PROCEDURES FOR SOIL ANALYSIS

Compiled and edited
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SIXTH EDITION

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CONTENTS

FOREWORD

This laboratory manual presents the procedures for soil analysis as they are in use at ISRIC at the time of writing. Indeed, because of changes within procedures or the introduction of new procedures and laboratory equipment such a manual can only be a snapshot of a moving scene. This touches on a dualism in soil analytical work: on the one hand there is the continuous pursuit of innovations and improvements and on the other the necessity of general acceptance and use of the same procedures by as many laboratories as possible. A number of the analyses described in this manual is aimed at characterisation of soils for the purpose of soil classification and correlation. Several classification criteria are based on specified, possibly archaic analytical procedures and the introduction of new and "better" techniques to replace the old may sometimes be a long-winded affair. An example is the CEC determination with the silver-thiourea method which is included in this manual because it seems to be a rapid and convenient substitute for the well-established but much abused ammonium acetate method.

Performance of an analysis according to more than one method, not only as a method-correlation exercise but also as a routine procedure, may in some cases be a rewarding informative investment, e.g. CEC at more than one pH value or particle size analysis with different pretreatments. Nevertheless, a good deal of the new developments, adaptations and improvements that become available regularly is useful and easy to adopt and it is foreseen that this manual has to be updated and extended regularly.

The procedures were compiled in cooperation with the laboratory staff of ISRIC: Messrs. J.G. ten Bokkel, J.R.M. Huting, B. van Lagen, A.J.M. van Oostrum, and R.A. Smaal. Much information was drawn from manuals in use by other laboratories working in the same field. These are mentioned under the references of the procedures concerned. The helpful discussions with Mr. L.Th. Begheijn and Dr. V.J.G. Houba of the Wageningen Agricultural University are gratefully acknowledged.

The editor welcomes any suggestion for the improvement of procedures as well as of the manual as a whole and invites readers to bring to his notice any error that almost inevitably escaped the weeding out.

Wageningen, June 1986 L.P. van Reeuwijk

In the second edition several changes, improvements and additions were made.

Wageningen, September 1987 L.P.v.R.

In the third edition again many corrections and other changes were made. The chapters are now all self-contained so that no longer reference is made to treatments in other procedures as was previously done for brevity's sake. Two procedures were added: the determination of clay and silt with the hydrometer in the particle-size analysis and a chapter on mineralogical analysis of the sand fraction.
The editor acknowledges typographical assistance of Ms. Y. Karpes, Mr. W.C.W.A. Bomer and Mr. J. Brunt.

Wageningen, October 1991. L.P.v.R.

In addition to some minor corrections, in the fourth edition the pretreatment of the particle-size analysis (Chapter 3) was revised: according to the forthcoming ISO standard the removal of carbonates is now done with acetic acid instead of with acetate buffer. The sample preparation for sand mineral analysis was simplified (Chapter 19). The order of the carbonate removal and hydrogen peroxide treatment was reversed (Chapters 3, 15, 16 and 19).

Wageningen, March 1993. L.P.v.R.

In the fifth edition, the particle-size analysis (Chapter 3) was changed in that the carbonate removal is now only optionally done using HCl (the latter was changed in the final version of ISO Standard 11277 in 1995). The percolation and washing procedures of the CEC by NH_4OAc (Chapter 9) were improved.
As several of the procedures in this manual are suitable and/or prescribed to determine taxonomic criteria for soil classification according to the Legend of the FAO-Unesco Soil Map of the World, FAO consented that its logo be added to the cover. The responsibility for the contents of this manual remains with the editor, however.

Wageningen, December 1995. L.P.v.R

The sixth edition was expanded with two procedures used in soil characterisation: ODOE (Optical Density of the Oxalate Extract) and the determination of the Melanic Index.

Wageningen, January 2002. L.P.v.R.

TECHNICAL REMARKS

For several analyses for soil characterisation, Analytical Reagent (A.R.) quality of chemicals is not essential and is chemically pure grade satisfactory ("purified", "reinst", "Baker grade", etc.). When A.R. is required, this is specifically stated.

When water is used, demineralised or deionised water is meant. The electrical conductivity should be < 2 µS/cm at 25 °C and the pH > 5.6 (Grade 2 water according to ISO Standard 3696). Distilled water can be used in all procedures but only where it is essential this is specifically stated.

The use of SI units (Système Internationale) is not consequently followed out in this manual but popular units such as **ppm** and **me** have been abandoned. The notation ***M*** for mol/l has been maintained in this edition for convenience. The old unit of ion exchange capacity, **me/100 g**, has been replaced by **$cmol_c$/kg** rather than by **$mmol_c$/kg** to facilitate direct comparison with old data.
For conversion to or from non-SI units the following list can be used:

non-SI units	SI units
1 ppm	1 mg dm^{-3} or mg/l, 1 mg kg^{-1} or mg/kg, 1 µg ml^{-1}, 1 µg g^{-1}
1 me (milli-equivalent)	1 mmol Na^+, 1 mmol ½Ca^{2+}, etc. 1 mmol Cl^-, 1 mmol ½SO_4^{2-}, etc. general notation: $mmol_c$ (i.e. mmol of charge)
1 me/100 g (for CEC and AEC)	1 $mmol_c$/100 g = 1 $cmol_c$/kg = 10 $mmol_c$/kg
1 Å	0.1 nm
1 bar	100 kPa

The notation % (percent) is not unambiguous. In cases where doubt may exist the following additions were used: *v/v* (= volume per volume, *vol%*), *w/w* (=weight per weight, *wt%*), and *w/v* (=weight per volume).
Note in 6th Edition: *m/m* (mass/mass) is preferred to *w/w*.

The abbreviations AAS and FES stand for *atomic absorption spectrometry* and *flame emission spectrometry* respectively.

It is assumed that normal laboratory equipment and glassware is available for the procedures e.g., test tubes, beakers, funnels, filter paper, thermometers, stopwatch. These are, therefore, in most cases not specifically listed with the necessary equipment.

In dilution and dispensing procedures, pipetting can often conveniently be done with diluters and dispensers.

Although many laboratories work with autoanalysers, the present procedures do not anticipate this. It is usually simpler to adapt general procedures for autoanalyser application than the other way round.

In several procedures specific brands of apparatus and chemicals are mentioned. These are brands that are in use in the ISRIC laboratory at the time of writing and the mentioning is intended as a description only and not as a recommendation for their use. In many cases, if not all, other brands may be suitable.

For internal laboratory quality control, in most procedures the use of a *control sample* in each batch is required. For soil characterisation, commercial reference samples are hard to obtain or not available. Therefore, samples with appropriate values for the various parameters should be selected. The repeated analysis makes this sample increasingly valuable (make *control charts*!) particularly if they are also analysed by other laboratories. Therefore, it is advisable to prepare as large a control sample as possible (say 25 or 50 kg or even more, depending on the consumption rate) so that it can serve for considerable time. Before depletion of the stock a new control sample should be prepared so that it can be analysed at least 10 times concurrently with the old one. External quality control, equally important, can be obtained by having the control samples analysed by a number of other laboratories and by participation in interlaboratory cross-checking programmes*. Quality Management in soil and plant analytical laboratories is dealt with in a separate volume (Van Reeuwijk, 1998).

* For instance, the International Soil-Analytical Exchange (ISE) of WEPAL, the Wageningen Evaluating Programmes for Analytical Laboratories, P.O. Box 8005, 6700 EC Wageningen, the Netherlands (http://www.benp.wau.nl/wepal).

1. SAMPLE PREPARATION

Transfer field sample to a plastic tray for air-drying. Take care of proper labelling to avoid identification errors during transfer. Break up large clods to speed up drying. Remove large plant residues. Avoid placing in direct sunlight. After drying, weigh the total sample (or a subsample sufficiently large to serve as laboratory sample). Sieve through a 2 mm sieve. Clods, not passing through the sieve are carefully crushed (not ground!) by a pestle and mortar and sieved again. Gravel, rock fragments etc. not passing through the sieve, after removal of any adhering finer particles, are weighed and their content is reported as fraction of the whole (sub)sample. (It is unavoidable that this procedure is liable to subjectivity and practical experience.) If desired, special features such as coarse concretions are picked out as quantitatively as possible and their content is determined separately. The fraction < 2 mm (*air-dry fine earth*) is homogenized and constitutes the sample that is subjected to the usual laboratory procedures. Store the samples thus obtained in labelled plastic boxes (e.g. refrigerator boxes). If only one label is used, stick this on the box, not on the lid. Mainly to reduce sub-sampling bias, for a number of analyses the use of sample material < 0.25 mm is recommended (e.g. Chapters 5, 6, 10, 12). For this purpose, crush 25 g of fine earth in a mortar to pass it through a 0.25 mm sieve (ISO Standard 11464). Store this in a small labelled box or bottle and keep this in the sample box with the fine earth. If necessary, the coarse fraction > 2 mm can be treated according to an individual programme of analysis.

When air-drying causes unacceptably large irreversible changes in certain soil properties, such as particle-size analysis, CEC, specific surface area, etc., samples have to be kept and treated in the field-moist state (e.g. peat; some soils with andic properties). Fine earth of the moist sample can be obtained by transferring (part of) the field sample to a 2 mm sieve and, after removal of plant residues, passing it through with the help of a plastic or wooden spatula. Another part of the sample can be air-dried and treated as above. The moist fine earth should be kept cool and in the dark and be analyzed as soon as possible.

2. MOISTURE CONTENT

2-1 PRINCIPLE

Calculation of the results of soil analysis is done on basis of "oven-dry" soil*. The moisture content of the sample should be determined shortly before soil analysis.

2-2 APPARATUS

Moisture tins or flasks with fitting lid.
Drying oven.

2-3 PROCEDURE

1. Transfer approx. 5 g fine earth to a tared moisture tin and weigh with 0.001 g accuracy (***A*** gram).
2. Dry overnight at 105°C (lid removed).
3. Remove tin from oven, close with lid, cool in desiccator and weigh (***B*** gram).

2-4 CALCULATION

The *moisture content in wt% (m/m)* is obtained by:

$$\text{Moist (wt\%)} = \frac{A-B}{B-\text{tare tin}} \times 100$$

The corresponding *moisture correction factor* (*mcf*) for analytical results or the multiplication factor for the amount of sample to be weighed in for analysis is:

$$\text{Moisture correction factor} = \frac{100+\%\text{moist}}{100}$$

* In view of soil-plant relationship it may be argued that for a number of soil attributes it is relevant to express values on a soil *volume* basis (w/v) rather than on the usual soil *weight* basis (w/w). Soil weight can be converted to volume by means of the bulk density (see Chapter 18). Thus, for instance, a soil with a CEC of 10 $cmol_c/kg$ and a bulk density of 1.50 kg/dm^3 would have a CEC of 15 $cmol_c/dm^3$.

3. PARTICLE-SIZE ANALYSIS

3-1 PRINCIPLE

Separation of the mineral part of the soil into various size fractions and determination of the proportion of these fractions. The analysis comprises all material, i.e. including gravel and coarser material (see Chapter 1) but the procedure below is applied to the fine earth (<2 mm) only.

Of paramount importance in this analysis is the pretreatment of the sample aimed at complete dispersion of the primary particles. Therefore, cementing materials (usually of secondary origin) such as organic matter and calcium carbonate may have to be removed. In some cases also sesquioxides may need to be removed. It may be argued, however, that for agricultural purposes it is often not relevant or even fundamentally wrong to remove these components. Thus, depending on the aim of study, all pretreatments are to be considered optional. For soil characterization purposes, in the ISRIC laboratory removal of organic matter by H_2O_2 and of carbonates by HCl is routinely carried out*.

After shaking with a dispersing agent, sand is separated from clay and silt with a 50 µm sieve**. The sand is fractionated by dry sieving, the clay and silt fractions are determined by the pipette method or, alternatively, by the hydrometer method.

3-2 APPARATUS

Water bath
Hot plate
End-over-end shaking machine
Sieving machine (e.g. Fritsch Analysette, by vibration)
Set of sieves, including bottom (diameter 20 cm)
Heavy brass funnel (diameter approx. 23 cm) on stand
Small 50 µm sieve (diameter 8 cm)
Glass sedimentation cylinders, marked at 1 litre
Drying oven
Moisture tins
Stopwatch

3-3 REAGENTS

Hydrogen peroxide, 30%.

Dispersing agent: Sodium hexametaphosphate 4% and soda 1% solution ("Calgon"-type). Dissolve 40.0 g $(NaPO_3)_6$ and 10.0 g Na_2CO_3 in water in a 1 l volumetric flask and make to volume. Both chemicals should be dried overnight at 105°C prior to use (therefore, hydrated soda qualities may be used).

Calcium chloride solution, 1 M. Dissolve 147 g $CaCl_2.2H_2O$ in 1 l water.

3-4 PROCEDURE

3-4.1 Oxidation of organic matter

1. Weigh out approx. 20 g fine earth into a 1 l beaker (at carbonate contents exceeding 10% and carbonate is to be removed, weigh out proportionally more soil).

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* In the ISRIC laboratory carbonates (when present) have always routinely been removed, previously with a Na-acetate buffer pH 5 and lately with a 10% acetic acid treatment. The accepted (1995) ISO/DIS (Draft International Standard) 11277 states that removal of carbonate (and oxides) is only done optionally. However, the new Standard 11277 is not accompanied by performance validation data and according to Good Laboratory Practice, a laboratory planning to (drastically) change its procedure should carry out a programme of validation and correlation of the new procedure against the old one, e.g. repeated analysis (min. 10×) of relevant control samples. Therefore, until such validation has been done, the ISRIC laboratory will continue to remove carbonates as a rule, be it with 1 M HCl (see Section 3-4.2).
Some other essential steps of Standard 11277 have also been accommodated in the present procedure.

** In the 1995 ISO/DIS 11277 the 50 µm boundary has been changed into a 63 µm boundary. In view of homogeneity of its database (ISIS), ISRIC has decided to postpone introduction of this boundary in soil characterization.

2. Add 15 ml water and 15 ml H_2O_2 30%. Cover beaker with watch-glass. In case of strong frothing place beaker in basin with cold water. In addition, frothing can be tempered by adding a few drops of ethanol.
3. Let stand overnight.
4. The next day, place beaker on water bath (80°C) and regularly add 5-10 ml increments of H_2O_2 30% until decomposition of organic matter is completed (usually the supernatant is clear then).
5. Add water to a volume of about 300 ml.
6. Place on hot plate and carefully boil for 1 hour to remove any remaining H_2O_2.
7. Remove beaker from hot place and allow to cool.
8. Centrifuge and decant or, alternatively, allow material to settle in the beaker and siphon off.

   Note: Flocculation may be enhanced by adding 25 ml 1 *M* $CaCl_2$ solution with a measuring cylinder. The washings have to be repeated until the dark residues of the organic matter have gone. Check that the EC of the washings is below 0.4 mS/cm before attempting to disperse the residue (this would leave a max. of 0.02 g salt in the sample, corresponding with an error in the correction for dispersing agent of max. 2% which is negligible).

   If presence of salts or gypsum is suspected (e.g. from EC check in pH-H_2O extract) measure electrical conductivity of supernatant solution.
9. If EC of supernatant solution is higher than 0.4 mS/cm, add about 250 ml water, cap centrifuge tube and shake in end-over-end shaker for one hour (or stir from time to time for one hour) and repeat Steps 8 and 9 until EC of supernatant solution < 0.4 mS/cm.

Proceed with Dispersion (3-4.4) unless carbonates (3-4.2) and/or iron oxides (3-4.3) are removed.

3-4.2 **Removal of carbonate** (optional)

3-4.2.1 Reagent

Hydrochloric acid, 1 M. Add 87 ml conc. HCl to 900 ml water and make to 1 l with water (use fume cupboard!).

3-4.2.2 Procedure

1. To the residue of 3-4.1 add 25 ml HCl 1 *M* plus 4 ml of the same for each percent of carbonate in the soil (if about 20 g of sample was used). If proportionally more soil was used (3-4.1 Step 1), calculate weight of carbonate in sample and add 25 ml HCl 1 *M* plus 1 ml of the same for each 50 mg of carbonate.
   If carbonate is less than 2% then only an initial 25 ml of the acid is required (if in this case flocculation is not adequate, add 20 ml 1 *M* $CaCl_2$ solution).
   Make up to about 250 ml with water.
2. Place suspension on water bath at approx. 80°C for about 15 min., stirring from time to time.
3. Remove suspension from water bath and leave to stand overnight.
4. If the soil flocculates to leave a perfectly clear supernatant, then this can be siphoned off or decanted, otherwise centrifugation will be necessary.
5. Repeat washing with water and siphoning off or decantation until EC of supernatant < 0.4 mS/cm.

Note: A few minerals might not survive this treatment e.g., some zeolites, chlorite, and allophane. If this is suspected to be quantitatively significant, the treatment should be milder. Several means can be considered; 1. omit heating. 2. Use a 10% acetic acid solution (vol/vol) instead of hydrochloric acid. 3. Use a 1 *M* Na-acetate buffer pH 5.
This consideration is also important when the clay fraction of the particle-size analysis is afterwards used for X-ray diffraction (as is done in some laboratories). Clay separation for XRFS and XRD using the mild acetate buffer is described in Chapters 15 and 16 respectively.

3-4.3 **Deferration** (optional)

If applied, this treatment is usually done after the other pretreatments prior to dispersion.

3-4.3.1 Reagents

Buffer solution 0.3 M sodium citrate and 0.1 M sodium bicarbonate. Dissolve 88 g Na-citrate.$2H_2O$ and 8.4 g $NaHCO_3$ in water and make to 1 l.
Sodium dithionite (powder).
Sodium chloride solution 1 M. Dissolve 58.5 g NaCl in water and make to 1 l.

3-4.3.2 Procedure

1. Weigh out approx. 20 g fine earth in a 1 l beaker and add 200 ml buffer solution.
2. Heat on a water bath to 75°C (do *not* exceed 80°C as elemental sulphur will then precipitate).
3. Add approx. 1 g sodium dithionite with a spoon and stir constantly for about a minute and then occasionally for 5 minutes.
4. Repeat Step 3 two more times.
5. Centrifuge and decant or allow to settle and siphon off.
6. For samples containing more than 5% extractable Fe_2O_3, repeat the procedure once or twice: a brownish or reddish colour of the sample may indicate still incomplete deferration.
7. Wash once more with 250 ml 1 *M* NaCl when centrifuging, or 500 ml when siphoning.
8. Proceed with 3-4.1 Step 8.

3-4.4 Dispersion

1. Transfer suspension quantitatively to a 1 l polythene bottle (if no pretreatment is given, weigh out approx. 20 g fine earth into this bottle).
2. Add 20.00 ml dispersing agent, make the volume to about 400 ml with water and cap the bottle.
3. Shake overnight (16 hrs.) on an end-over-end shaker at a speed of about 30 rpm.

3-4.5 Separation of fractions

1. Pass the suspension through a 50 µm sieve which is placed in a funnel positioned above a sedimentation cylinder with a stand and clamp. Use a wide (3 cm) rubber policeman.
2. Make to 1 litre mark with water. Proceed with this according to 3-4.7.
   Note: Include a blank (cylinder with water from same source plus dispersing agent) for temperature measurement in clay determination and for correction of dispersing agent addition.
3. Wash the sand fraction remaining on the sieve quantitatively into a porcelain dish, evaporate on water bath and dry at 105°C for at least an hour.

3-4.6 Determination of sand fractions

1. Transfer the dried sand of 3-4.5 Step 3 to the top sieve of a stacked set of sieves of the following mesh sizes: 1000 µm; 500 µm; 250 µm; 100 µm; 50 µm; bottom. (Or any other set of desired sizes.)
2. Sieve for 10 minutes on the sieving machine at the settings: amplitude 7.0 and interval 4. (At this setting the sieves vibrate at a frequency of 3000× per minute and an amplitude of 2 mm for 4-second periods interrupted for ½ second.)
3. Empty each sieve into a tared weighing dish by tapping it upside down on the brass funnel placed above the dish. Weigh with 0.01 g accuracy (net weights ***A*** through ***E***, individual sand fractions).
4. If any material is collected in sieve bottom (<50 µm) transfer this to suspension in sedimentation cylinder mentioned in 3-4.5.
   Note: If pipetting of the silt fraction is done before the sieving, then the collected material (which usually is very little) should be weighed and the weight added to weight ***M*** (silt fraction 20-50 µm, see Section 3-5) or to weight ***P*** (silt fraction 2-50 µm, see Section 3-6). These are the fractions where the material is assumed to be mainly derived from.

3-4.7 Determination of silt and clay

3-4.7.1 Calibration of pipette

The pipette method described here is based on sampling a 1 l suspension with a 20.00 ml pipette. Therefore, in the calculations a multiplication factor of 1000/20 = 50 is used (see Section 3-5). Unless a calibrated volumetric pipette is used, calibration of the pipette is necessary. This can be done by pipetting water and weighing the aliquot (accuracy 0.01 g). Repeat this ten times and take the mean (exclude outliers).
If the volume is not 20.00 ml, the multiplication factor of 50 should be changed accordingly.

3-4.7.2 Blank determination

Although the dispersing agent is prepared precisely, a possible error will be multiplied by 50. It is therefore good practice that this is checked in each batch of analyses. This is done by pipetting the blank cylinder as described for the silt and clay fractions below. (Net weight *Z* for dispersing agent.)

3-4.7.3 Fraction <50 µm

1. After adding material <50 µm possibly collected during sieving (see 3-4.6, Step 4) close the sedimentation cylinder with a rubber stopper and shake well.
2. Place the cylinder on the table, remove stopper and immediately pipette 20 ml from the centre of the cylinder.
3. Transfer the aliquot to a tared moisture tin, evaporate on water bath and dry overnight at 105°C.
4. Remove tin from drying oven, close with lid and cool in desiccator. Weigh with 0.001 g accuracy (net weight *F* for fraction <50 µm).

3-4.7.4 Fraction <20 µm

5. After measuring the temperature of the suspension, again stopper the cylinder and shake well.
6. Place the cylinder on a vibration-free table under the pipette-assembly.
7. After exactly 5 minutes pipette 20 ml at a depth indicated in Table 3-1.
8. Transfer aliquot to tared moisture tin, evaporate on water bath and dry overnight at 105°C.
9. Remove tin from drying oven, close with lid and cool in desiccator. Weigh with 0.001 g accuracy (net weight *G* for fraction <20 µm).

Table 3-1. Depth (in cm) at which fractions <20 µm and <2 µm are pipetted as a function of the temperature and after indicated settling time.

Temp. °C	5 mins. <20µm	5½ hrs. <2µm	Temp. °C	5 mins. <20µm	5½ hrs. <2µm
19	10.5	6.9	28	13.0	8.6
20	10.8	7.1	29	13.3	8.8
21	11.0	7.2	30	13.6	9.0
22	11.3	7.4	31	13.9	9.1
23	11.6	7.6	32	14.2	9.3
24	11.9	7.8	33	14.4	9.5
25	12.1	8.0	34	14.8	9.7
26	12.4	8.2	35	15.1	9.9
27	12.7	8.4	36	15.4	10.1

3-4.7.5 Fraction <2 µm

10. After 5½ hours measure temperature in blank cylinder and pipette 20 ml at a depth indicated in Table 3-1. *Note:* If this temperature differs from initial temperature (measured in 3-4.7.4 Step 5), use mean of this and initial temperature.
11. Transfer aliquot to tared moisture tin, evaporate on water bath and dry overnight at 105°C.
12. Remove tin from drying oven, close with lid and cool in desiccator. Weigh with 0.001 g accuracy (net weight *H* for fraction <2 µm).

Remark 1: In case only the clay fraction is to be determined (and not the silt) proceed according to Steps 1, 6, 10, 11 and 12 respectively of this section 3-4.7. Measure initial temperature of suspension.

