamination from, for example, dust, smoke, cleaning materials and perspiration.

A6.3 **Filtration apparatus – Funnels,** fitted with 12.5 cm filter papers (0.4–1.1 microns mean pore space has been found suitable)

A6.4 **Flasks** – 250 ml graduated.

A6.5 **pH meter,** readable to ± 0.05 pH unit and fitted with suitable electrodes.

A6.6 **A flame photometer** using an appropriate interference filter and equipped for an air/fuel flame. The fuel may be town gas, propane or butane.

A6.7 **An atomic absorption spectrophotometer** equipped for use with a nitrous oxide/butane flame and with a calcium hollow cathode lamp. The same spectrophotometer equipped for use with an air/acetylene flame and with a magnesium hollow cathode lamp.

A7 Sample Preparation

The determination is carried out on previously dried soils, related materials and sewage sludges (1.10). Sewage sludge should be dried at a temperature not exceeding 105°C.

A8 Analytical Procedure

Read Section on Hazards Before Starting this Procedure

Step	Procedure	Notes
	Leaching	
A8.1	Weigh 5.0 ± 0.05 g of the prepared sample into a 50 ml beaker. Add 20 ± 1 ml M ammonium acetate solution, stir, cover with a watch glass and allow to stand overnight.	(a) When the calcium carbonate in the original sample exceeds 0.4% employ method B for the leaching of exchangeable calcium. For Saline soils, high in water extractable soluble salts, see Introduction 2.

Step	Procedure	Notes
A8.2	Transfer the contents of the beaker to a funnel fitted with a 12.5 cm filter paper and collect the filtrate in a 250 ml graduated flask. Allow to drain. Leach the sample with 9 successive 25 ± 1 ml volumes of M ammonium acetate solution; allow to drain between each addition. Collect successive leachates in the flask containing the filtrate.	
A8.3	Dilute to volume with M ammonium acetate solution and retain this solution for the determination of calcium (note a.), magnesium, potassium and sodium (note b.). Carry out a blank determination.	(b) Carry out the determination of sodium immediately. Alternatively store both the solution and blank in polyethylene containers.
	Method of measurement	
A8.4	Sodium and potassium are determined by flame photometry. Calcium is determined by atomic adsorption spectrophotometry using a nitrous oxide/butane flame and magnesium similarly using an air/acetylene flame. For each element calibration standards are required and should be freshly prepared by diluting suitable aliquots of the appropriate standard solutions (see sections A5.5 to 5.9). (see also Refs 5–9).	
	Flame photometer stage for sodium and potassium	
A8.5	Perform all determinations (i.e. standards, blanks and samples) for Sodium, then perform all the determinations for potassium.	
	Blank determination	
A8.6	A blank must be run with each batch (e.g. up to 12 samples) of determinations for exchangeable cations, using the same batch of reagents as for samples. Carry out steps A8.1 to 8.3 omitting the sample and using the M ammonium acetate solution only and then proceed to step 8.7 treating the solution as if it were a sample.	
	General Procedure	
A8.7	For all samples, blanks and standards, transfer 20 ± 0.1 ml of well-mixed solution into a clean, dry polyethylene tube. Add 5 ± 0.1 ml of solution containing 2500 mg/l strontium and 0.5 ± 0.05 ml of glacial acetic acid. (see sections A5.12 and 5.13). Mix thoroughly (note c).	(c) All samples, blanks and standards must be processed to this stage, before proceeding to the flame photometer or atomic absorption stage. A rapid dispenser unit is suitable for adding these solutions.
	Determination of sodium	
	Preparation of the calibration curve (note d)	
A8.8	To a series of 200 ml calibrated flasks add 0, 1.0, 2.0, 4.0 and 10 ml (all ± 0.02 ml) of standard sodium solution B and dilute with M ammonium acetate solution to the mark. These solutions contain 0, 0.5, 1.0, 2.0 and 5.0 mg/l Na respectively.	(d) This calibration procedure must be carried out before analysis of each batch of samples.