Remark 2: In some cases peptization of the suspension is not or incompletely achieved. This can easily be observed by flocculation in the cylinder. In this case only the determination of the total fraction < 50 µm is possible, whereas clay and silt cannot be determined. This occurs mainly with calcareous soils, and the removal of carbonate (3-4.2) is then indicated.

3-5 CALCULATIONS

The basis of the calculations is the oven-dry sample weight after all treatments. It is obtained by summation of all individual fractions:

Clay (<2 μm)	$= (H \times 50) - (Z \times 50)$	(wt. K)
Silt (2-20 μm)	$= (G \times 50) - (Z \times 50) - K$	(wt. L)
Silt (20-50 μm)	$= (F \times 50) - (Z \times 50) - K - L$	(wt. M)
Sand (>50 μm)	$= A + B + C + D + E$	(wt. N)

Sample weight $= K + L + M + N$ (all weights in gram)

where
A through E = weight individual sand fractions
F = weight 20 ml pipette aliquot of fraction <50 μm
G = weight 20 ml pipette aliquot of fraction <20 μm
H = weight 20 ml pipette aliquot of fraction < 2 μm
Z = weight 20 ml pipette aliquot of blank

The proportional amounts of the fractions can now be calculated by:

$$\%\,\text{clay}\ (<2\mu\text{m}) = \frac{K}{\text{sample wt.}} \times 100$$

$$\%\,\text{silt}\ (2\text{–}20\mu\text{m}) = \frac{L}{\text{sample wt.}} \times 100$$

$$\%\,\text{silt}\ (20\text{–}50\mu\text{m}) = \frac{M}{\text{sample wt.}} \times 100$$

$$\%\,\text{sand}\ (1000\text{–}2000\mu\text{m}) = \frac{A}{\text{sample wt.}} \times 100$$

$$\%\,\text{sand}\ (500\text{–}1000\mu\text{m}) = \frac{B}{\text{sample wt.}} \times 100$$

$$\%\,\text{sand}\ (250\text{–}500\mu\text{m}) = \frac{C}{\text{sample wt.}} \times 100$$

$$\%\,\text{sand}\ (100\text{–}250\mu\text{m}) = \frac{D}{\text{sample wt.}} \times 100$$

$$\%\,\text{sand}\ (50\text{–}100\mu\text{m}) = \frac{E}{\text{sample wt.}} \times 100$$

Note: With this calculation, the clay, silt and sand fractions are obtained in percentages of the *fine earth* (minus carbonate and organic matter which have been removed). The coarse fraction >2 mm, if present, is reported in percentage of the *total soil* (see Chapter 1). If all fractions need to be reported on *total soil* basis convert above obtained figures for clay, silt and sand as follows:

$$\%\,\text{clay, silt, sand of } \textit{total soil} = \frac{100 - \%(\text{fraction}>2\text{mm} + \text{carbonate} + \text{org.matter})}{100} \times \%\,\text{clay, silt, sand of } \textit{fine earth}$$

In case deferration was applied the percentage "free iron" (see 12-1) should be included between the parentheses. The determination of the organic matter and carbonate contents is described in Chapters 5 and 7 respectively.

3-6 THREE FRACTIONS ONLY (Sand, Silt, Clay)

If only the sand (50-2000 µm), silt (2-50 µm) and clay (<2 µm) fractions are to be determined, the procedure described above is modified as indicated below.

Note: If only the *clay fraction* is required, then still the silt and sand fractions have to be determined in the present procedure as they are needed for calculating the sample weight. This can be avoided by weighing a precise amount of sample at the outset (in the calculation, if necessary, correct for moisture, organic matter, calcium carbonate and iron oxides).

Down to the last step of Section 3-4.5 no modifications are introduced.

3-6.1 Sand

To Section 3-4.5 (separation of fractions) is added:

4. Weigh sand fraction (net weight ***N***, total sand).
   Note: This is the same *N* as obtained by summation of the sand subfractions *A* through *E* of Section 3-4.6.

3-6.2 Silt

For this, proceed as indicated in Section 3-4.7.3 and determine weight ***F***. Omit the subsequent Section 3-4.7.4 (fraction <20 µm) but observe instructions of Sections 3-4.7.1 and 2.

3-6.3 Clay

No change, proceed as indicated in Section 3-4.7.5 and determine weight ***H***.

3-6.4 Calculations

The basis of the calculations is the oven-dry sample weight after all treatments. It is obtained by summation of the individual fractions:

Clay (<2 µm)	$= (H \times 50) - (Z \times 50)$	(wt. *K*)
Silt (2-50 µm)	$= (F \times 50) - (Z \times 50) - K$	(wt. *P*)
Sand (>50 µm)	= weighed	(wt. *N*)

Sample weight $= K + P + N$ (all weights in gram)

where
F = weight 20 ml pipette aliquot of fraction <50 µm
H = weight 20 ml pipette aliquot of fraction < 2 µm
Z = weight 20 ml pipette aliquot of blank

The proportional amounts of the fractions can now be calculated by:

$$\%\,\text{clay}\ (<2\mu\text{m}) = \frac{K}{\text{sample wt.}} \times 100$$

$$\%\,\text{silt}\ (2\text{-}50\mu\text{m}) = \frac{P}{\text{sample wt.}} \times 100$$

$$\%\,\text{sand}\ (50\text{-}2000\mu\text{m}) = \frac{N}{\text{sample wt.}} \times 100$$

Note: The Note added to the calculations of Section 3-5 applies here too.

3-7 FINE CLAY (<0.2 μm)

3-7.1 Principle

Because of the low settling velocity of these small particles, sedimentation in cylinders is not suitable for the determination of this fraction. This is overcome by using a centrifuge to increase the gravity force.

3-7.2 Apparatus

Centrifuge (preferably with refrigeration).

3-7.3 Procedure

1. After pipetting the fraction <2 µm (3-4.7.5, Step 10), stopper the cylinder and shake well.
2. Allow to stand for an hour and transfer about 200 ml suspension to a 250 ml centrifuge bottle. Measure temperature of the suspension. During spinning, the distance between surface of suspension and centre of centrifuge should be 16 cm.
3. Spin at 1800 rpm during the time indicated in Table 3-2 (excluding starting and stopping).
   Note: Spinning at 2500 rpm reduces the time needed. In this case plastic centrifuge bottles should be used. Before spinning a next batch, allow centrifuge to cool for at least an hour or use centrifuge with refrigeration. To gauge temperature increase during spinning, spin a blank batch (water) prior to spinning suspensions. A mean temperature can then be used.
4. Stop centrifuge without using the brake.
5. Gently remove bottles from centrifuge and place under pipette.
6. Pipette 20 ml aliquot at 4.5 cm depth. Measure temperature of suspension.
7. Transfer aliquot to tared moisture tin, evaporate on water-bath and dry overnight at 105°C.
8. Remove tin from drying oven, close with lid and cool in desiccator, weigh with 0.001 g accuracy (net weight *Q*).

Table 3-2. Centrifuge speed and spinning time in minutes as function of the temperature for determination of the fine clay fraction <0.2 µm.

Temp. °C	1800 rpm	2500 rpm	Temp °C	1800 rpm	2500 rpm	Temp °C	1800 rpm	2500 rpm
20	32.0	16.5	27	27.0	14.0	34	23.0	12.0
21	31.0	16.1	28	26.5	13.5	35	22.5	11.8
22	30.0	15.7	29	26.0	13.3	36	22.0	11.5
23	29.5	15.3	30	25.0	13.0	37	22.0	11.3
24	29.0	15.0	31	24.5	12.8	38	21.5	11.1
25	28.0	14.6	32	24.0	12.5	39	21.0	10.9
26	27.5	14.2	33	23.5	12.3	40	20.5	10.6

3-7.4 Calculation

$$\% \text{ fine clay } (<0.2\mu m) = \frac{(Q-Z)\times 50}{\text{sample wt.}} \times 100$$

where
Q = 20 ml aliquot weight of fraction <0.2 µm
Z = 20 ml aliquot weight of blank (see Section 3-4)
sample wt. is here the same as in Section 3-5 or 3-6.

3-8 WATER-DISPERSABLE CLAY (or: "natural clay")

3-8.1 Principle

This is the clay content found when the sample is dispersed with water without any pretreatment to remove cementing compounds and without use of a dispersing agent. The proportion of natural clay to total clay is used as a structure stability indicator.

3-8.2 Procedure

1. Weigh about 10 g fine earth (accuracy 0.01 g) into a 1 l polythene bottle.
2. Add 400 ml water and shake overnight in an end-over-end shaker at about 30 rpm.
3. Transfer to a 1 l sedimentation cylinder and make to the mark with water.
4. Pipette a 20 ml aliquot after 5½ hours at a depth indicated by Table 3-1.
5. Transfer aliquot to tared moisture tin, evaporate on water bath and dry overnight at 105°C.
6. Remove tin from drying oven, close with lid and cool in desiccator. Weigh with 0.001 g accuracy (net weight *R* g).

3-8.3 Calculation

$$\%\ \text{water-dispersable clay} = \frac{50 \times R}{s} \times 100 \times \text{mcf}$$

where
R = 20 ml aliquot weight of suspension
s = air-dry sample weight in gram
mcf = moisture correction factor

A parameter derived from the water-dispersable clay is the "Index of Structure" ranging from 0 to 100:

$$\text{Index of Structure} = 100 \times \left(1 - \frac{\%\ \text{water-dispersable clay}}{\%\ \text{total clay}}\right)$$

where *total clay* is the clay content found when pretreatment and dispersing agent are applied (i.e. *% clay* in Section 3-5 or 3-6).

References

Day, *in*: Black (1965), p. 545
Gee and Bauder, *in*: Klute (1986) p. 383
Jackson (1969)
SNLCS, EMBRAPA, 1979 *(Natural clay,* their method 1.17)
Sombroek (1966, p. 122: *Index of Structure)*
USDA, SCS (1972, 1982)

3-9 HYDROMETER METHOD

3-9.1 Principle

The clay and silt fractions in particle-size analysis can conveniently be determined with a hydrometer instead of with the pipette method. It is basically a measurement of the density of the suspension which is a function of the concentration and kind of particles present (after a certain time of settling).
The pretreatment of the soil is the same as described for the pipette method. After shaking with the dispersing agent, sand is separated from clay and silt with a 50 μm sieve. The sand is fractionated by dry sieving, the clay and silt fractions are determined by hydrometer readings.

3-9.2 Requisites

Standard hydrometer, ASTM no. 152H or D422, with Bouyoucos scale in g/l
Stopwatch
Amyl alcohol

3-9.3 Procedure

1. The suspension <50 μm obtained in 3-4.5 Step 2 is used. (Also use the blank described there: water containing 1 g/l dispersing agent).
2. Allow time for the suspension in the sedimentation cylinder to equilibrate thermally and record temperature.
3. Close the sedimentation cylinder with a rubber stopper and shake well. Add a drop of amyl alcohol if the surface of the suspension is covered with foam. As soon as mixing is completed, carefully lower the hydrometer into the suspension and take a reading when the hydrometer is stable but not later than 50 seconds after completion of the mixing.
4. Remove the hydrometer, rinse, and wipe it dry.
5. Reinsert the hydrometer carefully about 10 seconds before each reading and take readings at 5, 120 and 960 or 1440 minutes. (Readings at other times are possible.)
6. Remove and clean the hydrometer after each reading.
7. Record the reading R each time.
8. Place hydrometer in the blank solution, and record the blank reading as R_{bl} and the temperature each time.

3-9.4 Calculation

1. Determine the *concentration of soil in suspension,* ***C*** in g/l, by

$$C = R\text{-}R_{bl}$$

where R = uncorrected hydrometer reading in g/l
R_{bl} = hydrometer reading of the blank solution.

2. Determine the *summation percentage* ***P*** for the taken time-interval, i.e. the weight percentage of all particles still present at the depth of measurement after the time of settling, by

$$P = \frac{C}{C_0} \times 100$$

where $C_0 = C_{50\,sec}$ + total weight sand fractions.

(Note that C_0 = *weight total sample,* $C_{50\,sec}$ = *weight silt + clay fractions,* and that *total weight sand fractions* is weight N as calculated in Section 3-5).

3. Determine ***X*** *(mean particle diameter* in µm) in suspension at time *t*, using:

$$X = 1000\sqrt{(Bh')}\,/\sqrt{t}$$

where: $B = 30\eta\ /\ \{g(\rho_s-\rho_l)\}$ (see Table 3-3)
$h' = -0.164R + 16.3$

and with the terms expressed in the following units:

h' = effective hydrometer depth, cm
η = fluid viscosity, poise (= 100 mPa.s)
g = gravitational constant, 985 cm/s^2
ρ_s = soil particle density, 2.60 g/cm^3
ρ_l = solution density, g/cm^3
t = time, minutes

Solution density (g/cm^3): $\rho_l = \rho^\circ\ (1 + 0.630\ Cs)$

where ρ° = water density in g/cm^3 at temperature t
Cs = concentration dispersing agent in g/cm^3

Viscosity (cp): $\eta = \eta^\circ\ (1 + 4.25\ Cs)$

where η° = viscosity water in centipoise (mPa.s or g.m^{-1}.s) at temperature t

Table 3-3. The factor *B* calculated as a function of the temperature.

Temp. °C	***B*** ×10^{-4}	Temp. °C	***B*** ×10^{-4}	Temp. °C	***B*** ×10^{-4}
19	1.90	27	1.57	35	1.32
20	1.85	28	1.54	36	1.30
21	1.81	29	1.50	37	1.27
22	1.76	30	1.47	38	1.25
23	1.72	31	1.44	39	1.22
24	1.68	32	1.41	40	1.20
25	1.64	33	1.38		
26	1.60	34	1.35		

4. Plot a *summation percentage curve* (*P vs. X*; use log scale for *X*) using the hydrometer readings and the sieve data. From this curve derive silt and clay percentages (and total sand by subtraction from 100%). An example of this procedure is given next in Section 3-9.5.

References

Gee and Bauder, *in*: Klute (1986) p. 383
CRC Handbook of Chemistry and Physics, e.g. 69th ed. (1988-1989) or later.

3-9.5 Calculation example

Temperature = 22°C
Blank reading R_{bl} = 2.0
Weight total sand = 4.50 g

	50 sec.	5 min.	120 min.	1440 min.
Readings *(R)*	16.0	13.0	6.2	5.6
C $(=R-R_{bl})$	14.0	11.0	4.2	3.6

Then: total sample weight $\boldsymbol{C_0} = C_{50\,sec}$ + weight sand = 14.0 + 4.5 = 18.5

And: Calculation of $\boldsymbol{X}$ (particle diameter):

time (min.)	h'	X
0.83	(-0.164×16.0) + 16.3 = 13.68	$1000 \times \sqrt{(1.76\times10^{-4}\times13.68)} / \sqrt{0.83} = 54.0$ μm
5	(-0.164×13.0) + 16.3 = 14.17	$1000 \times \sqrt{(1.76\times10^{-4}\times14.17)} / \sqrt{5} = 22.3$ μm
120	(-0.164×6.2) + 16.3 = 15.28	$1000 \times \sqrt{(1.76\times10^{-4}\times15.28)} / \sqrt{120} = 4.7$ μm
1440	(-0.164×5.6) + 16.3 = 15.38	$1000 \times \sqrt{(1.76\times10^{-4}\times15.38)} / \sqrt{1440} = 1.4$ μm

Then: Calculation of $\boldsymbol{P}$ (summation percentage) presented with corresponding X:

	50 sec.	5 min.	120 min.	1440 min.
$P \quad (= \frac{C}{18.5} \times 100)$	75.7	59.5	22.7	19.5
X (μm)	54.0	22.3	4.7	1.4

These results have been plotted in Fig. 3-1 (squares □). Note that for the particle size at 50 seconds (0.83 min.) not 54 μm should be taken but 50 μm since particles >50 μm are not present in the suspension. (This means that in practice the first reading can be taken up to just under 1 minute after mixing.)
In this graph, determine the summation percentages of the fractions wanted, usually 2 μm, 20 μm and 50 μm (indicated by circles O). These are:

<2 μm: 20.5%, <20 μm: 57.0%, <50 μm: 75.7%

Remark: Obviously, the decimals cannot be read accurately and also the interpolation between the determined points by straight lines gives rise to some uncertainty. Therefore, the final results should be rounded off to whole figures.

Hence, the contents of the various fractions are (in % of the total sample):

clay (<2 μm)	= 20.5%	= 21%
silt (2-20 μm)	= 57.0 - 20.5 = 36.5%	= 37%
silt (2-50 μm)	= 75.7 - 20.5 = 55.2%	= 55%
silt (20-50 μm)	= 75.7 - 57.0 = 18.7%	= 19%
sand (50-2000 μm)	= 100 - 75.7 = 24.3%	= 24%

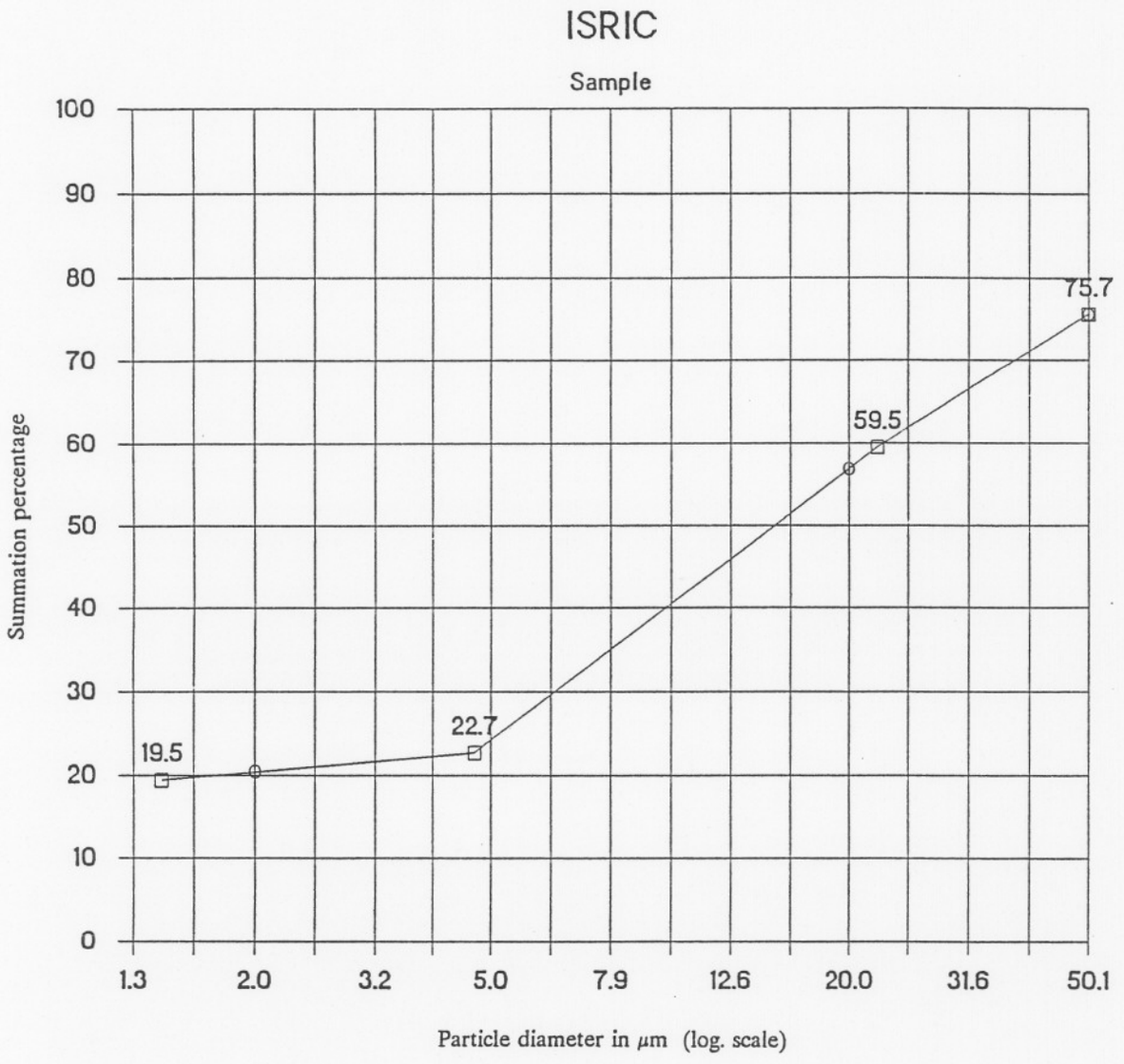

Fig. 3-1. Summation graph of an example particle-size analysis with the hydrometer (see text).

4. pH

4-1 pH-H_2O AND pH-KCl

4-1.1 Principle

The pH of the soil is potentiometrically measured in the supernatant suspension of a 1:2.5 soil:liquid mixture. The liquid is either water (pH-H_2O) or a 1 *M* KCl solution (pH-KCl).

4-1.2 Apparatus

pH meter with glass-calomel combination electrode
Reciprocating shaking machine

4-1.3 Reagents

Potassium chloride solution, 1 M. Dissolve 74.5 g KCl in water and make to 1 l.
Buffer solutions, pH 4.00, 7.00 and 9.00 (or 10.00). Dilute standard analytical concentrate ampoules according to instruction.

4-1.4 Procedure

1. Weigh 20 g fine earth into a 100 ml polythene wide-mouth type bottle. Include a blank.
2. Add 50 ml liquid (water or 1 *M* KCl solution) and cap the bottle.
3. Shake for 2 hours.
4. Before opening the bottle for measurement, shake by hand once or twice.
5. Immerse electrode in upper part of suspension.
6. Read pH when reading has stabilized (accuracy 0.1 unit).
   Note: The reading is considered stable when it does not change more than 0.1 unit per 30 seconds (or 0.02 units per 5 secs.). In calcareous soils stabilization may be difficult to achieve because of non-equilibrium conditions.

Remarks

1. Prior to reading, calibrate the pH meter with buffer solutions for the range in which is measured. Because of differences in slope of the calibration line measurements outside a calibration range may be in error.
2. Buffer solutions should not be stored for too long. Especially the pH 9 and 10 solutions are sensitive to CO_2 and may soon become unreliable.
3. For the identification of a "sulphuric horizon" a 1:1 soil:water ratio is used.
4. The presence of soluble salts in the soil can conveniently be detected by measuring the electrical conductivity of the pH-H_2O extract ($EC_{2.5}$). For this measuring procedure see 13-4.

Reference

Peech, *in*: Black (1965), Part 2, p. 914.

4-2 pH-NaF

4-2.1 Principle

The presence of *"active aluminium"* in soils is assessed by measuring the pH increase of a 1 *M* NaF solution upon a two-minute reaction with soil in a 50:1 ratio.

4-2.2 Reagent

Sodium fluoride solution, 1 M (saturated). Add 1 l water to 45 g NaF in a 1 l polythene bottle. Let stand for 2 days but shake occasionally. On the third day, after excess NaF has settled, decant or pass the solution through a filter. Transfer a 50 ml aliquot to a 100 ml beaker and measure the pH which should be between 7.2 and 8.1. If this is not the case (the pH is often higher), then bring down the pH with a few drops of 0.1 *M* HCl or HNO_3*.

4-2.3 Apparatus

pH meter with combination electrode
Stopwatch

4-2.4 Procedure

1. Weigh 1 g fine earth into a 100 ml beaker.
   Note: when moist samples are used weigh 1 g × *moisture correction factor* (see Chapter 2).
2. Add 50 ml NaF 1 *M* and start stopwatch.
3. Stir suspension for 1 minute with glass rod.
4. Immerse electrode in upper part of suspension.
5. Continue stirring and read pH exactly 2 minutes after adding NaF solution.
6. *Optional:* read pH again after 60 minutes.

Warning: The pH also increases by reaction of NaF with gibbsite and calcite.