Step	Procedure	Notes
A8.9	Set up the flame photometer according to the manufacturer's instructions for determining sodium. Aspirate the zero standard solution and adjust the scale reading to 0%. Aspirate the 5 mg/l Na standard and adjust the scale reading at 100%. Repeat the aspiration of water and 5 mg/l sodium until the 0% and 100% reading respectively are obtained without the need for further adjustment. Aspirate water.	
A8.10	Aspirate the 0.5 mg/l Na standard and measure the instrument response. Aspirate water. Aspirate the other calibration standards with an aspiration of water after each and measure the instrument response of each standard. Construct a calibration curve of sodium concentration against the instrument response.	
	Dilution of samples (note e)	
A8.11	If the sample contains or is likely to contain more than 5 mg/l sodium then an appropriate volume, V_1 ml, of the sample should be diluted with M ammonium acetate solution to an appropriately larger volume, V_2 ml, so that the expected sodium concentration is less than 5 mg/l. The dilution factor $F = \frac{V_2}{V_1}$	(e) If the sodium concentration is expected to be less than 5 mg/l proceed directly to steps A8.13 and A8.12. (f) The blank should give a zero reading indicating no contamination from the reagents used. If the blank is significant the reagents and cleaning of apparatus must be checked. (g) Aspirate a 5 mg/l sodium standard after every 10 samples and readjust the instrument if necessary
A8.12	Aspirate the blank and measure the maximum instrument response (note f). Aspirate water.	
	Analysis of samples	
A8.13	Aspirate a sample and measure the instrument response. Aspirate water. Aspirate the remaining samples with an aspiration of water after each and measure the instrument response (note g).	
A8.14	When all standards, blanks and samples have been aspirated, water should be aspirated for at least two minutes to cleanse the instrument.	
	Calculation of the result	
A8.15	If the samples were aspirated without dilution, the sodium concentration in solution is read directly from the calibration graph. If the sample was diluted step (A8.11) determine the sodium concentration, A, in the diluted sample from the calibration graph and calculate the exchangeable sodium concentration, B, in the original soil sample from $B = A \times F \times 50$ mg/kg Na.	

Step	Procedure	Notes
	Determination of potassium	
	Preparation of calibration curve (note h)	
A8.16	To a series of 100 ml calibration flasks add 0.0, 1.00, 2.50, 5.00, 7.50 and 10.00 ml (all ± 0.02 ml) of standard potassium solution B and dilute with M ammonium acetate solution to the mark. These solutions contain 0.0, 1.0, 2.5, 5.0, 7.5 and 10 mg/l K respectively.	(h) This calibration procedure mus be carried out before analysis of each batch of samples.
A8.17	Set up the flame photometer according to the manufacturers instructions for determining potassium. Aspirate the standards, blanks and samples for potassium using the same procedure as that for the determination of sodium (steps A8.8 to 8.15), calibrating over the range 0 to 10.0 mg/l K.	
	Atomic absorption stage for calcium and magnesium	
A8.18	Perform all determinations (i.e. standards, blanks and samples) for calcium, then perform all the determinations for magnesium.	
	Blank determination	
A8.19	See Section A8.6	
	Determination of calcium	
	Preparation of the calibration curve	
A8.20	Duplicate calibration standards must be run with each batch (e.g. up to 12 samples) of determinations, using the same batch of reagents as for the samples.	
A8.21	To a series of 100 ml calibrated flasks add 0, 1.5, 3.0, 6.0 and 15.0 ± 0.02 ml of standard calcium solution and dilute to the mark with M ammonium acetate solution. Mix well. These flasks contain 0, 15, 30, 60 and 150 mg/l Ca respectively.	
	General procedure	
A8.22	For all samples, blanks and standards, proceed as in Section A8.7	
A8.23	Set up a nitrous oxide/butane flame instrument according to the manufacturer's instructions for determining calcium. The wavelength required is 422.7 nm.	
A8.24	Aspirate the zero standard solution and adjust the transmittance scale reading to 0. Aspirate the 150 mg/l Ca standard and adjust the transmittance scale reading to 100 (corresponding to zero absorbance) (note i). Repeat the aspiration of water and 150 mg/l Ca until the 0 and 100 transmittance readings respectively are obtained without the need for further adjustment. Aspirate water.	(i) If difficulty is experienced in obtaining a transmittance reading of 100, the alignment of the burner slot can be adjusted to facilitate this operation.

Step	Procedure	Notes
A8.25	Aspirate the blank and measure the maximum instrument response (note j). Aspirate water.	(j) The blank should give a zero reading indicating no contamination from the reagents used. If the blank reading is significant, the reagents and cleaning of apparatus must be checked.
A8.26	Aspirate the samples with an aspiration of water after each. Measure the instrument response of the samples S.	
A8.27	After each batch (e.g. 12 samples) reaspirate the zero and 150 mg/l Ca standard solutions to ensure that there is no instrument drift.	
A8.28	Calculate the concentration of calcium in the sample solutions from the calibration curve. The calibration curve is normally linear to 150 mg/l Ca (≡ 118 mg/l Ca in the solution analysed) but the linearity of the calibration curve must be regularly checked. Calculate the exchangeable calcium concentration, C, in the original soil sample from $C = S \times 50$ mg/kg Ca.	
	Dilution of samples	
A8.29	If the sample contains more than 150 mg/l of calcium then an appropriate volume, V_1 ml, of the sample should be diluted with M ammonium acetate solution to an appropriately larger volume, V_2 ml, so that the expected calcium concentration is less than 150 mg/l. The dilution factor F is then $\frac{V_2}{V_1}$ and this must be used in the calculation of the result.	
	Determination of magnesium	
	Preparation of the calibration curve	
A8.30	To a series of 100 ml calibrated flasks add 0.0, 5.0, 10.0, 15.0, 20.0 and 25.0 ml (all ± 0.02 ml) of standard magnesium solution A and dilute with M ammonium acetate solution to the mark. These solutions contain 0.0, 5.0, 10.0, 15.0, 20.0 and 25.0 mg/l Mg respectively.	
A8.31	Set up an air/acetylene flame instrument according to the manufacturer's instructions for determining magnesium. The wavelength required is 285.2 nm.	
A8.32	Aspirate the standards, blanks and samples for magnesium using the same procedure as that for the determination of calcium (steps A8.22-8.27 and 8.29), calibrating over the range 0 to 25 mg/l Mg.	
A8.33	Calculate the exchangeable magnesium concentration in the soil sample as in step A8.28.	