References

Fieldes and Perrott (1966)
Peech, *in*: Black (1965), Part 2, p. 914
USDA, SCS (1972)

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* Since the NaF test is only a qualitative test (the pH-NaF having been abandoned as a soil classification criterion) it is preferred to rectify the pH in this way rather than to comply with the former tedious practice which was as follows: "Add 3 to 5 drops of a 0.1% phenolphthalein indicator solution (in ethanol) and titrate with 0.01 M NaOH standard solution until the colour is just pink. This should take less than 1.25 ml NaOH (corresponding with 0.25 me titratable acidity). If either of these two requirements is not met try another brand of NaF" (USDA-SCS, 1972).

5. ORGANIC CARBON

5-1 PRINCIPLE

The *Walkley-Black* procedure is followed. This involves a wet combustion of the organic matter with a mixture of potassium dichromate and sulphuric acid at about 125 °C. The residual dichromate is titrated against ferrous sulphate. To compensate for incomplete destruction an empirical correction factor of 1.3 is applied in the calculation of the result.

5-2 APPARATUS

Burette
Safety pipette 10 ml
Illuminated magnetic stirrer
Measuring cylinder 25 ml

5-3 REAGENTS

Potassium dichromate standard solution, 0.1667 M. Dissolve 49.04 g $K_2Cr_2O_7$ A.R. (dried at 105°C) in water in a 1 l volumetric flask and make to volume with water.
Concentrated sulphuric acid (96%).
Concentrated phosphoric acid (85%).
Barium diphenylamine sulphonate, 0.16% (indicator). Dissolve 1.6 g barium diphenylamine sulphonate in 1 l water.
Ferrous sulphate solution, 1 M (approx.). Dissolve 278 g $FeSO_4.7H_2O$ in ca. 750 ml water and add 15 ml conc. H_2SO_4. Transfer to a 1 l volumetric flask and make to volume with water.

5-4 PROCEDURE

1. Grind approx. 5 g fine earth to pass a 0.25 mm sieve.
2. Weigh 1 g of this material (accuracy 0.01 g) into a 500 ml wide-mouth erlenmeyer flask. Include a control sample.
   Note: In case of soils containing more than 2.5% C proportionally less sample should be weighed in.
3. Add 10.00 ml dichromate solution. Include two blanks (erlenmeyer flasks without soil) to determine the molarity of the ferrous sulphate solution.
4. Carefully add 20 ml sulphuric acid with a measuring cylinder, swirl the flask and allow to stand on a pad for 30 minutes (in fume cupboard!).
5. Add about 250 ml water and 10 ml phosphoric acid with a measuring cylinder and allow to cool.
6. Add 1 ml indicator solution and titrate with ferrous sulphate solution while the mixture is being stirred. Near the end-point the brown colour becomes purple or violet-blue and the titration must be slowed down. At the end-point the colour changes sharply to green. If more than 8 of the 10 ml dichromate added has been reduced then repeat the determination with less soil (see also Step 2).
   Note: The end-point is easily overshot, in that case add 0.50 ml of the dichromate solution and titrate again drop-wise (change calculation accordingly).

5-5 CALCULATION

The carbon content of the soil is obtained by:

$$\%C = M \times \frac{V1 - V2}{s} \times 0.39 \times mcf$$

where

M = molarity of ferrous sulphate solution (from blank titration)
V1 = ml ferrous sulphate solution required for blank
V2 = ml ferrous sulphate solution required for sample
s = weight of air-dry sample in gram
0.39 = $3 \times 10^{-3} \times 100\% \times 1.3$ (3 = equivalent weight of carbon)
mcf = moisture correction factor

Note: The factor 1.3 is a compensation factor for the incomplete combustion of the organic matter in this procedure. This ineffectiveness varies with the type of organic matter and the factor 1.3 is a compromise.

Conversion of the **% *carbon*** to **% *organic matter*** is done by multiplying with the empirical factor **2**:

$$\%\ \text{organic matter} = 2 \times \%\ \text{carbon}$$

Note: Formerly a conversion factor of 1.72 was used, but there is evidence that unless specific information about the organic matter concerned is available a factor 2 is more appropriate (Nelson & Sommers, 1982).

Remark: In reporting the results the used correction and conversion factors should be stated.

REFERENCES

D.W. Nelson and L.E. Sommers, *in*: Page (1982), p. 539
USDA, SCS, (1982)

6. NITROGEN

6-1 PRINCIPLE

The micro-Kjeldahl procedure is followed. The sample is digested in sulphuric acid and hydrogen peroxide with selenium as catalyst and whereby organic nitrogen is converted to ammonium sulphate. The solution is then made alkaline and ammonia is distilled. The evolved ammonia is trapped in boric acid and titrated with standard acid. The procedure determines all soil nitrogen (including adsorbed NH_4^+) except that in nitrates.

6-2 APPARATUS

Digestor (Kjeldahl digestion tubes in heating block)
Steam-distillation unit (fitted to accept digestion tubes)
Burette 25 ml

6-3 REAGENTS

Sulphuric acid - selenium digestion mixture. Dissolve 3.5 g of selenium powder in 1 l concentrated (96%) sulphuric acid by mixing and heating at approx. 350°C. The dark colour of the suspension turns into clear light-yellow. When this is reached, continue heating for 2 hours.

Hydrogen peroxide 30%.

Sodium hydroxide solution, 38%. Dissolve 1.90 kg NaOH pellets in 2 l water in a heavy-walled 5 l flask. Cool the solution with the flask stoppered to prevent absorption of atmospheric CO_2. Make up the volume to 5 l with freshly boiled and cooled deionized water. Mix well.

Mixed indicator solution. Dissolve 0.13 g methyl red and 0.20 g bromocresol green in 200 ml ethanol.

Boric acid-indicator solution, 1%. Dissolve 10 g H_3BO_3 in 900 ml hot water, cool and add 20 ml mixed indicator solution. Make to 1 l with water and mix thoroughly.

Hydrochloric acid, 0.010 M standard. Dilute standard analytical concentrate ampoule according to instruction.

6-4 PROCEDURE

6-4.1 Digestion

1. Grind approx. 5 g fine earth to pass a 0.25 mm sieve.
2. Weigh 1 g of this material (accuracy 0.01 g) into a digestion tube. Of soils, rich in organic matter (>10%), 0.5 g is weighed in (see Remark 1). In each batch, include two blanks and a control sample.
3. Add 2.5 ml digestion mixture.
4. Add successively 3 aliquots of 1 ml hydrogen peroxide. The next aliquot can be added when frothing has subsided. If frothing is excessive, cool the tube in water.
   Note: In Steps 3 and 4 use a measuring pipette with balloon or a dispensing pipette.
5. Place the tubes on the heater and heat for about 1 hour at moderate temperature (200°C).
6. Turn up the temperature to approx. 330°C (just below boiling temp.) and continue heating until mixture is transparent (this should take about two hours).
7. Remove tubes from heater, allow to cool and add approx. 10 ml water with a wash bottle while swirling.

6-4.2 Distillation

1. Add 20 ml boric acid-indicator solution to a 250 ml beaker and place beaker on stand beneath the condenser tip.
2. Add 20 ml NaOH 38% to digestion tube and distil for about 7 minutes during which approx. 75 ml distillate is produced.
   Note: the distillation time and amount of distillate may need to be increased for complete distillation (see Remark 2).
3. Remove beaker from distiller, rinse condenser tip, and titrate distillate with 0.01 *M* HCl until colour changes from green to pink.
   Note: When using automatic titrator: set end-point pH at 4.60.

Remarks

1. The described procedure is suitable for soil samples with a nitrogen content of up to 10 mg N. This corresponds with a carbon content of roughly 10% C. Of soils with higher contents, less sample material is weighed in. Sample sizes of less than 250 mg should not be used because of sample bias.
2. The capacity of the procedure with respect to the amount of N that can be determined depends to a large extent on the efficiency of the distillation assembly. This efficiency can be checked, for instance, with a series of increasing amounts of $(NH_4)_2SO_4$ or NH_4Cl containing 0-50 mg N.

6-5 CALCULATION

$$\%\,N = \frac{a-b}{s} \times M \times 1.4 \times mcf$$

where

a = ml HCl required for titration sample
b = ml HCl required for titration blank
s = air-dry sample weight in gram
M = molarity HCl
1.4 = $14 \times 10^{-3} \times 100\%$ (14 = atomic weight of nitrogen)
mcf = moisture correction factor

REFERENCES

Bremner and Mulvaney, *in*: Page (1982) p. 595
Hesse (1971)

7. CARBONATE

7-1 PRINCIPLE

The "rapid titration method" by Piper, also called "acid neutralization method", is used. The sample is treated with dilute acid and the residual acid (not consumed by carbonate) is titrated. The results are referred to as "calcium carbonate equivalent" since the dissolution is not selective for calcite, but also other carbonates such as dolomite will be dissolved to some extent.

7-2 APPARATUS

Burette
Polythene wide-mouth shaking bottles 250 ml
Reciprocating shaking machine

7-3 REAGENTS

Hydrochloric acid, 0.2 M[*]. Add about 4 l water to a graduated erlenmeyer flask, slowly add 85 ml conc. HCl under constant stirring. Cool and make to 5 l with water.

Hydrochloric acid, 0.100 M standard solution[*]. Dilute standard solution concentrate ampoule according to instruction.

Sodium hydroxide solution, 0.1 M. Standardized[*]. Dissolve 4 g NaOH pellets in 1 l water. Standardize by titrating immediately before use against 0.100 *M* standard HCl using phenolphthalein as indicator.
Note: This is an alternative for making this solution with a standard solution concentrate ampoule (which may be used also). Sodium hydroxide standard solutions have a short life and need to be re-standardized after storage: the effect of a CO_2 trap is limited by (frequent) opening of the bottle.

Phenolphthalein indicator solution, 0.1%. Dissolve 100 mg phenolphthalein in 100 ml ethanol 96%.

7-4 PROCEDURE

1. Weigh 5 g fine earth (accuracy 0.01 g) into a shaking bottle. Include two blanks and a control sample or 500 mg $CaCO_3$ powder[*].
2. Add 100 ml 0.2 *M* HCl by pipette and swirl.
3. Loosely screw on lid (do *not* tighten: CO_2!) and swirl occasionally during the next hour. Let then stand overnight.
4. The next day, indent the bottle by hand, tighten the lid and shake for 2 hours in reciprocating shaker.
5. Let the suspension settle (or filter off), pipette 10 ml supernatant solution into 100 ml erlenmeyer flask and add about 25 ml water.
6. Add a few drops phenolphthalein indicator and titrate with 0.1 *M* NaOH.
   Note: When using automatic titrator: set end-point pH at 7.80.

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[*] These concentrations or amounts are used for the low carbonate content range (<10%). For higher contents either use less sample or higher concentrations of reagents, e.g. 5×. At very high contents (>50%) both higher concentrated reagents and less sample should be used.

7-5 CALCULATION

$$\% \ CaCO_3 \text{ equivalent} = M \times \frac{a-b}{s} \times 50 \times mcf$$

where

a = ml NaOH used for blank
b = ml NaOH used for sample
s = air-dry sample weight in gram
M = molarity of NaOH solution
50 = 50 x 10^{-3} × 10 × 100% (50 = equivalent weight of $CaCO_3$)
mcf = moisture correction factor

Remarks

1. By this method, the calcium carbonate equivalent may be somewhat overestimated because some non-carbonate components of the soil may react with HCl. Thus, at very low carbonate contents (<1%) the error could be relatively large. However, many other and more complicated methods cannot claim a high accuracy in this range either and the present method in most cases offers a good compromise between convenience of operation and accuracy.
2. The analysis is not normally carried out on soils with a pH-H_2O ≤6.5 as carbonate is then assumed to be absent.

REFERENCES

Allison and Moodie, *in*: Black (1965) Part 2, p. 1387
Hesse (1971), p. 52

8. GYPSUM

8-1 PRINCIPLE

Gypsum is dissolved by shaking the sample with water. It is selectively precipitated from the extract by adding acetone. This precipitate is redissolved in water and the gypsum is determined by measuring the Ca concentration in the solution with AAS.

8-2 APPARATUS

Polythene bottles, wide-mouth, 250 ml
Reciprocating shaking machine
Centrifuge
Atomic absorption spectrophotometer

8-3 REAGENTS

Acetone.

Barium chloride solution, 1 M. Dissolve 60 g $BaCl_2.2H_2O$ in a graduated erlenmeyer flask and make to 250 ml with water.

Hydrochloric acid, 1 M. Dissolve 21 ml conc. HCl (37%) in 200 ml water in a 250 ml graduated erlenmeyer and make to 250 ml with water.

Nitric acid, 6 M. Add 380 ml conc. HNO_3 (70%) to approx. 500 ml water and make to 1 l with water.

Gypsum, $CaSO_4.2H_2O$ powder A.R. (optional).

Lanthanum suppressant solution, 1%. Dissolve 35.2 g La_2O_3 in 160 ml HNO_3 6 *M* and dilute to 3 l with water (excess acid: 0.1 *M*).

Standard solution, 1000 mg/l Ca. Dilute a standard analytical concentrate ampoule (1 g/l) according to instruction.

Standard series. Of the 1000 mg/l Ca standard solution pipette 25 ml into a 250 ml volumetric flask and make to volume with water. Of this 100 mg/l Ca standard solution pipette 0-5-10-15-20-25 ml into 100 ml volumetric flasks respectively, add 50 ml La suppressant solution and make to volume with water. The standard series is then 0-5-10-15-20-25 mg/l Ca.

8-4 PROCEDURE

1. Weigh 10 g of fine earth (accuracy 0.1 g) into a 250 ml polythene bottle (see Remark below). Include a control sample or 100 mg $CaSO_4.2H_2O$.
2. Add 100 ml water by pipette.
3. Screw cap on bottle and shake overnight.
4. Centrifuge the suspension until the supernatant is clear.
   Note: If the supernatant does not become clear, absence of gypsum must be inferred (when gypsum is present clay is usually well flocculated).
5. *Test for sulphate:* Transfer approx. 3 ml extract to a test tube and add 10 drops of 1 *M* HCl and 2 ml 1 *M* $BaCl_2$ solution. Only if a turbidity develops the analysis is proceeded. If not, gypsum can be assumed absent in the sample.
   Note: For this test, the extract of the pH-H_2O determination can be used also. Centrifuge first.
6. Pipette 20 ml extract into a 50 ml centrifuge tube. Add 20 ml acetone, mix thoroughly and let stand for 10 minutes.
7. Centrifuge until the supernatant solution is clear.
8. Decant the liquid taking care that no precipitate is lost.
9. Redisperse the precipitate with 10 ml of acetone by blowing the acetone from a pipette along the wall of the centrifuge tube.

10. Centrifuge and decant.
11. Dry the tube with precipitate in drying oven at about 50°C leaving oven-door ajar.
    Warning: When large numbers of tubes are to be dried, the oven should be placed in a fume-cupboard.
12. Add 40 ml of water by pipette, stopper the tube and shake until the precipitate has dissolved.
13. Pipette 2 ml of this solution and 2 ml La suppressant solution into a (short) test tube, homogenize and measure Ca by AAS at a wavelength of 422.7 nm.

8-5 CALCULATION

$$\% \text{ gypsum} = (\text{reading mg/l Ca}) \times \frac{0.172}{s} \times \text{dilution factor} \times \text{mcf}$$

where

$0.172 = \frac{2 \times 40}{1000} \times 10^{-3} \times \frac{100}{20} \times \frac{172.17}{40.08} \times 100\%$

172.17 = molecular weight of gypsum
40.08 = atomic weight of calcium
dilution factor = correction for possible dilution of final solution to bring within measuring range
s = air-dry sample in gram
mcf = moisture correction factor

Remark: The solubility of gypsum in water is approx. 2 g/l. In the present procedure, this corresponds with 2% gypsum in a sample using a 1:10 soil:water ratio. Considering the slow solubility near saturation, for practical reasons the maximum content should be set at 1.5%. At higher contents a proportionally larger ratio should be used, i.e. up to 3%: 5 g soil in 100 ml water (1:20); up to 4.5%: 5 g soil in 150 ml water (1:30), etc.

REFERENCES

Hesse (1971), p. 85
Nelson, *in*: Page et al (1982), p. 194

9. CATION EXCHANGE CAPACITY (CEC) and EXCHANGEABLE BASES

(ammonium acetate method)

9-1 PRINCIPLE

The sample is percolated with ammonium acetate and the bases are measured in the percolate. The sample is subsequently percolated with sodium acetate, the excess salt is then removed and the adsorbed sodium exchanged by percolation with ammonium acetate. The sodium in this percolate is a measure for the CEC.

Alternatively, after percolation with ammonium acetate, the sample can be washed free of excess salt, the whole sample is distilled and the evolved ammonia determined. The advantage of the former is the ease of determination of Na, the advantage of the latter is the omission of one percolation step.

Two procedures are described, they differ only in technique, not in principle:

1. ***Percolation tube*** procedure
2. ***Mechanical extractor*** procedure

The *flow diagram* of the method is given in Diagram 9-1 on p. 9-2.

9-2 APPARATUS

Either : Percolation tubes, 2-2.5 cm diameter, approx. 30 cm length (or a 60 ml syringe), with adjustable outlet (rubber or plastic tube with screw-clamp or stopcock), see Figure 9-1.
Or : Mechanical extractor* (Holmgren et al., 1977), see Figure 9-2.
pH-meter
Atomic absorption spectrophotometer

9-3 REAGENTS

Either : **For percolation tubes:** *ignited and washed sea-sand; cotton wool.*
Or : **For mechanical extractor**: *ignited and washed sea-sand; filter pulp, standard* grade.
Ethanol 96%.
Ethanol 80%. Make 4.17 l ethanol 96% to 5 l with water.
Note: For a comment on the use of ethanol 80% see Remark 3 at the end of Section 9-6.
Sodium hydroxide solution, 1 M. Dissolve 20 g NaOH in about 400 ml water in a graduated 500 ml beaker and make to 500 ml with water.
Ammonium hydroxide solution, 1 M. Add 35.5 ml conc. ammonia to about 400 ml water in a graduated 500 ml beaker and make to 500 ml with water.
Acetic acid 10%. Add 50 ml glacial acetic acid to about 400 ml water in a graduated 500 ml beaker and make to 500 ml with water.
Ammonium acetate solution, 1 M. Dissolve 385 g NH_4OAc in water in a 5 l beaker and make to 5 l. Adjust the pH to 7.0 with ammonia 1 *M* or acetic acid 10%.
Sodium acetate 0.9 M / sodium chloride 0.1 M solution. Dissolve 612 g $NaOAc.3H_2O$ and 29 g NaCl in water in a 5 l beaker and make to 5 l. Adjust the pH to 7.0 with sodium hydroxide 1 *M* or acetic acid 10%.
Note: If desired, both acetate solutions may be adjusted to pH 8.2 (for CEC at pH 8.2 of calcareous soils).
Silver nitrate 1 M (test) solution. Dissolve 8.5 g $AgNO_3$ in 50 ml water and transfer to dropping bottle.

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* Sample Tek #24VE, manufactured by Mavco Industries Inc., 5300 N. 57th Str., Lincoln, NE 68507, USA.

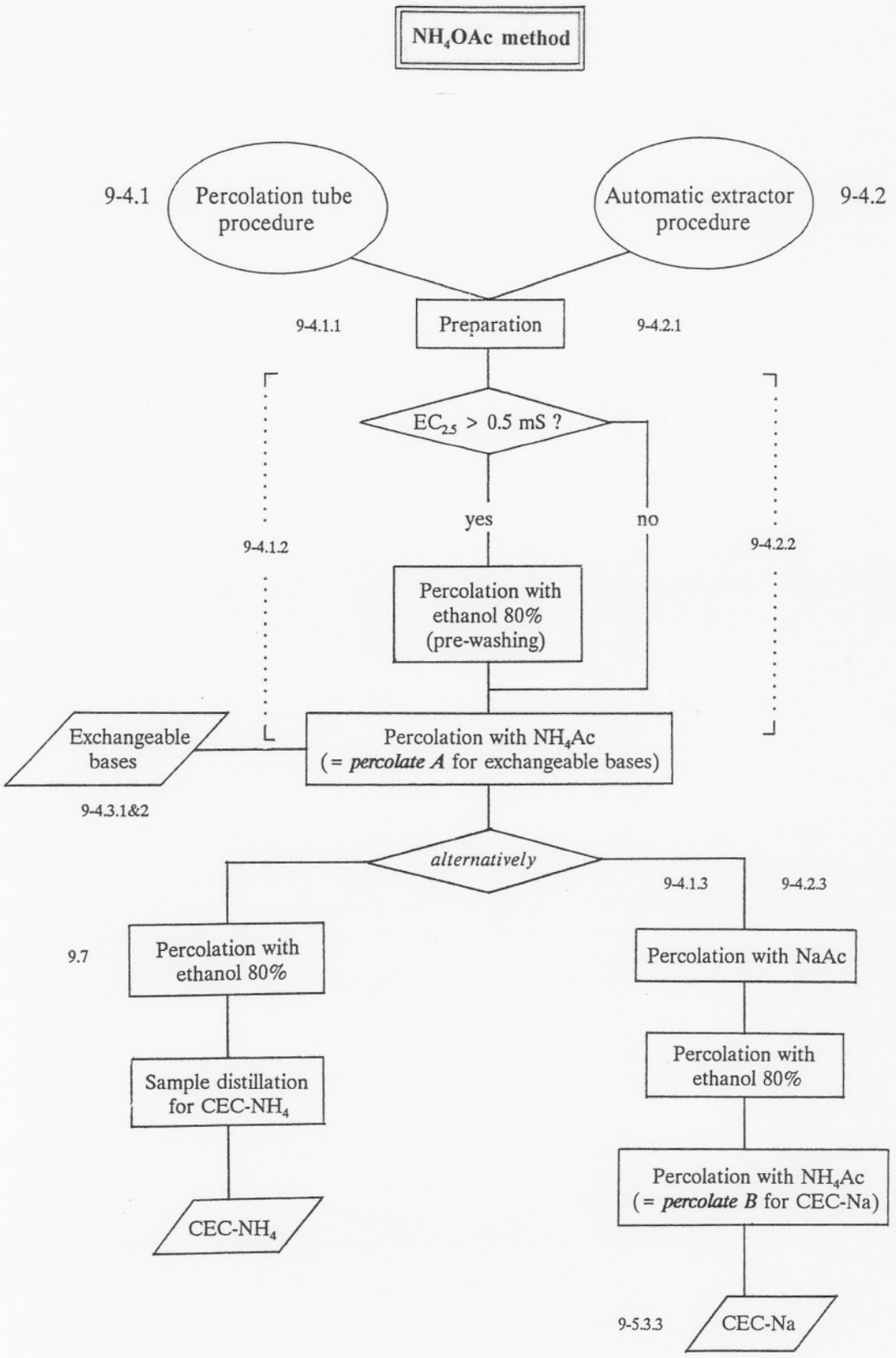

Diagram 9-1. Flow diagram of ammonium acetate method for exchangeable bases and CEC.

9-4 PERCOLATION

Two alternative techniques are described successively:

9-4.1 the ***percolation tube*** procedure
9-4.2 the ***mechanical extractor*** procedure.

9-4.1 Percolation tube procedure

9-4.1.1 Preparation

1. Install percolation tube in vertical position in a stand or rack.
2. Close the bottom of the tube with some cotton wool, compress with a plunger. Add two tea-spoons of sea-sand (approx. 10 g, giving a layer of about 1 cm thick).
3. Weigh 5 g of sample (accuracy 0.01 g) into a porcelain dish, add approx. 25 g sea-sand and mix well with a spatula.
4. Transfer quantitatively to the percolation tube and level the mixture with a long spatula or rod.
5. Add two tea-spoons of sea-sand to make an approx. 1 cm cover on the sample (to avoid splashing and compaction of the sample). Include two blanks (approx. 45 g sea-sand on cotton wool, no soil) and a control sample.

The set-up is schematically drawn in Figure 9-1.

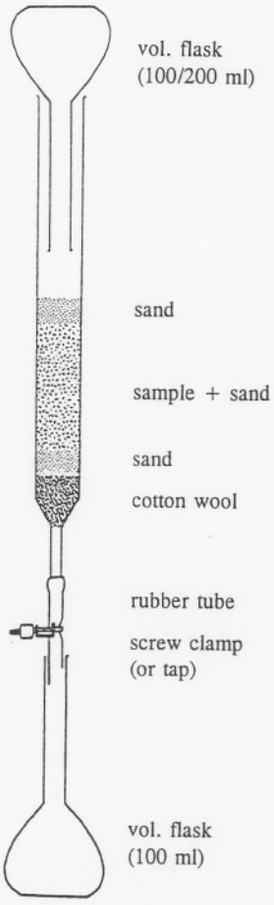

Fig. 9-1. Percolation assembly

9-4.1.2 Exchangeable bases

The presence of soluble salts may give an unacceptable overestimate of the "exchangeable bases". Therefore, in the procedure, a distinction can be made on basis of the presence or absence of soluble salts. Usually the conductivity of the pH-H_2O suspensions (Chapter 4) is used to test this:

a. $EC_{2.5} \geq 0.5$ mS: soluble salts need to be washed out first
b. $EC_{2.5} < 0.5$ mS: soluble salts negligible, no pre-washing needed.

Warning: Washing out the soluble salts will change the so-called *Reduced Ratio* of the soil solution (~ *Sodium Adsorption Ratio, SAR;* see Section 13-5.5.3, p. 13-6). Consequently, the composition of the exchange complex will be changed (upon dilution the proportion of monovalent cations will be reduced) which leads to erroneous results. In cases where these errors are suspected to be unacceptably high, the determination of exchangeable bases should be regarded as impossible and procedure 9-4.1.2 is skipped.
Note: When soluble salts are present an estimate of the adsorbed Na can be obtained from the SAR value of the saturation extract or other extracts (see 13-5.5.4, p. 13-6).

a. If $EC_{2.5} \geq 0.5$ mS (pre-washing)

1. Place 150 ml beaker under outlet of percolation tube and open outlet.
2. From a 100 ml volumetric flask, filled approx. to the mark with ethanol 80%, add about 25 ml to the tube.
3. When the first drops come from the outlet, close this. (The outlet was open to facilitate air expulsion from the sample.)
4. Check tube on entrapped air-bubbles and, if necessary, try to remove these by light tapping against the tube. Should this fail, then carefully disturb the soil/sand mixture with an extended mounting needle. Allow to stand for 20 minutes.
5. Place volumetric flask, with the remainder of the ethanol, upside down in the percolation tube.
   Note: When using a relatively short percolation tube such as a syringe, the flask has to be supported above this tube by a stand or rack. Adjust distance between sample and flask-mouth to approx. 5 cm.
6. Open and adjust outlet to percolate the 100 ml in 2 hours (approx. 20 drops/min.).
7. Discard percolate and place a 100 ml volumetric flask under outlet.

8. From a 100 ml volumetric flask filled with NH_4OAc 1 *M* almost to the mark add about 25 ml to the tube and then place the flask upside down in the tube.
9. Adjust outlet so that the 100 ml percolates in 4 hours (approx. 10 drops/min.).

   Note: this tube and sample can subsequently be used for CEC determination (see 9-4.1.3).

10. Make collecting volumetric flasks to volume with NH_4OAc 1 *M,* homogenize (= ***percolate A***).
11. Measure Ca, Mg, K, and Na in this percolate (see 9-5.3.1 and 9-5.3.2).

b. If $EC_{2.5}$ <0.5 mS (no pre-washing)

1. Place 100 ml volumetric flask under outlet of percolation tube and open outlet.
2. From a 100 ml volumetric flask filled almost to the mark with NH_4OAc 1 *M*, add about 25 ml to the tube.
3. When the first drops come from the outlet, close this. (The outlet was open to facilitate air expulsion from the sample.)
4. Check tube on entrapped air bubbles and, if necessary, try to remove these by light tapping against the tube. Should this fail, then carefully disturb the soil/sand mixture with an extended mounting needle. Allow to stand for 20 minutes.
5. Place volumetric flask with the remainder of the NH_4OAc solution upside down on the percolation tube and allow to stand for 20 minutes.

   Note: When using a relatively short percolation tube such as a syringe, the flask has to be supported above this tube by a stand or rack. Adjust distance between sample and flask-mouth to approx. 5 cm.
6. Open and adjust outlet to percolate the 100 ml in 4 hours (approx. 10 drops/min.).

   Note: This tube and sample are subsequently used for CEC determination (see 9-4.1.3).

7. Make collecting volumetric flask to volume with NH_4OAc 1 *M,* homogenize (= ***percolate A***)
8. Measure Ca, Mg, K and Na in this percolate (see 9-5.3.1 and 9-5.3.2).

9-4.1.3 Cation exchange capacity (CEC)

Generally, this determination is done immediately following the determination of exchangeable bases using the same sample and tube. If only the CEC is determined (without the bases), procedure 9-4.1.2 can be skipped. After preparation (9-4.1.1) the first step will then be Step 2 below.

1. After percolation with NH_4OAc (Steps *a.*9 or *b.*6, previous section) place a 250 ml beaker under the tube.
2. From a 200 ml volumetric flask filled almost to the mark with NaOAc/NaCl 0.9/0.1 *M* add about 25 ml to the tube and then place the flask upside down in tube.

   Note: When exchangeable bases are not determined, read Steps a.4 and a.5 or b.4 and b.5 of the previous section (9-4.1.2) for tips on proper percolation.
3. Adjust outlet so that the 200 ml percolates in 4 hours (approx. 20 drops/min.).
4. Discard percolate and replace beakers under tubes.
5. Rinse wall of tube with about 15 ml ethanol 80%.
6. From a 100 ml volumetric flask filled approx. to the mark with ethanol 80% add about 25 ml to the tube and then place the flask upside down in tube.
7. Adjust outlet to percolate the 100 ml in 2 hours (approx. 20 drops/min.)
8. Rinse the wall of the tube once more with about 10 ml ethanol 96%, collect 3 to 4 ml of the last part of this percolate and test for chloride with a drop of 1 *M* $AgNO_3$ solution.
9. If turbidity develops repeat Step 8, if no turbidity develops proceed with Step 10.
10. After dripping from the outlet has ceased, also rinse outlet and then place 100 ml volumetric flask under outlet.
11. From a 100 ml volumetric flask filled with NH_4OAc 1 *M* solution almost to the mark add about 25 ml to the tube, remove entrapped air-bubbles, and then place flask upside down in tube. Adjust outlet so that the 100 ml percolates in 4 hours (approx. 10 drops/min.).
12. Fill up collecting volumetric flask to the mark with NH_4OAc 1 *M,* homogenize (= ***percolate B***).
13. Measure Na in this percolate (see 9-5).

Remark: Any anomaly observed in the percolates such as strong coloration (dissolution of humus) or turbidity (colloidal particles) should be recorded. Such anomalies, particularly the latter, may cause erroneous results. In some cases filtering or even (super-speed) centrifuging may be necessary to obtain a clear solution.

9-4.2 Mechanical extractor procedure

9-4.2.1 Preparation

1. "Close" the bottom of the sample tube with approx. 1 g of filter pulp. Compress with a plunger.
2. Weigh 2.5 g fine earth (accuracy 0.01 g) into a porcelain dish, add approx. 5 g sea-sand and mix well with a spatula.
   Note: In case of very clayey samples or samples with swelling clays (smectites), addition of 10 g of sea-sand instead of 5 g is recommended (include a corresponding blank!).
3. Transfer quantitatively to sample tube and place tube in upper disc of extractor. If necessary, level sample to even thickness with a spatula. Include a control sample and two blanks.
4. Connect sample tube with collecting syringe the plunger of which is inserted in slot of stationary disc of extractor.

The machine (with 24 places) is shown in Figure 9-2.

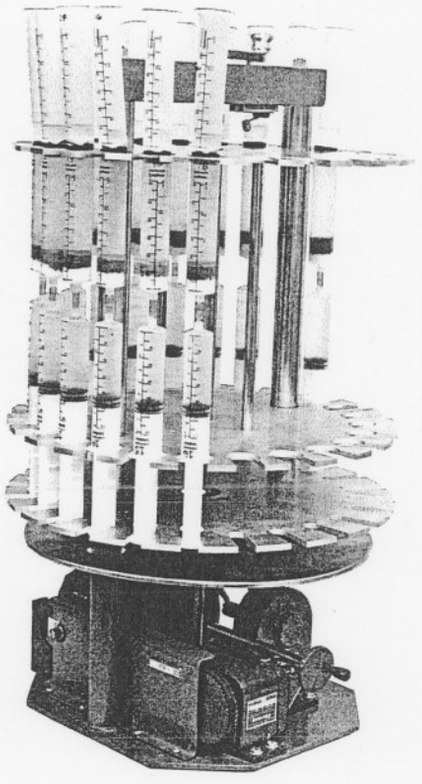

Fig. 9-2. Mechanical extractor.

9-4.2.2 Exchangeable bases

The presence of soluble salts may give an unacceptable overestimate of the "exchangeable bases". Therefore, in the procedure, a distinction can be made on basis of the presence or absence of soluble salts. Usually the conductivity of the pH-H_2O suspensions (Chapter 4) is used to test this:

a. $EC_{2.5} \geq 0.5$ mS: soluble salts need to be washed out first
b. $EC_{2.5} < 0.5$ mS: soluble salts negligible, no pre-washing needed.

Warning: Washing out the soluble salts will change the so-called *Reduced Ratio* of the soil solution (~ *Sodium Adsorption Ratio, SAR;* see Section 13-5.5.3, p. 13-6).
Consequently, the composition of the exchange complex will be changed (upon dilution the proportion of monovalent cations will be reduced) which leads to erroneous results. In cases where these errors are suspected to be unacceptably high, the determination of exchangeable bases should be regarded as impossible and procedure 9-4.2.2 is skipped.
Note: When soluble salts are present an estimate of the adsorbed Na can be obtained from the SAR value of the saturation extract or other extracts (see 13-5.5.4, p. 13-6).

a. If $EC_{2.5} \geq 0.5$ mS (pre-washing)

1. Rinse wall of sample tube with some ethanol 80% from wash bottle.
2. Carefully fill sample tube to the 25 ml mark with ethanol 80% and allow to stand for 20 minutes.
3. Check tube on entrapped air-bubbles and, if necessary, try to remove these by light tapping against the tube. Should this fail, then carefully disturb soil/sand mixture with an extended mounting needle.
4. If necessary, fill to 25 ml mark again and place reservoir tube on top of sample tube. Add about 40 ml ethanol 80% to reservoir tube, start extractor and complete percolation in 2 hours.
5. Remove both reservoir tube and collecting syringe. Discard percolate and replace collecting syringe by a clean one. Proceed with Step *b*.2 (next section).

b. If $EC_{2.5} < 0.5$ mS (no pre-washing)

1. Rinse wall of sample tube with some NH_4OAc 1 *M* from wash bottle.
2. Carefully fill sample tube to the 25 ml mark with NH_4OAc 1 *M*. Allow to stand for 20 minutes.
   Note: If pre-washed, omit standing for 20 minutes.
3. Check tube on entrapped air-bubbles and, if necessary, try to remove these by light tapping against the tube. Should this fail, then carefully disturb soil/sand mixture with an extended mounting needle.

4. If necessary, fill to 25 ml mark again and place reservoir tube on top of sample tube. Add about 40 ml NH_4OAc 1 *M* to reservoir tube, start extractor and complete percolation in 8 hours.
5. Disconnect collecting syringe, transfer contents quantitatively to 100 ml volumetric flask and make to volume with NH_4OAc 1 *M* solution (= ***percolate A***).
6. Measure Ca, Mg, K, and Na in this extract (see 9-5.3.1 and 9-5.3.2).
7. If CEC determination is to follow, remove reservoir tube, reset extractor in starting position and replace collecting syringe.

9-4.2.3 Cation exchange capacity (CEC)

Generally, this determination is done immediately following the determination of exchangeable bases using the same sample and tube. If only the CEC is determined (without the bases), procedure 9-4.2.2 can be skipped.

Note: For the alternative CEC measurement by ammonium distillation see Section 9-7.

1. Rinse wall of sample tube with some NaOAc/NaCl 0.9/0.1 *M* from wash bottle and carefully fill to 25 ml mark.
2. Check tube on entrapped air-bubbles and, if necessary, try to remove these by light tapping against the tube. Should this fail, then carefully disturb soil/sand mixture with an extended mounting needle.
3. Place clean reservoir tube on sample tube and add about 40 ml NaOAc/NaCl.
4. Start extractor and percolate in 4 hours. Discard percolate.
5. Remove reservoir tube, reset extractor in starting position and replace collecting syringe.
6. Rinse wall and outlet of sample tube with ethanol 80% and carefully fill to 25 ml mark.
7. Place clean reservoir tube and add about 40 ml ethanol 80%.
8. Start extractor and percolate in 2 hours. Discard percolate.
9. Remove reservoir tube, reset extractor in starting position and replace collecting syringe.
10. Rinse wall of sample tube with about 10 ml ethanol 96% and percolate this in ½ hour (timer position: 2 hrs.) Discard percolate.
11. Repeat Step 9 but before discarding percolate test this for chloride with a drop of $AgNO_3$ 1 *M*. If no turbidity develops proceed with Step 11. If turbidity develops repeat Step 10. Remove collecting syringe from those samples that do not need extra washing.
12. Reset extractor in starting position and place clean collecting syringe.
13. Carefully add NH_4OAc 1 *M* solution to the 25 ml mark of sample tube.
14. Place reservoir tube and add about 40 ml NH_4OAc 1 *M*.
15. Start the extractor and percolate in 8 hours.
16. Disconnect collecting syringe and transfer contents quantitatively to 100 ml volumetric flask and make to volume with NH_4OAc 1 *M* solution, homogenize (= ***percolate B***).
17. Measure Na in this percolate (see 9-5).

Remark: Any anomaly observed in the percolates such as strong coloration (dissolution of humus) or turbidity (colloidal particles) should be recorded. Such anomalies, particularly the latter, may cause erroneous results. In some cases filtering or even (super-speed) centrifuging may be necessary to obtain a clear solution.

9-5 MEASUREMENTS

9-5.1 Principle

Exchangeable Ca and Mg are measured by flame atomic absorption spectrophotometry (AAS) and exchangeable K and Na by flame emission spectrophotometry (FES) in ***percolate A***. The CEC is measured through Na by FES in ***percolate B***. For Ca and Mg measurement La (5000 mg/l or 0.5%) is introduced to prevent formation of refractory compounds of Ca and Mg in the flame. For Na and K measurement Cs (1000 mg/l or 0.1%) is introduced to overcome ionization interference.

9-5.2 Reagents

Standard solutions 1000 mg/l Ca, Mg, K, Na. Dilute standard analytical concentrate ampoules according to instruction.

Nitric acid, 6 M. Add 380 ml conc. HNO_3 (70%) to about 500 ml water and make to 1 l with water.

Lanthanum suppressant solution for Ca and Mg, 1% La. Dissolve 35.2 g La_2O_3 in 160 ml HNO_3 6 *M* and dilute to 3 l with water (excess acid: 0.1 *M*).
Ditto, 0.55% La (see Remark after 9-5.3.3). Dilute 550 ml of the 1% La suppressant solution to 1 l with water.
Cesium suppressant solution for K and Na, 2% Cs. Dissolve 25 g CsCl in water and dilute with water to 1 l.
Ditto, 0.2% Cs. Dilute 200 ml of the above 2% Cs suppressant solution to 2 l with water.
Ditto, 0.11% Cs. Dilute 110 ml of the 2% Cs suppressant solution to 2 l with water.

9-5.3 Procedure

9-5.3.1 Exchangeable Ca and Mg

Standard series

1. Dilute the 1000 mg/l Ca standard solution to 250 mg/l: pipette 50 ml into a 200 ml volumetric flask, make to volume with water.
2. Dilute the 1000 mg/l Mg standard solution to 25 mg/l: pipette 25 ml into a 1 l volumetric flask, make to volume with water.
3. Of the 250 mg/l Ca solution and the 25 mg/l Mg solution pipette a series of 0-5-10-15-20-25 ml into 250 ml volumetric flasks respectively.
4. To each flask add 25 ml NH_4OAc 1 *M* solution and 125 ml 1% La solution. Make to volume with water. The standard series are then: 0-5-10-15-20-25 mg/l Ca and 0-0.5-1.0-1.5-2.0-2.5 mg/l Mg.

Measurement

Pipette 1 ml of ***percolate A*** (see 9-4.2.2) and 9 ml of the 0.55% La suppressant solution into a test tube, homogenize and measure Ca and Mg in this solution by AAS at wavelengths of 422.7 and 285.2 nm respectively.

9-5.3.2 Exchangeable K and Na

Standard series

1. Dilute both the 1000 mg/l K and Na standard solutions to 100 mg/l: pipette 25 ml of each into one 250 ml volumetric flask and make to volume with water.
2. Of this mixed 100 mg/l standard solution pipette 0-5-10-15-20 ml into 200 ml volumetric flasks respectively.
3. To each flask add 100 ml NH_4OAc 1 *M* solution and 10 ml 2% Cs suppressant solution. Make to volume with water. The standard series are then 0-2.5-5-7.5-10 mg/l for both K and Na.

Measurement

Pipette 2 ml of ***percolate A*** (see 9-4.2.2) and 2 ml of the 0.2% Cs suppressant solution into a short test tube, homogenize and measure K and Na by FES at wavelengths of 766.5 and 589.0 nm respectively.

9-5.3.3 CEC-Na

Standard series

1. Dilute the 1000 mg/l Na solution to 250 mg/l: pipette 50 ml into a 200 ml volumetric flask and make up to volume with water.
2. Of this 250 mg/l Na solution pipette a series of 0-5-10-15-20-25 ml into 250 ml volumetric flasks respectively.
3. To each flask add 25 ml NH_4OAc 1 *M* solution and 12.5 ml 2% Cs suppressant solution. Make to volume with water. The standard series is then 0-5-10-15-20-25 mg/l Na.

Measurement

Pipette 1 ml of ***percolate B*** (see 9-4.2.3) and 9 ml of the 0.11% Cs suppressant solution into a test tube, homogenize and measure Na by FES at a wavelength of 589.0 nm.

Remark: The use of suppressant solutions with different concentrations is preferred to using one suppressant solution throughout (in varying quantities) as in the latter case always an additional amount of water needs to be added to arrive at the desired dilution of the percolate.

9-6 CALCULATIONS

9-6.1 Exchangeable bases

$$\text{Exch. Ca } (\text{cmol}_c/\text{kg soil}) = \frac{(a-b)\times 10\times 100\times \text{mcf}}{10\times 20.04\times s}$$

$$\text{Exch. Mg } (\text{cmol}_c/\text{kg soil}) = \frac{(a-b)\times 10\times 100\times \text{mcf}}{10\times 12.15\times s}$$

$$\text{Exch. K } (\text{cmol}_c/\text{kg soil}) = \frac{(a-b)\times 2\times 100\times \text{mcf}}{10\times 39.10\times s}$$

$$\text{Exch. Na } (\text{cmol}_c/\text{kg soil}) = \frac{(a-b)\times 2\times 100\times \text{mcf}}{10\times 23.00\times s}$$

$$\text{Base saturation } (\%) = \frac{\text{Exch. (Ca+Mg+K+Na)}}{\text{CEC}}\times 100$$

where
a = mg/l Ca, Mg, K or Na in the diluted sample percolate ***A*** (dilution 10× and 2× respectively)
b = ditto in the diluted blank percolate ***A*** (mean of two)
s = air-dry sample weight in gram
mcf = moisture correction factor

9-6.2 CEC

$$\text{CEC } (\text{cmol}_c/\text{kg soil}) = \frac{(a-b)\times 10\times 100\times \text{mcf}}{10\times 23\times s}$$

where
a = mg/l Na in 10x diluted sample percolate ***B***
b = mg/l Na in 10x diluted blank percolate ***B*** (mean of two)
s = air-dry sample weight in gram
mcf = moisture correction factor

9-6.3 Derived parameters

1. The "Effective CEC" or *ECEC* is obtained by:

Effective CEC (ECEC) = exchangeable bases + exchangeable acidity (see Chapter 11)

2. The *CEC of the clay* is obtained by:

$$\text{CEC}_{\text{clay}} \ (\text{cmol}_c/\text{kg clay}) = \text{CEC}_{\text{soil}} \times \frac{100}{\%\text{clay}}$$

where *%clay* is the clay content of the soil.
Note: This calculation is likewise applicable to the ECEC.

This calculation implies neglecting two errors both of which may be substantial:

a. Contribution to CEC by Organic Matter

The given calculation of the CEC_{clay} includes the contribution of organic matter to the CEC_{soil} and may, therefore, be (highly) inaccurate. A correction for this can be made by first subtracting this contribution from the CEC_{soil} yielding the contribution of the mineral part (and which can usually almost exclusively be ascribed to the clay fraction):

$$CEC_{soil\ (clay\ part)} = CEC_{soil} - CEC_{soil\ (organic\ part)}$$

A reasonable estimate for the (average*) organic matter contribution is:

$$CEC_{soil\ (organic\ part)} = 3.5^{*} \times \%\,Carbon$$

The corrected CEC of the clay is then obtained by:

$$CEC_{clay\ (corr.)}\ (cmol_c/kg\ clay) = CEC_{soil\ (clay\ part)} \times \frac{100}{\%\ clay}$$

b. Weight-basis error

The % clay used in the above calculations is based on the fine earth minus organic matter and optionally removed components (carbonates, free iron oxides; see p. 3-5). If the contents of the removed components are substantial the clay content can be corrected as follows:

$$\%\,clay_{corr.} = \%\,clay \times \frac{100 - (\%\,O.M. + \%\,carbonate + \%\,free\ iron)}{100}$$

3. The "exchangeable sodium percentage" *(ESP)* is calculated by:

$$\text{Exchangeable sodium percentage (ESP in \%)} = \frac{\text{Exch. Na}}{\text{CEC}} \times 100$$

Remarks

1. Application of the described method to calcareous (and gypsiferous) soils leads to erroneous results (as does application of many other methods). Dissolution of carbonates interferes particularly with the determination of exchangeable Ca (over-estimation) but to only a limited extent with that of the CEC. Results can be improved to some extent by raising the pH of both acetate buffer solutions to 8.2 where the solubility of calcium (and magnesium) carbonate is reduced. This can also be achieved by using acetate buffer(pH7)/ethanol mixtures (e.g. 1:1). Since in neither case the solubility is reduced to zero the results remain unreliable.
   A better alternative would seem to be the silver thiourea method (see Chapter 10).
2. The base saturation of calcareous and gypsiferous soils may safely be considered to be 100%.

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* Depending on the character of the organic matter, the CEC may range from 150 to over 750 $cmol_c/kg$ carbon. Unless a more accurate value is known in a particular case, the value of 350 $cmol_c/kg$ (~ 3.5 $cmol_c$ per % C) seems to be a workable approximation (Klamt & Sombroek, 1988).

9-7 CEC BY AMMONIUM DISTILLATION

9-7.1 Principle

After percolation with ammonium acetate to remove exchangeable bases, the excess salt is washed out with ethanol 80%, the whole sample is distilled and the evolved ammonia determined.