B Determination of Exchangeable Calcium only (including Water-Soluble) in Soils, Related Materials and Sewage Sludges containing more than 0.4% Calcium Carbonate

B1 Performance Characteristics of the Method

B1.1	Parameter determined	Exchangeable calcium
B1.2	Type of sample	Soils, related materials and sewage sludges containing more than 0.4% calcium carbonate.
B1.3	Basis of method	Replacement of the exchangeable calcium in the sample with the lithium ion by leaching with a lithium chloride – lithium acetate solution. The leachate obtained is analysed for the exchangeable calcium only. (10)
B1.4	Range of application	0–7500 mg/kg calcium
B1.5	Calibration function	Linear
B1.6	Standard deviation	See Table 2
B1.7	Limit of detection	0.5 mg/l
B1.8	Sensitivity	10 mg/l gives an absorbance of approximately 0.05
B1.9	Bias	None known
B1.10	Interferences	None known
B1.11	Time required for analysis	For 16 samples the analytical and operator times are the same at 5.5 hrs (excluding the overnight period). The analytical and operator times for the determination of Calcium in the extract is a further 1 hr.

Table 2 **Determination of exchangeable calcium only (including water-soluble) in soils, related materials and sewage sludges containing more than 0.4% calcium carbonate – Method B.**

Results expressed as mg/kg in <2 mm fine soil

	Soil A	Soil B
	1110	2100
	1120	2130
	1100	2170
	1100	2100
	1100	2120
	1090	2160
	1110	2130
	1110	2130
	1060	2060
	1070	2130
RMSD	± 18	± 30

Analyses carried out at the Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen.

B2 Principle

B2.1 Ammonium acetate at pH value 7.0 dissolves appreciable quantities of calcium carbonate when present in excess of 0.4% in the sample. The calcium content of such leachates will therefore represent both exchangeable and soluble calcium. The solubility of calcium carbonate in lithium chloride – lithium acetate solution at pH value 8.2 is 0.005% of the solubility in M ammonium acetate and this solution is therefore a suitable exchange reagent for use with samples containing more than 0.4% calcium carbonate. The conditions described in section A2.1, apply equally to this method.

B2.2 The sample is successively leached with aliquots of lithium chloride – lithium acetate solution. The combined leachate is examined for calcium only, using an appropriate method of analysis; the result is expressed as meq/kg.

B3 Interferences

None known

B4 Hazards

The exhaust fumes from the atomic absorption spectrophotometer are toxic and must be ducted away to the outside atmosphere.

B5 Reagents

Analytical grade reagent chemicals are suitable.

B5.1 Distilled or deionized water is suitable.

B5.2 **2% m/V Lithium hydroxide solution**

Dissolve 2 ± 0.1 g of lithium hydroxide in 100 ml water.

B5.3 **Lithium chloride, 0.8 M – lithium acetate, 0.2 M solution**

Dissolve 169.6 g of lithium chloride, dried at 100°C for one hour, and 102.02 g of lithium acetate ($CH_3C00\ Li\ 2H_20$) in approximately 2 litres of water and dilute to approximately 4.8 litres. Add approximately 2 ml of 2% w/V lithium hydroxide solution, drop by drop until the pH value is 8.20 ± 0.05. Dilute to 5 litres.

B6 Apparatus

As described under method A, sections A1 – 6.4 and 6.7

B7 Sample Preparation

See method A, section A.7

B8 Analytical Procedure

Step	Procedure
B8.1 –8.3	As described under method A but using lithium chloride, 0.08M – lithium acetate, 0.2 M (pH value 8.2) solution (B5.3) in place of M ammonium acetate solution (pH value 7.0) (A5.4). After dilution to volume, retain the solution for the determination of calcium. Carry out a blank determination. (See A8.6 and proceed to step A8.20).
B8.4	Carry out the determination of calcium as described in Method A, Steps A8.20 to 8.29.

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Note Refs 1, 5–9 and 11 are also part of the series *'Methods for the Examination of Waters and Associated Material'*.

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