9-7.2 Introductory remarks

Experiments in the ISRIC laboratory showed that the alternative determination of the CEC by direct distillation was as robust as the determination by Na saturation described above and somewhat quicker to perform. The alternative is described below for the **mechanical extractor procedure** only (9-4.2.3) but can similarly be applied in the percolation tube variant (9-4.1.3).

Generally, the CEC determination is done immediately following the determination of exchangeable bases using the same sample and tube (see 9-4.2.2). However, to facilitate the $AgNO_3$ test to check if the sample is washed free of salt, here the NH_4OAc saturating solution should contain chloride.
Although the determination of bases in this case is virtually identical to that described in Section 9-4.2, to avoid confusion it is described here in full rather than referring to that section.

9-7.3 Percolation

9-7.3.1 Reagents

Ethanol 96%.
Ethanol 80%. Make 4.17 l ethanol 96% to 5 l with water.
Ammonium hydroxide solution, 1 M. Add 35.5 ml conc. ammonia to about 400 ml water in a graduated 500 ml beaker and make to 500 ml with water.
Acetic acid 10%. Add 50 ml glacial acetic acid to about 400 ml water in a graduated 500 ml beaker and make to 500 ml with water.
Ammonium acetate 0.9 M / ammonium chloride 0.1 M solution. Dissolve 347 g NH_4OAc and 27 g NH_4Cl in water in a 5 l beaker and make to 5 l. Adjust the pH to 7.0 with ammonia 1 M or acetic acid 10%.
Silver nitrate 1 M (test) solution. Dissolve 8.5 g $AgNO_3$ in 50 ml water and transfer to dropping bottle.

9-7.3.2 Preparation

1. "Close" the bottom of the sample tube with approx. 1 g of filter pulp. Compress with a plunger.
2. Weigh 2.5 g fine earth (accuracy 0.01 g) into a porcelain dish, add approx. 5 g sea-sand and mix well with a spatula. Include two blanks and a control sample.
   Note: In case of very clayey samples or samples with swelling clays (smectites), addition of 10 g of sea-sand instead of 5 g is recommended (include a corresponding blank!).
3. Transfer quantitatively to sample tube and place tube in upper disc of extractor. If necessary, level sample to even thickness with a spatula. Include a control sample and two blanks.
3. Connect sample tube with collecting syringe the plunger of which is inserted in slot of stationary disc of extractor.

9-7.3.3 Exchangeable bases

The presence of soluble salts may give an unacceptable overestimate of the "exchangeable bases". Therefore, in the procedure, a distinction can be made on basis of the presence or absence of soluble salts. Usually the conductivity of the pH-H_2O suspensions (Chapter 4) is used to test this:

a. $EC_{2.5} \geq$ 0.5 mS: soluble salts need to be washed out first
b. $EC_{2.5} <$ 0.5 mS: soluble salts negligible, no pre-washing needed.

Warning: Washing out the soluble salts will change the so-called *Reduced Ratio* of the soil solution (~ *Sodium Adsorption Ratio, SAR;* see Section 13-5.5.3, p. 13-6). Consequently, the composition of the exchange complex will be changed (upon dilution the proportion of monovalent cations will be reduced) which leads to erroneous results. In cases where these errors are suspected to be unacceptably high, the determination of exchangeable bases should be regarded as impossible and procedure 9-4.2.2 is skipped.
Note: When soluble salts are present an estimate of the adsorbed Na can be obtained from the SAR value of the saturation extract or other extracts (see 13-5.5.4, p. 13-6).

a. If $EC_{2.5} \geq 0.5$ mS (pre-washing)

1. Rinse wall of sample tube with some ethanol 80% from wash bottle.
2. Carefully fill sample tube to the 25 ml mark with ethanol 80% and allow to stand for 20 minutes.
3. Check tube on entrapped air-bubbles and, if necessary, try to remove these by light tapping against the tube. Should this fail, then carefully disturb soil/sand mixture with an extended mounting needle.
4. If necessary, fill to 25 ml mark again and place reservoir tube on top of sample tube. Add about 40 ml ethanol 80% to reservoir tube, start extractor and complete percolation in 2 hours.
5. Remove both reservoir tube and collecting syringe. Discard percolate and replace collecting syringe by a clean one. Proceed with Step *b*.2 (next section).

***b*. If $EC_{2.5} < 0.5$ mS (no pre-washing)**

1. Rinse wall of sample tube with some NH_4OAc/NH_4Cl 0.9/0.1 *M* from wash bottle.
2. Carefully fill sample tube to the 25 ml mark with NH_4OAc/NH_4Cl solution. Allow to stand for 20 minutes. *Note:* If pre-washed, omit standing for 20 minutes.
3. Check tube on entrapped air-bubbles and, if necessary, try to remove these by light tapping against the tube. Should this fail, then carefully disturb soil/sand mixture with an extended mounting needle.
4. If necessary, fill to 25 ml mark again and place reservoir tube on top of sample tube. Add about 40 ml NH_4OAc/NH_4Cl to reservoir tube, start extractor and complete percolation in 8 hours.
5. Disconnect collecting syringe, transfer contents quantitatively to 100 ml volumetric flask and make to volume with NH_4OAc 1 *M* solution (= ***percolate A***).
6. Measure Ca, Mg, K, and Na in this extract (see 9-7.3.4.3 *a* and *b*).
7. If CEC determination is to follow, remove reservoir tube and reset extractor in starting position.

Remark: Any anomaly observed in the percolates such as strong coloration (dissolution of humus) or turbidity (colloidal particles) should be recorded. Such anomalies, particularly the latter, may cause erroneous results. In some cases filtering or even (super-speed) centrifuging may be necessary to obtain a clear solution.

9-7.3.4 Measurement of bases

9-7.3.4.1 Principle

Exchangeable Ca and Mg are measured by flame atomic absorption spectrophotometry (AAS) and exchangeable K and Na by flame emission spectrophotometry (FES) in ***percolate A***. For Ca and Mg measurement La (5000 mg/l or 0.5%) is introduced to prevent formation of refractory compounds of Ca and Mg in the flame. For Na and K measurement Cs (1000 mg/l or 0.1%) is introduced to overcome ionization interference.

9-7.3.4.2 Reagents

Standard solutions 1000 mg/l Ca, Mg, K, Na. Dilute standard analytical concentrate ampoules according to instruction.

Nitric acid, 6 M. Add 380 ml conc. HNO_3 (70%) to about 500 ml water and make to 1 l with water.

Lanthanum suppressant solution for Ca and Mg, 1% La. Dissolve 35.2 g La_2O_3 in 160 ml HNO_3 6 *M* and dilute to 3 l with water (excess acid: 0.1 *M*).

Ditto, 0.55% La (see Remark after 9-5.3.3). Dilute 550 ml of the 1% La suppressant solution to 1 l with water.

Cesium suppressant solution for K and Na, 2% Cs. Dissolve 25 g CsCl in water and dilute with water to 1 l.

Ditto, 0.2% Cs. Dilute 200 ml of the above 2% Cs suppressant solution to 2 l with water.

Ditto, 0.11% Cs. Dilute 110 ml of the 2% Cs suppressant solution to 2 l with water.

9-7.3.4.3 Procedure

a. Exchangeable Ca and Mg

Standard series

1. Dilute the 1000 mg/l Ca standard solution to 250 mg/l: pipette 50 ml into a 200 ml volumetric flask, make to volume with water.
2. Dilute the 1000 mg/l Mg standard solution to 25 mg/l: pipette 25 ml into a 1 l volumetric flask, make to volume with water.
3. Of the 250 mg/l Ca solution and the 25 mg/l Mg solution pipette a series of 0-5-10-15-20-25 ml into 250 ml volumetric flasks respectively.
4. To each flask add 25 ml NH_4OAc/NH_4Cl solution and 125 ml 1% La solution. Make to volume with water. The standard series are then: 0-5-10-15-20-25 mg/l Ca and 0-0.5-1.0-1.5-2.0-2.5 mg/l Mg.

Measurement

Pipette 1 ml of ***percolate A*** (see 9-7.3.3) and 9 ml of the 0.55% La suppressant solution into a test tube, homogenize and measure Ca and Mg in this solution by AAS at wavelengths of 422.7 and 285.2 nm respectively.

b. Exchangeable K and Na

Standard series

1. Dilute both the 1000 mg/l K and Na standard solutions to 100 mg/l: pipette 25 ml of each into one 250 ml volumetric flask and make to volume with water.
2. Of this mixed 100 mg/l standard solution pipette 0-5-10-15-20 ml into 200 ml volumetric flasks respectively.
3. To each flask add 100 ml NH_4OAc/NH_4Cl solution and 10 ml 2% Cs suppressant solution. Make to volume with water. The standard series are then 0-2.5-5-7.5-10 mg/l for both K and Na.

Measurement

Pipette 2 ml of ***percolate A*** (see 9-7.3.3) and 2 ml of the 0.2% Cs suppressant solution into a short test tube, homogenize and measure K and Na by FES at wavelengths of 766.5 and 589.0 nm respectively.

c. Calculations

$$\text{Exch. Ca } (\text{cmol}_c/\text{kg soil}) = \frac{(a-b)\times 10\times 100\times \text{mcf}}{10\times 20.04\times s}$$

$$\text{Exch. Mg } (\text{cmol}_c/\text{kg soil}) = \frac{(a-b)\times 10\times 100\times \text{mcf}}{10\times 12.15\times s}$$

$$\text{Exch. K } (\text{cmol}_c/\text{kg soil}) = \frac{(a-b)\times 2\times 100\times \text{mcf}}{10\times 39.10\times s}$$

$$\text{Exch. Na } (\text{cmol}_c/\text{kg soil}) = \frac{(a-b)\times 2\times 100\times \text{mcf}}{10\times 23.00\times s}$$

$$\text{Base saturation } (\%) = \frac{\text{Exch. (Ca + Mg + K + Na)}}{\text{CEC}}\times 100$$

where

a = mg/l Ca, Mg, K or Na in the diluted sample percolate *A* (dilution 10× and 2× respectively)
b = ditto in the diluted blank percolate *A* (mean of two).
s = air-dry sample weight in gram
mcf = moisture correction factor

9-7.3.5 CEC

9-7.3.5.1 Washing procedure

1. Rinse wall of sample tube with some ethanol 80% from wash bottle and fill to 20 ml mark with same.
3. Check tube on entrapped air-bubbles and, if necessary, try to remove these by light tapping against the tube. Should this fail, then carefully disturb soil/sand mixture with an extended mounting needle.
2. Place clean reservoir tube on sample tube and add about 40 ml ethanol 80%.
3. Start extractor and percolate in 2 hours. Discard percolate.
4. Remove reservoir tube, reset extractor in starting position and replace collecting syringe.
5. Rinse wall of sample tube with about 10 ml ethanol 96% and percolate this in ½ hour (timer position: 2 hrs.) Discard percolate.
6. Repeat Step 5 but before discarding percolate test this for chloride with a drop of $AgNO_3$ 1 *M.* If no turbidity develops proceed with Step 7. If turbidity develops repeat Step 6. (Samples that do not need extra washing may be removed from extractor to await Step 7).
7. Transfer sample and filter pulp quantitatively to distillation vessel by blowing through the outlet of the percolation tube with compressed air (or with the mouth using a piece of rubber tubing) and rinse with water from a wash bottle.

9-7.3.5.2 Distillation

a. Apparatus

Steam distillation unit (or other distillation assembly, see Fig. 9-3)

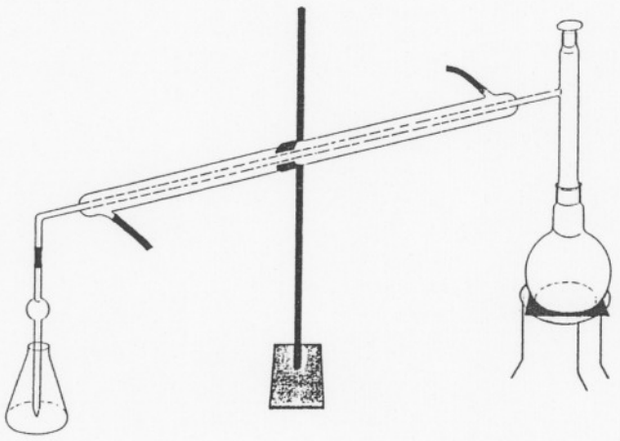

Fig. 9-3. A simple distillation assembly.

b. Reagents

Sodium hydroxide, 1 M. Dissolve 40 g NaOH in water in a graduated 1 l beaker and make to 1 l.
Mixed indicator solution. Dissolve 0.13 g methyl red and 0.20 g bromocresol green in 200 ml ethanol 96%.
Boric acid-indicator solution, 1%. Dissolve 10 g boric acid in water and add 20 ml mixed indicator solution. Make to 1 l with water and mix thoroughly.
Hydrochloric acid, 0.01 M standard. Dilute standard analytical concentrate ampoule according to instruction.

c. Procedure

1. Make volume in distillation vessel to approx. 100 ml with water (or follow instruction of steam distiller).
2. Add 20 ml boric acid-indicator solution to a 250 ml erlenmeyer or beaker and place this on stand under condenser tip (with tip just dipping in the boric acid solution).
3. Add a tea-spoon of solid NaCl and 10 ml NaOH 1 *M* to the distillation vessel, immediately close vessel and distil about 75 ml (taking 7-10 minutes).
   Note: the distillation time and amount of distillate may need to be increased for complete distillation (see Remark).
4. Remove erlenmeyer from distiller, rinse condenser tip and titrate distillate with 0.05 *M* HCl until colour changes from green to pink.
   Note: When using automatic titrator set end-point pH at 4.6.

Remark: The efficiency of the distiller may be insufficient at very high CEC values and should be checked. A "standard" series of 0-50 mg N as NH_4Cl or $(NH_4)_2SO_4$ could be used for this purpose. An efficiency of 20 mg N will be sufficient for CEC values of up 50 $cmol_c$/kg soil.
If using a home-made distillation assembly, its characteristics (volumes, duration of distillation etc.) should be established by trial and error.

d. Calculation

$$\text{CEC } (cmol_c/kg \text{ soil}) = \frac{(a-b) \times M \times 100 \times mcf}{s}$$

where
a = ml HCl required for titration sample
b = ml HCl required for titration blank
s = air-dry sample weight in gram
M = molarity of HCl
mcf = moisture correction factor

REFERENCES

Soil Laboratory Staff, Royal Tropical Institute (1984)
Houba et al. (1988)
Holmgren et al. (1977)
USDA, SCS (1972, 1982)

10. CATION EXCHANGE CAPACITY (CEC) and EXCHANGEABLE BASES

(silver thiourea method)

10-1 PRINCIPLE

This rapid and convenient method is based on the strong affinity of the monovalent silver thiourea complex cation (AgTU) for negatively charged colloid surfaces, mineral and organic alike. This allows a one-step centrifuge extraction with a 0.01 *M* AgTU solution in which complete exchange is achieved. Thus, the supernatant solution contains all exchangeable cations while the decrease in Ag concentration is a measure for the CEC.

10-2 APPARATUS

Atomic absorption spectrophotometer (with Ag hollow cathode lamp)
Reciprocating shaking machine
Centrifuge

10-3 REAGENTS

Silver nitrate solution, 0.04 M. Dissolve 3.4 g $AgNO_3$ in 500 ml of water. Store in the dark.

Thiourea, 0.2 M. Dissolve 15 g of thiourea in one litre of water. ***Warning:*** use gloves and avoid inhalation of thiourea dust (see Remark 1, p. 10-4).

Ammonium acetate solution, 0.4 M. Dissolve 15.5 g NH_4OAc in 400 ml of water, adjust the pH to 7.0 with dilute (0.1 *M*) ammonia or acetic acid and make to 500 ml with water.

Silver thiourea solution, 0.01 M Ag, 0.1 M TU (AgTU extractant).

1. **For CEC at pH of the soil** (see Remark 2): To 1 l thiourea 0.2 *M* solution add 500 ml of water. Homogenize. Then slowly add 500 ml of $AgNO_3$ 0.04 *M* solution under strong stirring. (***Warning:*** do not reverse this order).
2. **For CEC at pH 7**: To 1 l thiourea 0.2 *M* solution slowly add 500 ml $AgNO_3$ 0.04 *M* solution under strong stirring. Then similarly add 500 ml NH_4OAc 0.4 *M* pH 7 solution. (***Warning:*** do not reverse this order.) Readjust the pH to 7.0.

Note 1: During and after preparation of the solutions some turbidity may have formed. The solution should then be filtered through a hard filter (e.g. Whatman 42).

Note 2: These solutions should be stored in the dark.

Nitric acid, 1 M. Add 63 ml conc. HNO_3 (70%) with water to about 900 ml water and make to 1 l with water.

Standard solutions Ca, Mg, K, Na and Ag, all 1000 mg/l. Dilute standard analytical concentrate ampoules according to instruction.

Lanthanum suppressant solution for Ca and Mg, 1% La. Dissolve 58.6 g La_2O_3 in 265 ml HNO_3 6 *M* and dilute with water to 5 l (excess HNO_3: 0.1 *M*).

Ditto, 0.55% La. Dilute 2.75 l of the 1% La suppressant solution to 5 l with water.

Cesium suppressant solution for K and Na, 2% Cs. Dissolve 25 g CsCl in water and dilute with water to 1 l.

Ditto, 0.2% Cs. Add 200 ml HNO_3 1 *M* to 200 ml of the above 2% Cs suppressant solution and dilute to 2 l with water.

10-4 PROCEDURE

1. Crush (not grind) approx. 5 g of fine earth to pass a 0.5 mm sieve.
2. Weigh 1 g of this sample (accuracy 0.005 g) into a 50 ml centrifuge tube (see Remark 3). Include two blanks and a control sample.
3. Pipette 40 ml of the AgTU extractant into the tube and close this with a cap or rubber stopper.
4. Shake for 4 hours in reciprocating shaking machine.
   Note: Take care that the stoppers remain in place. If necessary, use sticky tape.
5. Centrifuge.
6. Measure Ca, Mg, K, Na and Ag in the clear supernatant extract.

10-5 MEASUREMENT

The obtained extract is equivalent to ***percolate A*** of the ammonium acetate method (see Section 9-4) and measurement of the exchangeable bases can be done using the same standard series with the difference that 1 *M* NH_4OAc is substituted by 0.1 *M* thiourea.

10-5.1 Exchangeable Ca and Mg

Standard series

1. Dilute the 1000 mg/l Ca standard solution to 250 mg/l: pipette 50 ml into a 200 ml volumetric flask, make to volume with water.
2. Dilute the 1000 mg/l Mg standard solution to 25 mg/l: pipette 25 ml into a 1 l volumetric flask, make to volume with water.
3. Of the 250 mg/l Ca solution and the 25 mg/l Mg solution pipette a series of 0-5-10-15-20-25 ml into 250 ml volumetric flasks respectively.
4. To each flask add 12.5 ml thiourea 0.2 *M* and 125 ml 1% La suppressant solution. Make to volume with water. The standard series are then: 0-5-10-15-20-25 mg/l Ca and 0-0.5-1.0-1.5-2.0-2.5 mg/l Mg.

Measurement

Pipette 1 ml of the extract and 9 ml of the 0.55% La suppressant solution into a test tube, homogenize and measure Ca and Mg in this solution by AAS at wavelengths of 422.7 and 285.2 nm respectively.

10-5.2 Exchangeable K and Na

Standard series

1. Dilute both the 1000 mg/l K and Na standard solutions to 100 mg/l: pipette 25 ml of each into one 250 ml volumetric flask and make to volume with water.
2. Of this mixed 100 mg/l solution pipette 0-5-10-15-20 ml into 200 ml volumetric flasks respectively.
3. To each flask add 20 ml HNO_3 1 *M*, 50 ml thiourea 0.2 *M* and 10 ml 2% Cs suppressant solution. Make to volume with water. The standard series are then: 0-2.5-5-7.5-10 mg/l for both K and Na.

Measurement

Pipette 2 ml extract and 2 ml 0.2% Cs suppressant solution into a (short) test tube, homogenize and measure K and Na by FES at wavelengths of 766.5 and 589.0 nm respectively.

10-5.3 CEC-Ag

Standard series

1. Dilute the 1000 mg/l Ag standard solution to 250 mg/l: pipette 50 ml into a 200 ml volumetric flask and make to volume with water.
2. Add 2.5 ml thiourea 0.2 *M* solution and 5 ml HNO_3 1 *M* to each of six 250 ml volumetric flasks.
3. Of the 250 mg/l Ag solution pipette 0-5-10-15-20-25 ml into these flasks respectively, while swirling. Make to volume with water and homogenize. The standard series is then 0-5-10-15-20-25 mg/l Ag.

Measurement

Add 5 ml HNO_3 1 *M* to a 100 ml volumetric flask, pipette 2 ml extract into this flask and make to volume with water. Homogenize and measure Ag by AAS at a wavelength of 328.1 nm.

10-6 CALCULATIONS

10-6.1 Exchangeable bases

$$\text{Exch. Ca } (\text{cmol}_c/\text{kg soil}) = \frac{(a-b)\times 10\times 100\times \text{mcf}}{25\times 20.04\times s} = \frac{(a-b)\times 2.00\times \text{mcf}}{s}$$

$$\text{Exch. Mg } (\text{cmol}_c/\text{kg soil}) = \frac{(a-b)\times 10\times 100\times \text{mcf}}{25\times 12.15\times s} = \frac{(a-b)\times 3.29\times \text{mcf}}{s}$$

$$\text{Exch. K } (\text{cmol}_c/\text{kg soil}) = \frac{(a-b)\times 2\times 100\times \text{mcf}}{25\times 39.10\times s} = \frac{(a-b)\times 0.205\times \text{mcf}}{s}$$

$$\text{Exch. Na } (\text{cmol}_c/\text{kg soil}) = \frac{(a-b)\times 2\times 100\times \text{mcf}}{25\times 23.00\times s} = \frac{(a-b)\times 0.348\times \text{mcf}}{s}$$

$$\text{Base saturation } (\%) = \frac{\text{Exch.}(\text{Ca}+\text{Mg}+\text{K}+\text{Na})}{\text{CEC}}\times 100$$

where
a = mg/l Ca, Mg, K or Na in the diluted extract
b = mg/l Ca, Mg, K or Na in the blank extract
s = air-dry sample weight in gram
mcf = moisture correction factor

10-6.2 CEC

$$\text{CEC } (\text{cmol}_c/\text{kg soil}) = \frac{(b-a)\times 50\times 100\times \text{mcf}}{25\times 107.87\times s} = \frac{(b-a)\times 1.85\times \text{mcf}}{s}$$

where
a = mg/l Ag in 50× diluted soil extract
b = mg/l Ag in 50× diluted blank extract
s = air-dry sample weight in gram
mcf = moisture correction factor

Remarks

1. Thiourea is suspected to be toxic and inhalation of the dust and swallowing of solutions should be avoided. While working with solutions, the use of gloves is recommended.
2. The AgTU-CEC at the pH of the soil (unbuffered) may be referred to as "effective CEC" *(ECEC)*.
3. The sample weight of 1 g should be used for CEC values between approximately 5 and 20 $cmol_c$/kg soil. When values outside this range are found the analysis has to be repeated with proportionally more or less sample respectively*. (Often, on basis of organic matter and clay content together with the clay mineralogy a reasonable prediction of the CEC can be made.) At very high CEC values (>40 $cmol_c$/kg soil) more extracting solution should be used, e.g. 0.5 g sample and 80 ml extractant (change the calculation accordingly). The use of sample material <0.25 mm is recommended to avoid sample bias.
4. Solutions of AgTU may "poison" the electrode of the pH meter. Therefore do not expose electrodes unnecessarily long to these solutions. Cleaning can be done by letting the electrode stand in a 0.2 *M* TU solution acidified with a few drops of HNO_3 1 *M*.
5. The use of 0.1 *M* NH_4OAc buffer has a slight influence on the CEC. The selectivity coefficient $AgTU^+/NH_4^+$ is about 500 so that at a molar ratio $AgTU^+/NH_4^+ = 1/10$ in the extracting solution the CEC is suppressed by 2%. If only the CEC is to be determined (and not the exchangeable bases) then a sodium buffer is preferred: the $AgTU^+/Na^+$ selectivity coefficient is about 5000!
6. In principle, the AgTU method can be applied with some confidence to calcareous, gypsiferous and saline soils provided the pH of the soil does not exceed 9 (precipitation of Ag may then occur).

REFERENCES

Chhabra, Pleysier and Cremers (1975)
Houba et al. (1986)
Pleysier and Juo (1980)

* At lower CEC values very little Ag is withdrawn from solution and the procedure becomes too insensitive. At higher values more than half of the Ag originally present is withdrawn whereby the non-proportional adsorption range is entered.

11. SOIL ACIDITY

Two fundamentally different methods for the determination of soil acidity are described:

1. **"Exchangeable acidity"**, the acidity (H + Al) released upon exchange by an unbuffered KCl solution. It may also be designated *actual acidity* and it is used to determine the so-called *effective cation exchange capacity* (ECEC) which is defined as *sum of bases + (H + Al)* (Coleman et al., 1959).
   When the exchangeable acidity is substantial, the Al may be determined separately in the extract as it may be toxic to plants.
   Because the contribution of H^+ is often (but not always!) negligible, some laboratories only determine exchangeable Al. In that case the ECEC is calculated as *(sum of bases + Al).*
2. **"Extractable acidity"**, the acidity extracted by a $BaCl_2$-TEA buffer solution pH 8.2. It may also be designated *potential acidity, maximal acidity* or *titratable acidity* and is sometimes, confusingly, referred to as *exchange acidity.* It is used (in Soil Taxonomy) to calculate the so-called *CEC by sum of cations* which is defined as *sum of bases + extractable acidity.*

11-1 EXCHANGEABLE ACIDITY AND ALUMINIUM

11-1.1 Principle

The sample is percolated with a 1 *M* KCl solution. The acidity brought into solution from various sources in the soil is measured by titration. In addition, one of the sources of acidity, exchanged aluminium, is measured separately.

11-1.2 Apparatus

Burette
Atomic absorption spectrophotometer

11-1.3 Reagents

Potassium chloride solution, 1 M. Dissolve 373 g KCl in water and make to 5 l.
Aluminium standard solution, 1000 mg/l. Dilute standard analytical concentrate ampoule (1 g/l) according to instruction.
Hydrochloric acid, 0.02 M (standard solution). Dilute standard analytical concentrate ampoule of 0.02 *M* HCl according to instruction.
Sodium hydroxide solution, approx. 0.02 M (standardized). Dissolve 1 g of NaOH in water in a 1 l volumetric flask. Cool and make to volume. Standardize this solution by titration against the 0.02 *M* standard HCl solution.
Note: This is an alternative for making this solution with a standard solution concentrate ampoule (which may be used also). Sodium hydroxide standard solutions have a limited life and need to be re-standardized after storage: the effect of a CO_2 trap is limited by (frequent) opening of the bottle.
Phenolphthalein indicator solution, 0.1%. Dissolve 100 mg phenolphthalein in 100 ml ethanol 96%.

11-1.4 Procedure

11-1.4.1 Percolation

1. Transfer 10 g fine earth (accuracy 0.05 g) to a dry filter paper in a funnel placed in a 100 ml volumetric flask. Include two blanks.
2. Add ten portions of 10 ml 1 *M* KCl solution with 15-minute intervals so that the percolation takes about 2½ hours.
3. After the last portion has percolated, remove the funnel and fill the volumetric flask to the mark with 1 *M* KCl solution and homogenize.

11-1.4.2 Determination of exchangeable acidity

1. Pipette a 25 ml aliquot of percolate into a 250 ml erlenmeyer flask and add 3-5 drops of phenolphthalein solution.
2. Titrate with 0.025 *M* NaOH until the colour turns just permanently pink (in practice: wait for 1 minute).
   Note 1: Weakening of the pink colour can be caused by the hydroxy-Al precipitate. This can be remedied by adding another drop of phenolphthalein.
   Note 2: When using automatic titrator: set end-point pH at 7.60.

Calculation

$$\text{Exchangeable acidity } (\text{cmol}_c/\text{kg soil}) = \frac{(a-b) \times M \times 4 \times 100 \times mcf}{s}$$

where
a = ml NaOH needed for percolate
b = ml NaOH needed for blank
M = molarity of NaOH solution
s = air-dry sample weight in gram
4 = aliquot factor
mcf = moisture correction factor

The "effective CEC" can then be calculated:

$$\text{Effective CEC } (\textit{ECEC} \text{ in } \text{cmol}_c/\text{kg soil}) = \text{Exchangeable (Na+K+Ca+Mg+acidity)}$$

Note: For determination of exchangeable bases, see Chapter 9 or 10.

11-1.4.3 Determination of exchangeable aluminium

Al is measured by AAS in a 1:1 diluted percolate using a 0-50 mg/l Al standard series.

1. Dilute the 1000 mg/l Al solution to 500 mg/l: pipette 100 ml into a 200 ml volumetric flask and make to volume with water.
2. Of this 500 mg/l Al solution pipette 0-5-10-15-20-25 ml into 250 ml volumetric flasks respectively.
3. To each of these flask add 125 ml 1 *M* KCl solution and make up to volume with water and homogenize. The standard series is then 0-10-20-30-40-50 mg/l Al.
4. Pipette equal volumes (e.g. 5 ml) of extract and water into a test tube, homogenize and measure Al by AAS at 309.3 nm using a nitrous oxide/acetylene flame.

Remark: If colorimetric determination of Al is preferred this can be done according to one of the procedures described by Barnhisel and Bertsch in Page (1982) p. 288.

Calculation

$$\text{Exchangeable Al } (\text{cmol}_c/\text{kg soil}) = \frac{(a-b) \times 2 \times 100 \times mcf}{10 \times 9 \times s} = \frac{(a-b) \times 2.22 \times mcf}{s}$$

where
a = mg/l Al in 1:1 diluted soil extract
b = mg/l Al in 1:1 diluted blank
2 = dilution factor
9 = equivalent weight of Al
s = air-dry sample weight in gram
mcf = moisture correction factor

Aluminium saturation

The "aluminium saturation" is the exchangeable aluminium expressed as a percentage of the CEC or ECEC:

$$\text{Exch. Al (\%)} = \frac{\text{Exch. Al}}{\text{CEC or ECEC}} \times 100$$

where
Exch. Al (in fraction) = exchangeable Al in $cmol_c/kg$ (calculated in this Section)
CEC and *ECEC* = cation exchange capacity and effective cation exchange capacity (in $cmol_c/kg$) as determined in Chapters 9 or 10.

Reference:

Thomas *in*: Page (1982) p. 159

11-2 EXTRACTABLE ACIDITY

11-2.1 Principle

The sample is shaken with a $BaCl_2$-TEA buffer solution pH 8.2. After centrifugation, an aliquot of the supernatant solution is titrated with acid to measure the residual base.

11-2.2 Apparatus

Burette
Polythene wide-mouth shaking bottles 50 or 100 ml, or screw-cap centrifuge tubes, 50 ml
End-over-end shaking machine
Centrifuge

11-2.3 Reagents

Extracting buffer solution, barium chloride 0.25 M, triethanolamine 0.2 M. Dissolve 61 g $BaCl_2.2H_2O$ and 27 ml TEA in water in a graduated beaker and make to 1 l. Adjust the pH to 8.2 with HCl 6 *M* (approx. 10 ml). Store in bottle with CO_2-trap (drying tube with $Ca(OH)_2$ or soda lime).
Hydrochloric acid, 0.100 M standard. Dilute standard analytical concentrate ampoule of 0.100 *M* HCl according to instruction.
Bromocresol green, 0.1%. Dissolve 250 mg bromocresol green in 250 ml water.
Mixed indicator. Dissolve 310 mg methyl red and 210 mg methylene blue in 250 ml ethanol 96%.

1-2.4 Procedure

1. Weigh 2.5 g fine earth (accuracy 0.01 g) into a shaking bottle or centrifuge tube. Include two blanks and a control sample.
   Note: Use 1 g in case of soils rich in organic matter or variable charge components (such as "free" oxides) combined with a low pH.
2. Add 25 ml buffer solution by pipette and shake overnight (16 hrs.) with an end-over-end shaker.
3. Centrifuge.
4. Transfer 10 ml aliquot to a 100 ml erlenmeyer flask and add about 20 ml water. Add 1 drop bromocresol green and 5 drops mixed indicator.
5. Titrate with 0.100 *M* HCl until first full purple colour (titrate blanks first to establish the point of colour change).
   Note: When using automatic titrator: set end-point pH at 4.60.

11-2.5 Calculation

$$\text{Extractable acidity } (\text{cmol}_c/\text{kg soil}) = \frac{(a-b)\times 0.1\times 100\times \text{mcf}}{s}\times\frac{25}{10} = \frac{(a-b)\times 25\times \text{mcf}}{s}$$

where
a = ml HCl used for blank
b = ml HCl used for sample
mcf = moisture correction factor
s = sample weight in gram

References

Blakemore et al. (1981, 1987)
USDA, SCS (1972, 1982)

12. EXTRACTABLE IRON, ALUMINIUM, MANGANESE AND SILICON

These analyses comprise:

1. "Free" iron, aluminium and manganese compounds in the soil extracted by a dithionite-citrate solution.
2. "Active" iron, aluminium and silica compounds extracted by an acid oxalate solution.
3. "Organically bound" iron and aluminium extracted by a pyrophosphate solution.

12-1 DITHIONITE EXTRACTABLE Fe, Al, Mn

Two procedures, the *Mehra & Jackson* and the *Holmgren* methods are described*.

12-1.1 Mehra & Jackson procedure

12-1.1.1 Principle

The sample is heated in a complexing buffer of sodium citrate/bicarbonate to which solid sodium dithionite is added as a reducing agent. Iron, aluminium, manganese and (optionally) silicon are measured in the extract by AAS.

12-1.1.2 Apparatus

Water bath
Centrifuge
Atomic absorption spectrometer (with nitrous oxide/acetylene flame)

12-1.1.3 Reagents

Buffer solution: sodium citrate 0.27 M and sodium bicarbonate 0.11 M. Dissolve 397 g Na-citrate.$2H_2O$ and 46.2 g $NaHCO_3$ in about 4 l water. Make to 5 l.

Sodium dithionite. Powder.

Potassium chloride, saturated solution. Dissolve 375 g KCl in 1 l warm water. Cool.

Standard solution of Fe, Al and Mn, 250 mg/l. Dilute standard analytical concentrate ampoules (1 g/l) according to instruction to make 1000 mg/l solutions. Dilute each to 250 mg/l by pipetting 50 ml into a 200 ml volumetric flask and making to volume with water.

Matrix solution for standard series. To a 1 l volumetric flask add 360 ml Na-citrate/bicarbonate buffer solution, 80 ml saturated KCl solution and 24 g $Na_2S_2O_4$. Dissolve and make to volume with water. *Note:* This solution can be kept for only a few days.

Mixed standard series of Fe, Al and Mn.

1. Of the 250 mg/l standard solutions pipette 0-5-10-25-50 ml into 250 ml volumetric flasks.
2. To each flask add 50 ml of the matrix solution, and make to volume with water. The standard series are then: Fe, Al, Mn: 0-5-10-25-50 mg/l.

Note: These solutions can be kept for about a week.

Remark: For certain purposes measurement of silicon in the extracts may be required. A 0-50 mg/l Si standard series can then be included similar to the other elements. In case Si is measured, use distilled water throughout the procedure rather than demineralized water.

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* The analytical results of these two methods are supposed to be comparable. The ISRIC laboratory has data indicating that this is the case.

12-1.1.4 Procedure

1. Crush approx. 5 g fine earth to pass a 0.25 mm sieve.
2. Weigh a suitable amount of this (accuracy 0.01 g) containing up to 0.5 g of extractable Fe_2O_3 into a 100 ml centrifuge tube (e.g. 4 g of sample with up to 9% Fe and 2 g of sample with up to 18% Fe). Include two blanks and a control sample.
3. Add 45 ml of buffer solution and place in water bath of 75°C. ***Warning***: the temperature should *not* exceed 80°C! (precipitation of elemental sulphur).
4. Add 1 g of solid $Na_2S_2O_4$ by means of a size scoop and stir the mixture constantly for one minute and then occasionally during the next 5 minutes with a glass or plastic rod.
5. Repeat Step 4 two more times.
6. Add 10 ml saturated KCl solution (while rinsing the rod) and warm again in water bath for 5 minutes.
7. Centrifuge and decant clear supernatant into a 250 ml volumetric flask.
9. Repeat Step 3 through 6 and add the second supernatant to the corresponding volumetric flask.
10. Make volumetric flasks to volume with water.
11. Prepare 5× and 50× dilutions:

    5× dilution

    Pipette 1 ml of extract and 4 ml water into a test tube and homogenize.

    50× dilution

    Pipette 1 ml extract and 9 ml matrix solution into a test tube and homogenize. Pipette 1 ml of this 10× diluted extract and 4 ml water into a test tube and homogenize.
12. Measure Fe by AAS at 248.3 nm using an air/acetylene flame.
13. Measure Al (usually in the 5× dilution) by AAS at 309.3 nm using a nitrous oxide/acetylene flame.
14. Measure Mn (usually in the 5× dilution) by AAS at 279.5 nm using an air/acetylene.
15. Measure Si (usually in the 5× dilution) by AAS at 251.6 nm using a nitrous oxide/acetylene flame.

Note: In case of overranged (diluted) extracts, dilute these once more 1+1 with the zero standard solution. Therefore, of the latter an extra 250 or 500 ml should be prepared. Change the calculation accordingly.

Remark: If desired, colorimetric determination of these elements can be done according to methods described in Page (1982): Fe, p. 304; Al, p. 288; Mn, p. 315; and Si, p. 270.

12-1.1.5 Calculation

$$\text{Fe, Al, Mn, Si (\%)} = \frac{(a-b)\times df}{s} \times \frac{250}{1000} \times mcf \times 100\% = \frac{(a-b)\times 25 \times df \times mcf}{s}$$

where

a = mg/l Fe, Al or Mn in diluted sample extract
b = ditto in diluted blank
df = dilution factor (5 or 50)
mcf = moisture correction factor
s = air-dry sample weight in milligram

Conversion factors for reporting:

$\%\ Fe_2O_3 = 1.43 \times \%\ Fe$
$\%\ Al_2O_3 = 1.89 \times \%\ Al$
$\%\ MnO_2 = 1.58 \times \%\ Mn$
$\%\ SiO_2 = 2.14 \times \%\ Si$

Reference: Mehra and Jackson (1960)

12-1.2 Holmgren procedure

12-1.2.1 Principle

The sample is shaken with a mixed complexing and reducing buffer solution of sodium citrate and sodium dithionite. Iron, aluminium, manganese and (optionally) silicon are measured in the extract by AAS.

12-1.2.2 Apparatus

Reciprocating shaking machine
Centrifuge
Polythene shaking bottles, wide mouth, 100 ml
Atomic absorption spectrometer (with nitrous oxide/acetylene flame)

12-1.2.3 Reagents

Extractant solution: sodium citrate 17%, and sodium dithionite 1.7%. Dissolve 510 g Na-citrate.$2H_2O$ in 2.5 l water. Add and dissolve 50 g $Na_2S_2O_4$ and make to 3 l. *Warning:* this solution can be kept for only a few days.

"Superfloc" solution, 0.2%. Dissolve 100 mg superfloc* in 50 ml water (stir overnight in the dark)
Note: Store in the dark. This solution can be kept for about a week.

Standard solution Fe, Al and Mn, 250 mg/l. Dilute standard analytical concentrate ampoules (1 g/l) according to instruction to make 1000 mg/l solutions. Dilute each to 250 mg/l by pipetting 50 ml into a 200 ml volumetric flask and make up to volume with water.

Mixed standard series of Fe, Al and Mn:

1. Of the 250 mg/l standard solutions pipette 0-5-10-25-50 ml into 250 ml volumetric flasks.
2. To each flask add 50 ml of the citrate/dithionite solution, and make to volume with water.

The standard series are then: Fe, Al, Mn, 0-5-10-25-50 mg/l.
Note: These solutions can be kept for about a week.

Remark: For certain purposes measurement of silicon in the extracts may be required. A 0-50 mg/l Si standard series can then be included similar to the other elements. In case Si is measured, use distilled water throughout the procedure rather than demineralized water.

12-1.2.4 Procedure

1. Weigh 1 g of fine earth (accuracy 0.01 g) into a 100 ml shaking bottle. Include two blanks and a control sample (see Remark 2 below).
2. Add 60 ml of the citrate/dithionite reagent, close the bottle and shake overnight (16 hrs).
   Note: This soil:reagent ratio is suitable for samples with iron oxide contents up to approx. 10% Fe (15% Fe_2O_3). For samples with contents up to 20% Fe use 120 ml reagent (in a 250 ml shaking bottle), up to 30%: 180 ml etc. In case no estimation can be made beforehand and the Fe content appears to be beyond the range, repeat the analysis with a lower soil:reagent ratio.
3. Transfer about 35 ml of suspension to a 50 ml centrifuge tube.
4. Add 3-4 drops of superfloc solution and swirl well (preferably on Vortex mixer) and centrifuge.
5. Prepare 5× and 50× dilutions:

   5× dilution

   Pipette 1 ml of the clear supernatant solution and 4 ml water into a test tube and homogenize.

   50x dilution

   Pipette 1 ml of the clear supernatant solution and 9 ml of the citrate/dithionite extractant solution into a test tube and homogenize.
   Pipette 1 ml of this 10× diluted extract and 4 ml water into a test tube and homogenize.

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* e.g. Cyanamid Superfloc N-100; Floerger Kemflock FA 20H.

6. Measure Fe by AAS at 248.3 nm using an air/acetylene flame.
7. Measure Al (usually in the 5× dilution) by AAS at 309.3 nm using a nitrous oxide/acetylene flame.
8. Measure Mn (usually in the 5× dilution) by AAS at 279.5 nm using an air/acetylene or nitrous oxide/acetylene flame.
9. Measure Si by AAS at 251.6 nm using a nitrous oxide/acetylene flame.

Note: In case of overranged (diluted) extracts, dilute these once more 1+1 with the zero standard solution. Therefore, of the latter an extra 250 or 500 ml should be prepared. Change the calculation accordingly.

Remarks

1. For colorimetric measurement see Remark in 12-1.1.4.
2. The original procedure by Holmgren prescribes the use of "fine-ground soil". Other workers use various other particle sizes, e.g. 80 mesh (≈0.18 mm)(USDA, SCS, 1972) and 0.25 mm (Blakemore et al., 1987). Comparison in the ISRIC laboratory of analyses of several particle-size fractions (obtained by crushing and grinding of fine earth) including fine earth, revealed no significant differences in the results. Hence the recommendation to use fine earth.

12-1.2.5 Calculation

$$\text{Fe, Al, Mn, Si (\%)} = \frac{(a-b)\times df}{s} \times \frac{60}{1000} \times mcf \times 100\% = \frac{(a-b)\times 6 \times df \times mcf}{s}$$

where

a = mg/l Fe, Al or Mn in diluted sample extract
b = ditto in diluted blank
df = dilution factor (5 or 50)
mcf = moisture correction factor
s = air-dry sample weight in milligram

(the factor 60 is based on 60 ml extractant but can be higher)

Conversion factors for reporting:

$\%\ Fe_2O_3 = 1.43 \times \%\ Fe$
$\%\ Al_2O_3 = 1.89 \times \%\ Al$
$\%\ MnO_2 = 1.58 \times \%\ Mn$
$\%\ SiO_2 = 2.14 \times \%\ Si$

References

Blakemore et al. (1987) p. 75
Holmgren (1967)

12-2 ACID OXALATE EXTRACTABLE Fe, Al, Si

12-2.1 Principle

The sample is shaken with a complexing acid ammonium oxalate solution dissolving the "active" or "short-range order" (≈ "amorphous") compounds of Fe, Al and Si which are determined in the extract by AAS.

12-2.2 Apparatus

Reciprocating shaking machine
Centrifuge
Atomic absorption spectrophotometer (with nitrous oxide/acetylene flame)
Polythene shaking bottles, wide mouth, 100 and/or 250 ml

12-2.3 Reagents

In this procedure *distilled* water is used since deionized water may contain Si.

Acid ammonium oxalate solution, 0.2 M in oxalate, pH 3. Dissolve 81 g $(COONH_4)_2.H_2O$ and 54 g $(COOH)_2.2H_2O$ in 4.5 l water and make to 5 l. Prepare 0.5 l of two separate 0.2 *M* solutions of NH_4-oxalate (28 g/l) and oxalic acid (25 g/l) and add some of either solution to the mixture until the pH is 3. Store in polypropylene bottle.

Alternative way of preparation:
Solution A (ammonium oxalate): Dissolve 142 g of $(COONH_4)_2.H_2O$ in 5 l water. *Solution B* (oxalic acid): dissolve 126 g of $(COOH)_2.2H_2O$ in 5 l water. Mix 4 parts of solution A with 3 parts of solution B. Adjust the pH of the acid oxalate solution by adding either solution A (base) or B (acid).

Potassium suppressant solution, 10,000 mg/l K. Dissolve 19 g KCl in 800 ml water and make up to 1 l.

"Superfloc" solution, 0.2%. Dissolve 0.1 g superfloc* in 50 ml water. Stir overnight in the dark.

Note: Store in the dark. This solution can be kept for about a week.

Diluent solution (5×). Make 2.38 g KCl and 25 ml conc. HCl to 1 l with water.

Diluent solution (20×). Make 2.01 g KCl, 210 ml acid ammonium oxalate solution and 21 ml conc. HCl to 1 l with water.

Standard solutions Fe, Al and Si, 250 mg/l. Dilute standard analytical concentrate ampoules (1 g/l) according to instruction to make 1000 mg/l solutions. Dilute each to 250 mg/l by pipetting 50 ml into a 200 ml volumetric flask and making up to volume with water.

Mixed standard series of Fe, Al and Si.

1. To each of five 250 ml volumetric flasks add 50 ml of the acid oxalate reagent, 25 ml of the KCl suppressant solution and 5 ml conc. HCl (or 10 ml of 6 *M* HCl).
2. Of each 250 mg/l standard solution pipette 0-5-10-25-50 ml into the 250 ml volumetric flask (same volumes into same flasks respectively) and make to volume with water.

The standard series are then: Fe, Al, Si, 0-5-10-25-50 mg/l.

12-2.4 Procedure

1. Weigh 1 g of fine earth (accuracy 0.01 g) into a 100 ml shaking bottle. Include two blanks and a control sample.
2. Add 50.0 ml acid oxalate reagent and close the bottle.
   Note: For soils with relatively high contents of oxalate-extractable material (Al, Fe > 2%) use 100.0 ml oxalate reagent and a 250 ml shaking bottle.
3. Shake for 4 hours in the dark.
4. Transfer about 35 ml to a 50 ml centrifuge tube.
5. Add 3-4 drops of superfloc solution and swirl well (preferably on Vortex mixer) and centrifuge.
6. Prepare 5× and 20× dilutions:

   5× dilution

   Pipette 1 ml of the clear supernatant and 4 ml of the diluent solution (5×) into a test tube and homogenize.

---

* e.g. Cyanamid Superfloc N-100; Floerger Kemflock FA 20H.

20× dilution

Pipette 1 ml of the clear supernatant solution and 19 ml (by varispenser or burette) of the diluent solution (20×) into a wide test tube or 25 ml beaker and homogenize.

7. Measure Fe by AAS at 248.3 nm using an air/acetylene flame.
8. Measure Al by AAS at 309.3 nm using a nitrous oxide/acetylene flame.
9. Measure Si by AAS at 251.6 nm using a nitrous oxide/acetylene flame.

Note: In case of overranged (diluted) extracts, dilute these once more 1+1 with the zero standard solution. Therefore, of the latter an extra 250 or 500 ml should be prepared. Change the calculation accordingly.

Remark 1: For colorimetric measurement see Remark in 12-1.1.4.

Remark 2: For the determination of ODOE (Optical Density of Oxalate Extract) the use of a mechanical extractor is prescribed rather than a shaking procedure (Chapter 20). We have data indicating that the present shaking procedure indeed yields less sensitive results for ODOE. Therefore, this procedure should **not** be used as a short-cut for the ODOE determination.

12-2.5 Calculation

$$\text{Fe, Al, Si (\%)} = \frac{(a-b)\times df}{s} \times \frac{\text{ml ox.}}{1000} \times \text{mcf} \times 100\% = \frac{(a-b)\times 0.1 \times df \times \text{ml ox.} \times \text{mcf}}{s}$$

where

a = mg/l Fe, Al or Si in diluted sample extract
b = ditto in diluted blank
df = dilution factor (5 or 20)
ml ox. = ml of oxalate reagent used (50 or 100)
mcf = moisture correction factor
s = air-dry sample weight in milligram

Conversion factors for reporting:

$\%\ Fe_2O_3 = 1.43 \times \%\ Fe$
$\%\ Al_2O_3 = 1.89 \times \%\ Al$
$\%\ SiO_2 = 2.14 \times \%\ Si$

References

Blakemore et al. (1987) p. 71
USDA, SCS (1972) p. 32
USDA, NRCS, NSSC (1996) p. 253

12-3 SODIUM PYROPHOSPHATE EXTRACTABLE Fe, Al

12-3.1 Principle

The sample is shaken with a sodium pyrophosphate solution which selectively extracts Fe and Al complexed to organic matter. Fe and Al are measured in the extract by AAS.

12-3.2 Apparatus

Reciprocating shaking machine
Centrifuge
Atomic absorption spectrophotometer (with nitrous oxide/acetylene flame)
Polythene shaking bottles, wide mouth, 250 ml

12-3.3 Reagents

Sodium pyrophosphate (diphosphate) solution, 0.1 M. Dissolve 223 g $Na_4P_2O_7.10H_2O$ in water and make to 5 l.
"Superfloc" solution, 0.2%. Dissolve 0.1 g superfloc* in 50 ml of water. Stir overnight in the dark.
Note: Store in the dark. This solution can be kept for about a week.
Standard solutions Fe and Al, 250 mg/l. Dilute standard analytical concentrate ampoules (1 g/l) according to instruction to make 1000 mg/l solutions. Dilute each to 250 mg/l by pipetting 50 ml into a 200 ml volumetric flask and making to volume with water.
Mixed standard series of Fe and Al.
1. To each of six 250 ml volumetric flasks add 50 ml of the pyrophosphate solution.
2. Of both 250 mg/l standard solutions pipette 0-5-10-25-50 ml into the 250 ml volumetric flask (same volumes into same flasks respectively) and make to volume with water.
The standard series are then: Fe, Al, 0-5-10-25-50 mg/l.

12-3.4 Procedure

1. Weigh 1 g of fine earth (accuracy 0.01 g) into a 250 ml shaking bottle. Include two blanks and a control sample.
2. Add 100 ml of pyrophosphate solution and close the bottle.
3. Shake overnight (16 hrs.).
4. Transfer about 35 ml of suspension to a 50 ml centrifuge tube.
5. Add 3-4 drops of superfloc and swirl well (preferably on Vortex mixer) and centrifuge.
Note: Because of peptization (phosphate!) it is often difficult to obtain a clear supernatant solution. Use of a superspeed unit in the centrifuge is then indicated, especially for certain "tropical" soils (see Remark 1 in 12-3.5).
6. Prepare a 5× dilution by pipetting 1 ml of the clear supernatant solution and 4 ml of water into a short test tube. Homogenize.
7. Measure Fe by AAS at 248.3 nm using an air/acetylene flame.
8. Measure Al by AAS at 309.3 nm using a nitrous oxide/acetylene flame.

Note: In case of overranged (diluted) extracts, dilute these once more 1+1 with the zero standard solution. Therefore, of the latter an extra 250 or 500 ml should be prepared. Change the calculation accordingly.

Remark: For colorimetric measurement see Remark in 12-1.1.4.

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*e.g. Cyanamid Superfloc N-100; Floerger Kemflock FA 20H.

12-3.5 Calculation

$$\text{Fe, Al (\%)} = \frac{(a-b)\times 5}{s} \times \frac{100}{1000} \times \text{mcf} \times 100\% = \frac{(a-b)\times 50 \times \text{mcf}}{s}$$

where

a = mg/l Fe or Al in 5× diluted sample extract
b = ditto in diluted blank
mcf = moisture correction factor
s = air-dry sample weight in milligram

Conversion factors for reporting:

$\%\ Fe_2O_3 = 1.43 \times \%\ Fe$
$\%\ Al_2O_3 = 1.89 \times \%\ Al$

Remarks

1. An important weakness of the method is the difficulty to obtain a clear supernatant solution. Also in routine work each supernatant solution has to be carefully inspected after centrifugation. Especially for certain "tropical" soils (i.e. soils rich in iron oxides) the use of superspeed centrifugation is recommended. Even this may not sediment all particles (particularly of goethite) and then use of ultrafiltration is indicated. (Schuppli et al., 1983).
2. If of interest, organic carbon can be determined in the extract also. Several procedures based on wet combustion by acid/dichromate may be successfully applied, e.g. Allison (1960), Walkley-Black (this volume), Begheijn (1976), Van Oostrum and Mokma (1982).

References

Blakemore et al. (1987) p. 75
USDA, SCS (1972) p. 32

13. SOLUBLE SALTS

13-1 PRINCIPLE

With "soluble salts" in soils are generally meant the salts with a higher solubility than gypsum. They are determined by measuring the cations and anions in water extracts. The procedures described are those for extracts of the water-saturated soil paste and the 1:5 soil:water mixture. The salinity of the soil is assessed by the electrical conductivity of the extract.

The *1:5 extract* is easier to obtain and gives a larger yield of extract than the saturation extract. However, the *saturation extract* is considered to give a better representation of the actual soil conditions with respect to plant environment.

13-2 PREPARATION OF THE EXTRACTS

13-2.1 Apparatus

Filter funnel
Büchner funnel with small suction/receiving flask (50 or 100 ml). See Figure 13-1.
Vacuum pump (electrical or water-jet)
Polythene bottles, wide-mouth, 250 ml
Reciprocating shaking machine

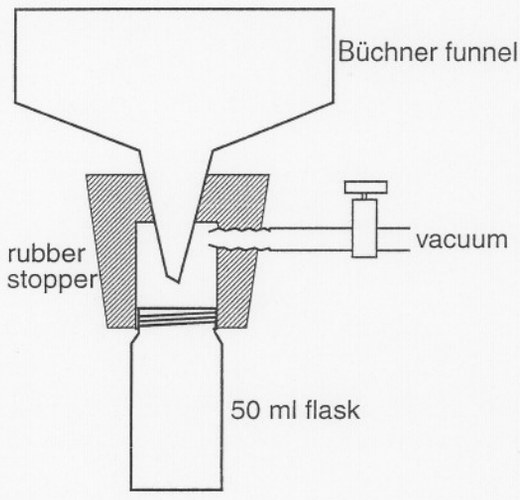

Fig. 13-1. Suction device for obtaining saturation extract (after a model by Dr. P.M. Driessen). The rubber stopper can be prepared with different gauges of cork-borers. The assembly is placed in a stand or a rack.

13-2.2 Reagents

Sodium hexametaphosphate solution, 0.1%. Dissolve 0.1 g of $(NaPO_3)_6$ in water and dilute to 100 ml.
Thymol.

13-2.3 Procedure for saturation extract

1. For about 40 ml extract, weigh 200 to 1000 g fine earth (accuracy 1 g) into a 500 or 1000 ml plastic beaker or plastic container with snap-tight lid (e.g. a refrigerator box). The higher the clay content of the sample, the less sample is needed.
2. Add a crystal of thymol to reduce bacterial growth.
3. Add just enough water to saturate the sample.
4. Stir gently with a spatula and add either water or some soil to reach a condition of saturation. The criteria for this condition are:
   - when the beaker is tapped on the bench, free water should not collect on the surface
   - the paste glistens as it reflects light
   - the paste flows slightly when the beaker is tipped
   - the paste slides freely and cleanly off the spatula (except in the case of high clay content)
5. Cover the beaker and leave to stand overnight. Include two beakers with 50 ml water as blanks.
6. The next day, check the paste on the above criteria and, if necessary, adjust the condition with some water or soil.
7. Take one or two teaspoons of paste for moisture content determination (see Chapter 2). This gives the ***Saturation Percentage:***

Saturation Percentage (wt%) = moisture content of saturated paste

8. Transfer the paste to the Buchner funnel (use a hardened, low-speed filter paper), apply suction and collect the filtrate. If the initial filtrate is turbid, return this to the funnel.
9. After filtration, immediately measure pH in the extract (see Section 13-3).
10. For measurement of ions (Sections 13-5 and 13-6), after pH measurement immediately dilute part of the extract 10× and 100× by pipetting 5 ml of extract into a 50 ml volumetric flask and 1 ml into a 100 ml volumetric flask respectively. Make to volume with water (= **solutions A_{10} and A_{100}**).
11. Add 1 drop of 0.1% sodium hexametaphosphate solution to the remaining extract (about 25 ml) to prevent precipitation of $CaCO_3$.
    Note: This quantity of sodium hexametaphosphate solution increases the sodium concentration by less than 0.5 mg/l, which is of little consequence as compared with the possible loss of $CaCO_3$.

13-2.4 Procedure for 1:5 extract

1. Weigh 30 g fine earth (accuracy 0.1 g) into a 250 ml polythene bottle and add 150 ml of water. Include two blanks.
   Note: Normally, no allowance is made for the water in air-dry samples. Only at higher contents (>5%) a correction of the added amount of water must be considered.
2. Stopper the bottle and shake mechanically for 2 hours and let stand for another 2 hours. However, if gypsum is suspected to be present*, after 1 hour add a crystal of thymol and let stand overnight (to allow dissolution of gypsum).
3. Filter the suspension using a hardened, low-speed filter paper. If the initial filtrate is turbid, return this to the funnel. If the filtrate remains turbid, try centrifugation, if necessary with the super-speed unit.
4. After filtration, immediately measure pH in the extract (see Section 13-3).
5. For measurement of ions (Sections 13-5 and 13-6), after pH measurement immediately dilute part of the extract 2× and 20× by pipetting 50 ml and 5 ml into 100 ml volumetric flasks respectively. Make to volume with water (= **solutions B_2 and B_{20}**)
6. To the remaining extract add 1 drop of 0.1% sodium hexametaphosphate solution for each 25 ml of extract to prevent precipitation of $CaCO_3$ (see note in 13-2.3, Step 10).

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* The presence of gypsum can be suspected when a well-flocculated suspension is noticed during pH and EC measurement. Also, an excessively high base saturation (>300%) found with the ammonium acetate CEC method (Chapter 9) can be an indication.

13-3 pH

Measure the pH directly in the (undiluted) extract using a combination electrode (for instruction see Chapter 4). Before each measurement rinse the electrode and wipe with soft tissue paper.

13-4 ELECTRICAL CONDUCTIVITY

13-4.1 Apparatus

Conductivity meter with dip cell and pipette cell

13-4.2 Reagent

Standard potassium chloride solution 0.01 M. Dilute standard analytical concentrate ampoule of 0.100 *M* KCl according to instruction. Pipette 10 ml of the standard 0.100 *M* KCl solution into a 100 ml volumetric flask and make to volume with water. Alternatively, dissolve 0.7456 g of oven-dried (105°C) KCl in water in a 1 l volumetric flask and make to volume with water.

13-4.3 Calibration of conductivity meter and measuring cell

1. Add about 30 ml standard 0.01 *M* KCl solution to a 50 ml beaker and measure the temperature.
2. Rinse and fill pipette cell with the standard KCl solution or insert dip cell in this solution.
3. Set temperature compensation dial at measured temperature and adjust reading of the meter to 1.412 mS/cm* with cell-constant dial. (This is the specific conductivity of the standard 0.01 *M* KCl solution at 25°C.)

13-4.4 Measurement

1. Measure the temperature of the extract and set temperature compensation dial at this temperature. (The reading is then automatically corrected to 25°C.)
2. Fill pipette cell with extract or insert dip cell into extract and read conductivity.
   Note: If not sufficient extract is available for rinsing the cell between measurements (usually the case with the saturation extract) then rinse the cell with water and acetone and dry with an air-jet.

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* 1 mS/cm = 1 dS/m = 1 mmho/cm

13-5 SOLUBLE CATIONS

13-5.1 Principle

Soluble Ca and Mg are measured by AAS and K and Na by FES in diluted extracts. Interferences in the measurements are suppressed by La and Cs additives respectively (see also 9-5.1). A major problem is the uncertainty about the concentration of the ions in the extract before analysis. Therefore, measurements will often have to be repeated using a higher or lower dilution of the extract.

13-5.2 Apparatus

Atomic absorption spectrophotometer
Diluter

13-5.3 Reagents

Standard solutions 1000 mg/l Ca, Mg, K, Na. Dilute standard analytical concentrate ampoules according to instruction.

Lanthanum suppressant solution for Ca and Mg, 1% La. Dissolve 23.4 g La_2O_3 in 106 ml HCl or HNO_3 6 *M* and dilute to 2 l with water (excess acid: 0.1 *M*).

Cesium suppressant solution for K and Na, 0.2% Cs. Dissolve 5 g CsCl in water and dilute with water to 2 l.

13-5.4 Procedure

13-5.4.1 Soluble Ca and Mg

Standard series

1. Dilute the 1000 mg/l Ca standard solution to 250 mg/l: pipette 50 ml into a 200 ml volumetric flask, make to volume with water.
2. Dilute the 1000 mg/l Mg standard solution to 25 mg/l: pipette 25 ml into a 1 l volumetric flask, make to volume with water.
3. Of the 250 mg/l Ca solution and the 25 mg/l Mg solution pipette a series of 0-5-10-15-20-25 ml into 250 ml volumetric flasks respectively.
4. To each flask add 125 ml of La suppressant solution. Make to volume with water. The standard series are then 0-5-10-15-20-25 mg/l Ca and 0-0.5-1.0-1.5-2.0-2.5 mg/l Mg.

Measurement

Pipette 2 ml of solutions $\boldsymbol{A_{10}}$ and $\boldsymbol{A_{100}}$ or $\boldsymbol{B_2}$ and $\boldsymbol{B_{20}}$ and 2 ml of the La suppressant solution into short test tubes, homogenize and measure Ca and Mg by AAS at wavelengths of 422.7 and 285.2 nm respectively.

Note: More often than not for Ca and Mg the high dilution factor is applicable, and it may be preferred to analyze solutions $\boldsymbol{A_{100}}$ or $\boldsymbol{B_{20}}$ first.

13-5.4.2 Soluble K and Na

Standard series

1. Dilute the 1000 mg/l K standard solution to 100 mg/l: pipette 25 ml into a 250 ml volumetric flask and make to volume with water.
2. Dilute the 1000 mg/l Na standard solution to 250 mg/l: pipette 50 ml into a 200 ml volumetric flask and make to volume with water.
3. Of the 100 mg/l K and the 250 mg/l Na solution pipette a series of 0-5-10-15-20-25 ml into 250 ml volumetric flasks respectively.
4. To each flask, add 125 ml of Cs suppressant solution. Make to volume with water. The standard series are then 0-2-4-6-8-10 mg/l K and 0-5-10-15-20-25 mg/l Na.

Measurement

Pipette 2 ml of solutions A_{10} and A_{100} or B_2 and B_{20} and 2 ml of the Cs suppressant solution into short test tubes, homogenize and measure K and Na by FES at wavelengths of 766.5 and 589.0 nm respectively.
Note: Usually for K the low dilution factor is applicable and for Na the high one.

13-5.5 Calculations

The soluble salt content of soils can be expressed in several ways. Two most usual ones are given here:

1. ***cation concentration of the extract,*** expressed in *$mmol_c$/litre* (formerly *me/l)*
2. ***cation content of the soil***, expressed in *$mmol_c$/kg* or *$cmol_c$/kg* (formerly in *me/100 g)**.

The two parameters are related to each other by the soil:liquid ratio of the extract. In case of the saturation extract this ratio is not fixed but determined by the Saturation Percentage (see 13.2.3).

Remark: The *cation content of the soil* can be expressed in *mg/kg* by multiplying the result in *$mmol_c$/kg* by the *equivalent weight* of the ions. Values for the latter are given below (e.g. 13-5.5.1).

13-5.5.1 Saturation extract

1. The *cation concentration of the* ***extract*** is obtained by:

$$\text{Soluble Ca, Mg, Na, K } (\text{mmol}_c\text{/l extract}) = \frac{(a-b)\times d}{\text{Eq. wt.}}$$

where
a = mg/l Ca, Mg, K or Na in the (diluted) extract
b = ditto for blank
d = dilution factor (for A_{10}: d=20; for A_{100}: d=200)
Eq.wt. = equivalent weight (Ca=20.04; Mg=12.15; Na=23.00; K=39.10)

2. The *cation content of the* ***soil*** is obtained by:

$$\text{Soluble Ca, Mg, Na, K } (\text{mmol}_c\text{/kg soil}) = \text{Soluble Ca, Mg, Na, K } (\text{mmol}_c\text{/l extract}) \times \frac{SP}{100}$$

where *SP* = Saturation Percentage (see 13-2.3)

13-5.5.2 1:5 Extract

1. The *cation concentration of the* ***extract*** is obtained by:

$$\text{Soluble Ca, Mg, Na, K } (\text{mmol}_c\text{/l extract}) = \frac{(a-b)\times d}{\text{Eq. wt.}}$$

where
a = mg/l Ca, Mg, Na, or K in the (diluted) extract
b = ditto for blank
d = dilution factor (for B_2: d=4; for B_{20}: d=40)
Eq.wt. = equivalent weight (Ca=20.04; Mg=12.15; Na=23.00; K=39.10)

---

* 1 me/l extract = 1 $mmol_c$/l extract, and 1 me/100 g soil = 1 $cmol_c$/kg soil = ***10*** $mmol_c$/kg soil.

2. The *cation content of the* ***soil*** is obtained by:

$$\text{Soluble Ca, Mg, Na, K } (\text{mmol}_c/\text{kg soil}) = \text{Soluble Ca, Mg, Na, K } (\text{mmol}_c/\text{l extract}) \times 5 \times \text{mcf}$$

where *mcf* = moisture correction factor

13-5.5.3 Sodium Adsorption Ratio (SAR)

The Sodium Adsorption Ratio (SAR) of solutions is defined as:

$$SAR = \frac{Na}{\sqrt{½ \times (Ca + Mg)}}$$

where *Na, Ca* and *Mg* are concentrations expressed in *mmol$_c$/l* as calculated above for both the saturation extract and the 1:5 extract.

13-5.5.4 Estimation of ESP from SAR

The Exchangeable Sodium Percentage (ESP) follows directly from the determination of the CEC and exchangeable bases (see Chapter 9 or 10). However, it can also be estimated with the empirical equation below. This may particularly be useful in saline soils where the determination of exchangeable bases is generally unreliable (if not impossible).

$$ESP\ (\%) = \frac{100 \times (-0.0126 + 0.01475 \times SAR)}{1 + (-0.0126 + 0.01475 \times SAR)} = \frac{1.475 \times SAR - 1.26}{0.01475 \times SAR + 0.9874}$$

where SAR is the Sodium Adsorption Ratio of the saturation extract*.

A graphical representation of this equation can be found in *Handbook 60,* pp. 73 and 103 (Richards, ed., 1954, 1969) and in *Booker Tropical Soil Manual*, p.165 (Landon ed.,1984, 1991).

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* ESP values can likewise be calculated from SAR values of the 1:5 extract (and of irrigation water). However, because the soil solution is usually more concentrated than these solutions, such ESP values usually give an *underestimation* of the actual ESP.

13-6 SOLUBLE ANIONS

This involves the determination of carbonate and bicarbonate, chloride and sulphate.

13-6.1 Carbonate and bicarbonate (alkalinity)

13-6.1.1 Principle

Carbonate and bicarbonate are determined by potentiometric titration of the extract with HCl to pH 8.4 and 4.4 respectively.

13-6.1.2 Apparatus

Automatic potentiometric titrator

13-6.1.3 Reagents

Hydrochloric acid standard solution 0.020 M. Dilute a 0.010 *M* HCl standard solution ampoule to 500 ml or a 0.020 *M* HCl ampoule to 1 l according to instruction.
Freshly boiled water. Boil 2 l water for 15 minutes and cool.

13-6.1.4 Procedure

1. Determine the aliquot of extract for the titration using the electrical conductivity according to the following table:

   EC < 1 mS : 10 ml
   EC = 1-10 mS : 5 ml
   EC > 10 mS : 2 ml

   (Alternatively, instead of the extracts themselves, use a proportional amount of the diluted extracts A_{10}, A_{100} or B_2, B_{20}. See Section 13-2).
   For the blank titration, use 10 ml of the blank extract.
2. Pipette an appropriate aliquot into measuring vessel, if necessary add water until electrode is submerged (use freshly boiled and cooled water).
3. Measure the pH. *Note*: Calibrate pH meter with buffers of pH 4 and 7.
4. If pH is 8.7 or higher, set end-point at 8.40 and titrate. *Note*: Below pH 8.7 insufficient carbonate is present for a meaningful determination (thus, the blank titration needs only to be carried out for bicarbonate).
5. When titration has stopped, record ml titrant used.
6. Switch end-point to pH 4.40 and continue titration
7. When titration has ended, again record ml titrant used.

Remark: When these titrations are performed manually, use phenolphthalein and methyl-orange respectively as indicators or, alternatively, a pH meter to read above indicated end-points.

13-6.1.5 Calculations

Like the cation contents, the anion contents can also be expressed as:

1. ***anion concentration of the extract,*** in *mmol$_c$/litre* (formerly *me/l)*
2. ***anion content of the soil***, in *mmol$_c$/kg* or *cmol$_c$/kg* (formerly in *me/100 g)**.

The two parameters are related to each other by the soil:liquid ratio of the extract. In case of the saturation extract this ratio is not fixed but determined by the Saturation Percentage.

Remark: The *anion content of the soil* can be expressed in *mg/kg* by multiplying the result in *mmol$_c$/kg* by the *equivalent weight* of the ions. Values for the latter are given at the end of this chapter.

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* 1 me/l = 1 mmol$_c$/l, and 1 me/100 g = 1 cmol$_c$/kg = ***10*** mmol$_c$/kg

13-6.1.5.1 *Saturation extract*

1. The carbonate and bicarbonate *concentration in the **extract*** is obtained by:

$$CO_3 \text{ (mmol}_c\text{/l extract)} = \frac{2 \times V \times M \times 1000}{a}$$

$$HCO_3 \text{ (mmol}_c\text{/l extract)} = \frac{(T - 2V - b) \times M \times 1000}{a}$$

where

V^* = ml HCl needed to titrate to pH 8.4
M = molarity of HCl
a = aliquot of (undiluted) extract in ml (2, 5 or 10)
T = total ml HCl needed to titrate to pH 4.4
b = $a/10$ × ml HCl needed to titrate 10 ml blank to pH 4.4

2. The carbonate and bicarbonate *content of the **soil*** is obtained by:

$$CO_3, HCO_3 \text{ (mmol}_c\text{/kg soil)} = CO_3, HCO_3 \text{ (mmol}_c\text{/l extract)} \times \frac{SP}{100}$$

where SP = Saturation Percentage (see 13-2.3).

13-6.1.5.2 1:5 Extract

1. The carbonate and bicarbonate *concentration in the **extract*** is obtained by:

$$CO_3 \text{ (mmol}_c\text{/l extract)} = \frac{2 \times V \times M \times 1000}{a}$$

$$HCO_3 \text{ (mmol}_c\text{/l extract)} = \frac{(T - 2V - b) \times M \times 1000}{a}$$

where

V^* = ml HCl needed to titrate to pH 8.4
M = molarity of HCl
a = aliquot of (undiluted) extract in ml (2, 5 or 10)
T = total ml HCl needed to titrate to pH 4.4
b = (a/10) × ml HCl needed to titrate 10 ml blank to pH 4.4

2. The carbonate and bicarbonate *content of the **soil*** is obtained by:

$$CO_3, HCO_3 \text{ (mmol}_c\text{/kg soil)} = CO_3, HCO_3 \text{ (mmol}_c\text{/l extract)} \times 5 \times \text{mcf}$$

where *mcf* = moisture correction factor.

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* $2 \times V$ in the equation because CO_3^{2-} is determined by titration of only one of its valencies.

13-6.2 Chloride

13-6.2.1 Principle

Chloride is titrated coulometrically. The chloride in the extract is titrated with silver ions generated from a silver electrode by a stabilized electrical current.
The end-point of the titration is reached when the Ag ions are no longer precipitated by chloride. This excess of Ag ions causes a sudden change in the electrical potential between two sensor electrodes and hence a detection of the end-point. The result is given by the number of pulses on a counter which by means of standard determination is converted to $mmol_c/l$.

13-6.2.2 Apparatus

Chlor-O-Counter chloride titrator (Marius)

13-6.2.3 Reagents

Basic solution I. Add 100 ml glacial acetic acid (A.R.) and 7 ml conc. nitric acid (70%, A.R.) to a 1000 ml volumetric flask, make to volume with water and mix well. This solution can be kept unlimited.

Basic solution II. Soak 600 mg gelatin (pure granular grade "Album") in 50 ml water in a 100 ml beaker during 2 hours at room temperature. Then heat on a water bath or burner till the gelatine has been dissolved and transfer content to a 100 ml volumetric flask. Add 10 mg thymol (to prevent mould), 10 mg thymol-blue and make to volume with water.

Note: The solution can be kept for 1 or 2 weeks in a refrigerator. Prior to use, check by smelling if the solution is not "off".

Chloride standard solution, 10 $mmol_c/l$. Dissolve 3.728 g KCl (oven-dried, 105°C) in water in a 500 ml volumetric flask. Make to volume with water and mix well. Of this 100 $mmol_c/l$ solution, pipette 10 ml into a 100 ml volumetric flask. Make to volume with water.

13-6.2.4 Procedure

1. Clean electrodes according to instruction of apparatus.
2. Transfer to a 50 ml beaker: 20 ml of Basic solution I and 1 ml of Basic solution II. Add a few drops of the chloride standard solution.
3. Place beaker on a test platform and raise this to measuring position.
4. Set current dial at 10×10^{-9} eq/pulse, the digital counter at zero and push *stirrer* button.
5. After a few seconds push *titration* button and, after finishing the titration, push *pipette* button. The titrator is now ready for operation (free of Cl^-; the formed AgCl precipitate accelerates the rate of reaction).
6. Calibrate by pipetting 1 ml Cl-standard solution into the 50 ml beaker (still containing the Basic solutions) and titrate as in Steps 4 and 5. Repeat this two or three times and take average of readings (1 ml standard solution corresponds to approximately 1000 pulses in dial position 10).
7. Pipette 1 ml diluted extract (usually solutions A_{10} or B_2, see Section 13-2)) into the 50 ml beaker and titrate as above. Repeat and take average reading.

Remarks

1. In each beaker containing fresh Basic solutions usually about 10 titrations can be made. Continue until the beaker is full or when the thymol blue indicator colour turns from red to blue: the pH is then too high). Each newly prepared mixture of Basic solutions I and II should be titrated with a few drops of standard Cl solution.
2. Titrations are best carried out when sample readings are within a range of 400 to 1000 pulses in dial position 10. If the number of pulses is below 400 use more sample. If the reading is considerably higher than 1000, dilute the extract or set dial at higher current position.
3. The electrodes need to be cleaned regularly.
4. The blank gives no meaningful measurement, it is assumed to be incorporated in the standard.

13-6.2.5 Calculations

13-6.2.5.1 Saturation extract

1. The chloride *concentration of the **extract*** is obtained by:

$$\text{Cl (mmol}_c\text{/l)} = \frac{a \times 10 \times d}{b}$$

where

a = counts of pulses of diluted extract (solution ***A***)
b = ditto of Cl standard (1 ml of 10 mmol$_c$/l Cl)
d = dilution factor of solution ***A*** (10 or 100)
10 = mmol$_c$/l of standard

Note: If the dial settings during titration of the extract and the standard solution are not the same, the calculation has to be changed accordingly.

2. The chloride *content of the soil* is obtained by:

$$\text{Cl (mmol}_c\text{/kg soil)} = \text{Cl (mmol}_c\text{/l extract)} \times \frac{SP}{100}$$

where *SP* = Saturation Percentage (see 13-2.3)

13-6.2.5.2 1:5 extract

1. The chloride *concentration of the **extract*** is obtained by:

$$\text{Cl (mmol}_c\text{/l)} = \frac{a \times 10 \times d}{b}$$

where

a = counts of pulses of diluted extract (solution ***B***)
b = ditto of Cl standard (1 ml of 10 mmol$_c$/l Cl)
d = dilution factor of solution ***B*** (2 or 20)
10 = mmol$_c$/l of standard

Note: If the dial settings during titration of the extract and the standard solution are not the same, the calculation has to be changed accordingly.

2. The chloride *content of the soil* is obtained by:

$$\text{Cl (mmol}_c\text{/kg soil)} = \text{Cl (mmol}_c\text{/l extract)} \times 5 \times \text{mcf}$$

where *mcf* = moisture correction factor

13-6.3 Sulphate

13-6.3.1 Principle

Sulphate is precipitated as barium sulphate and determined turbidimetrically.

13-6.3.2 Apparatus

Spectrophotometer or colorimeter (with 2 cm cuvette)

13-6.3.3 Reagents

Barium chloride solution, 10%. Acidified. Dissolve 25 g $BaCl_2.2H_2O$ in about 200 ml water to which 12.5 ml conc. HCl is added. Make to 250 ml with water.
Glycerol reagent (1:1). Mix 500 ml glycerol with 500 ml water.
Standard solution 1000 mg/l SO_4. Dilute standard analytical concentrate ampoule according to instruction.
Standard series.

1. Dilute the 1000 mg/l SO_4 standard solution to 100 mg/l: pipette 25 ml into a 250 ml volumetric flask and make to volume with water.
2. Of this 100 mg/l SO_4 solution pipette a series of 0-5-10-20-30 ml into 100 ml volumetric flasks respectively. Make to volume with water. The standard series is then: 0-5-10-20-30 mg/l SO_4.

13-6.3.4 Procedure

1. Pipette 5 ml aliquot of the diluted extract (solution ***A*** or ***B***, see Section 13-2) and the standard series (zero standard = blank) into a 50 ml beaker. Add 10.0 ml water and stir with a glass rod or magnetic stirrer (leave rod or magnetic bar in beaker throughout).
   Note: The aliquot may contain up to 0.6 mg SO_4. At higher contents pipette less aliquot and add proportionally more water.
2. Add 10.0 ml glycerol reagent (1:1) and stir thoroughly for 15 seconds.
3. Place in refrigerator to cool to about 15°C.
4. Remove from refrigerator and, while stirring, add 2.0 ml $BaCl_2$ reagent. Stir for 10 seconds.
5. Allow to stand at room temperature for 30 minutes.
6. Measure transmittance with spectrophotometer at 600 nm.

13-6.3.5 Calculation

Construct calibration curve from standard series.

13-6.3.5.1 Saturation extract

1. The sulphate *concentration in the **extract*** is obtained by:

$$SO_4 \text{ (mmol}_c\text{/l extract)} = \frac{a \times d}{48}$$

where
a = mg/l SO_4 in diluted extract (solution ***A***)
d = dilution factor of solution ***A*** (10 or 100)
48 = weight of 1 $mmol_c$ SO_4 (= equivalent weight)

2. The sulphate *content of the* ***soil*** is obtained by:

$$SO_4 \text{ (mmol}_c\text{/kg soil)} = SO_4 \text{ (mmol}_c\text{/l extract)} \times \frac{SP}{100}$$

where *SP* = saturation percentage (see 13-2.3)

13-6.3.5.2 1:5 extract

1. The sulphate *concentration in the* ***extract*** is obtained by:

$$SO_4 \text{ (mmol}_c\text{/l extract)} = \frac{a \times d}{48}$$

where
a = mg/l SO_4 in diluted extract (solution ***B***)
d = dilution factor (2 or 20)
48 = weight of 1 $mmol_c$ SO_4 (= equivalent weight)

2. The sulphate *content of the* ***soil*** is obtained by:

$$SO_4 \text{ (mmol}_c\text{/kg soil)} = SO_4 \text{ (mmol}_c\text{/l extract)} \times 5 \times \text{mcf}$$

where *mcf* = moisture correction factor.

Remark: To express the ion content in ***mg/kg soil***, multiply the content in *$mmol_c$/kg* by the *equivalent weight* of the ions concerned. Equivalent weights of the anions discussed above are:

CO_3^{2-} = 30.00
HCO_3^- = 61.01
Cl^- = 35.45
SO_4^{2-} = 48.03

REFERENCES

Landon (1984, 1991)
Beatty and Loveday, *in:* Loveday (1974) p. 108
Richards (1954, 1969)

14. PHOSPHORUS

Two methods are described for "available" phosphorus: *Bray I* and *Olsen,* the former being suitable for acid soils and the latter for other soils.

The extraction of phosphorus by *citric acid,* in long-ago days also used for available phosphorus, is included for soil classification purposes: required to establish "anthropic" influence.

The *phosphate retention* determination is described to obtain a measure for the capacity of the soil to take up phosphate from solution: required to establish "andic" properties.

14-1 PHOSPHORUS SOLUBLE IN DILUTE ACID-FLUORIDE

(Extraction according to *Bray & Kurtz no. I*)

14-1.1 Principle

The readily acid-soluble forms of P are extracted by a combination of HCl and NH_4F. Phosphate in the extract is determined colorimetrically with the blue ammonium molybdate method with ascorbic acid as reducing agent.

14-1.2 Apparatus

Spectrophotometer (with 10 mm cuvette)

14-1.3 Reagents

Ammonium fluoride solution, 1 M. Dissolve 3.7 g NH_4F in water and make to 100 ml (store in polythene bottle).

Hydrochloric acid, 0.5 M. Dilute 8.3 ml HCl 6 *M* (or 4.3 ml conc. HCl, 37%) to 100 ml with water.

Extracting solution Bray I (0.03 M NH_4F and 0.025 M HCl). Add 15 ml NH_4F 1 *M* and 25 ml HCl 0.5 *M* to approx. 400 water and fill up to 500 ml with water.

Sulphuric acid, 2.5 M. Slowly add 35 ml conc. H_2SO_4 (96%) to 150 ml water under constant stirring. After cooling make to 250 ml with water.

Ammonium molybdate solution, 4%. Dissolve 4 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ in water and make to 100 ml. Store in polythene or pyrex bottle in the dark.

Potassium antimony tartrate solution, 0.275% (1000 mg/l Sb). Dissolve 0.275 g $KSbOC_4H_4O_6$ in water and make to 100 ml.

Ascorbic acid solution, 1.75%. Dissolve 1.75 g ascorbic acid in water and make to 100 ml.
Prepare fresh daily.

Mixed reagent. Successively add with a measuring cylinder to a 500 ml polythene or pyrex bottle and homogenize after each addition:
- 50 ml of 2.5 *M* H_2SO_4
- 15 ml of NH_4-molybdate solution
- 30 ml of ascorbic acid solution
- 5 ml of KSb-tartrate solution
- 200 ml water

Prepare fresh daily.

Boric acid solution, 1%. Dissolve 1 g H_3BO_3 in 100 ml water.

Standard phosphate solution, 100 mg/l P. Dilute standard analytical concentrate ampoule (1 g/l) according to instruction. Pipette 50 ml of this 1000 mg/l solution into a 500 ml volumetric flask and make to volume with extracting solution. (Alternatively: dissolve 0.4390 g KH_2PO_4 in extracting solution in a 1 l volumetric flask and make to volume.)

Standard phosphate solution, 12 mg/l P. Pipette 30 ml of the 100 mg/l P standard solution into a 250 ml volumetric flask and make to volume with water.

Standard series. Pipette into 100 ml volumetric flasks 0-10-20-30-40-50 ml of the 12 mg/l P standard solution respectively. Make to volume with water. The standard series is then 0-1.2-2.4-3.6-4.8-6.0 mg/l P.

14-1.4 Procedure

1. Weigh 2 g fine earth (accuracy 0.01 g) into a wide test tube (50 ml) or shaking bottle. Include two blanks and a control sample.
2. Add 14.0 ml of extracting solution Bray I.
3. Shake for 1 minute by hand and then immediately filter through a hardened filter (e.g. Whatman 42). In case the filtrate is turbid filter again through the same filter. Filtration procedure not to exceed 10 minutes.
4. Pipette into (short) test tubes 1 ml of the standard series, the blanks and the sample extracts, 2 ml boric acid and 3 ml of the mixed reagent. Homogenize.
5. Allow solutions to stand for at least 1 hour for the blue colour to develop its maximum (see Remark below).
6. Measure absorbance on spectrophotometer at 882 or 720 nm.

14-1.5 Calculation

$$P\ (mg/kg\ soil) = (a-b) \times \frac{14}{1000} \times \frac{1000}{s} \times mcf = (a-b) \times \frac{14}{s} \times mcf$$

where

a = mg/l P in sample extract
b = ditto in blank
s = sample weight in gram
mcf = moisture correction factor

Conversion factor for reporting:
$P_2O_5 = 2.31 \times P$

Remark: With the acid molybdate solution phosphate forms phospho-molybdenic acid which is reduced to phospho-molybdenic-blue with ascorbic acid. The antimony accelerates the development of the blue colour and stabilizes this for up to 24 hours. With this method interference of Si is not to be expected. Should such an interference still occur (blue coloured zero standard) then repeat procedure using distilled water.

References

Bray and Kurtz (1945)
Houba et al. (1988)
Olsen and Sommers, *in:* Page et al. (1982), p. 416
Soil Laboratory Staff, Royal Tropical Institute (1984)

14-2 PHOSPHORUS SOLUBLE IN SODIUM BICARBONATE

(Extraction according to *Olsen et al.*)

14-2.1 Principle

The sample is extracted with a sodium bicarbonate solution of pH 8.5. Phosphate in the extract is determined colorimetrically with the blue ammonium molybdate method with ascorbic acid as reducing agent. The high pH of the extracting solution renders the method suitable for calcareous, alkaline or neutral soils containing Ca-phosphates because the Ca concentration in solution is suppressed by precipitation of $CaCO_3$. As a result, the phosphate concentration in solution can increase.
The procedure can, in principle, also be applied to acid soils as the relatively high pH of the carbonate buffer suppresses the solubility of Al and Fe and thus allows the phosphate concentration to increase.

14-2.2 Apparatus

Spectrophotometer (with 10 mm cuvette)
Polythene shaking bottles 250 ml
Reciprocating shaking machine

14-2.3 Reagents

Sodium bicarbonate solution, 0.5 M, pH 8.5 (extracting solution). Dissolve 42 g $NaHCO_3$ in water and make to 1 l. Adjust the pH to 8.5 by adding NaOH 1 *M* (4 g/100 ml). In case of overshooting pH 8.5 add some $NaHCO_3$ 0.5 *M.*

Note: Check and re-adjust the pH after storage.

Sulphuric acid, 4 M. Slowly add 56 ml concentrated H_2SO_4 (96%) to about 150 ml water in a graduated beaker under constant stirring. After cooling make to 250 ml with water.

Ammonium molybdate solution, 4%. Dissolve 4 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ in water and make to 100 ml. Store in polythene or pyrex bottle.

Potassium antimony tartrate solution, 0.275% (1000 mg/l Sb). Dissolve 0.275 g $KSbOC_4H_4O_6$ in water and make to 100 ml.

Ascorbic acid solution, 1.75%. Dissolve 1.75 g ascorbic acid in water and make to 100 ml.
Prepare fresh daily.

Mixed reagent. Successively add with a measuring cylinder to a 500 ml polythene or pyrex bottle and homogenize after each addition:

- 50 ml of 4 *M* H_2SO_4
- 15 ml of NH_4-molybdate solution
- 30 ml of ascorbic acid solution
- 5 ml of KSb-tartrate solution
- 200 ml water

Prepare fresh daily.

Standard phosphate solution, 100 mg/l P. Dilute standard analytical concentrate ampoule (1 g/l) according to instruction. Pipette 100 ml of this 1000 mg/l solution into a 1 l volumetric flask and make to volume with water. (Alternatively: dissolve 0.4390 g KH_2PO_4 in water in a 1 l volumetric flask and make to volume.)

Standard phosphate solution, 4 mg/l P. Pipette 10 ml of the 100 mg/l P standard solution into a 250 ml volumetric flask and make to volume with extracting solution.

Standard series. Pipette into 100 ml volumetric flasks 0-10-20-30-40-50 ml of the 4 mg/l P standard solution. Make to volume with extracting solution. The standard series is then 0-0.4-0.8-1.2-1.6-2.0 mg/l P.

14-2.4 Procedure

1. Weigh 5 g fine earth (accuracy 0.01 g) into a 250 ml polythene shaking bottle. Include two blanks and a control sample.
2. Add 100 ml of the extracting solution.
3. Shake for 30 minutes.
4. Filter through a hardened filter (e.g. Whatman 42).
5. Pipette into (short) test tubes 3 ml of the standard series, the blanks and the sample extracts.
6. Slowly add 3 ml of the mixed reagent by pipette and swirl (CO_2 evolution!).
7. Allow the solutions to stand for at least 1 hour for the blue colour to develop its maximum (see Remark below).
8. Measure absorbance on spectrophotometer at 882 or 720 nm.

14-2.5 Calculation

Plot a calibration graph of absorbance against P concentration.

$$\text{P (mg/kg soil)} = (a-b) \times \frac{100}{1000} \times \frac{1000}{s} \times \text{mcf} = (a-b) \times \frac{100}{s} \times \text{mcf}$$

where

a = mg/l P in sample extract
b = ditto in blank
s = sample weight in gram
mcf = moisture correction factor

Conversion factor for reporting:
$P_2O_5 = 2.31 \times P$

Remark: With the acid molybdate solution phosphate forms phospho-molybdenic acid which is reduced to phospho-molybdenic-blue with ascorbic acid. The antimony accelerates the development of the blue colour and stabilizes it for up to 24 hours. With this method interference of Si is not to be expected. Should such an interference still occur (indicated by a blue coloured zero standard) then repeat procedure using distilled water.

References

Olsen et al. (1954)
Olsen and Sommers, *in:* Page et al. (1982), p. 421
Soil Laboratory Staff, Royal Tropical Institute (1984)

14-3 PHOSPHORUS SOLUBLE IN CITRIC ACID

This is an ancient determination of available P. The method still needs to be used to determine the P content of the *"Fimic horizon"* (Revised FAO/Unesco Soil Map of the World Legend) and the *"Anthropic epipedon"* (Soil Taxonomy). It is also still in use in archaeology and in fertilizer quality control.

14-3.1 Principle

The sample is extracted with a 1% citric acid solution. Phosphate in the extract is determined colorimetrically with the blue ammonium molybdate method with ascorbic acid as reducing agent.

14-3.2 Apparatus

Spectrophotometer (with 10 mm cuvette)
Polythene shaking bottles 100 ml
Reciprocating shaking machine

14-3.3 Reagents

Citric acid solution, 1%. Dissolve 11 g C_3H_4OH $(COOH)_3.H_2O$ in water and make to 1 l. Prepare on the day of use.

Sulphuric acid, 5 M. Slowly add 140 ml concentrated H_2SO_4 (96%) to about 325 ml water under constant stirring. After cooling make to 500 ml with water.

Potassium antimony tartrate solution, 0.5%. Dissolve 0.50 g $KSbOC_4H_4O_6$ in water and make to 100 ml.

Stock solution for mixed reagent. Dissolve 12 g ammonium molybdate in about 300 ml water. Slowly add 450 ml 5 *M* sulphuric acid under constant stirring. Add 100 ml 0.5% potassium antimony tartrate solution. Make to 1 l with water. Store in the dark.

Mixed reagent. Dissolve 1.5 g ascorbic acid in 100 ml stock solution. Prepare on the day of use.

Standard phosphate solution, 200 mg/l P. Dilute standard analytical concentrate ampoule (1 g/l) according to instruction. Pipette 100 ml of this 1000 mg/l solution into a 500 ml volumetric flask and make to volume with water. (Alternatively: dissolve 0.4390 g KH_2PO_4 in water in a 500 ml volumetric flask and make to volume.)

Standard series. Pipette into 100 ml volumetric flasks 0-10-20-30-40-50 ml of the 200 mg/l P standard solution. Make to volume with water. The standard series is then 0-20-40-60-80-100 mg/l P.

14-3.4 Procedure

14-3.4.1 Extraction

1. Weigh 5 g fine earth (accuracy 0.01 g) into a 100 ml polythene shaking bottle.
2. If the soil contains less than 0.3 % calcium carbonate equivalent, add 50.0 ml of the 1% citric acid solution. If the soil contains more than 0.3% carbonate, first add 7 mg solid citric acid for each 0.1 % carbonate and then 50 ml citric acid solution. Include two blanks and a control sample.
3. Shake for 2 hours. ***Warning***: In case carbonate is present, do not stopper the shaking bottle until effervescence has ceased.
4. Let stand for 20 hours.
5. Shake again for 1 hour.
6. Filter through a hardened filter. In case the filtrate is turbid filter again through the same filter.
7. Pipette 1 ml of the standards, blanks and filtrate into a 100 ml volumetric flask and add water to a volume of approx. 80 ml.
8. Add 10.0 ml mixed reagent and homogenize.
9. Make to volume with water, homogenize and allow to stand for at least 2 hours for the blue colour to develop its maximum.
10. Measure absorbance on spectrophotometer at 882 or 720 nm.

Remark: The described dilution procedure is suitable for soils with extractable phosphorus up to 2300 mg/l P_2O_5 (1000 mg/l P). To cope with higher contents a smaller aliquot of the filtrate can be used (e.g. 0.5 ml) or a pre-dilution with water (e.g. 1:1) followed by 1:100 as described (change calculation accordingly). Because of the lower citrate concentration in this case the colour development is faster but this has no consequence for its maximum intensity. Note that the standards contain no citrate.

14-3.4.2 Calculation

Plot a calibration graph of absorbance against P concentration.

$$P\ (mg/kg\ soil) = (a-b) \times \frac{50}{1000} \times \frac{1000}{s} \times mcf = (a-b) \times \frac{50}{s} \times mcf$$

where

a = mg/l P in sample extract
b = ditto in blank
s = sample weight in gram
mcf = moisture correction factor

Conversion factor for reporting:
$P_2O_5 = 2.31 \times P$

Remarks

1. The method described is suitable for citrate concentrations up to 0.42 mmol/100 ml (final concentration) without digestion of the extract by oxidation. This corresponds with $CaCO_3$ contents in the soil of up to 50%.
2. Experiments at ISRIC with a number of "anthropic" samples indicated that digestion of the extracts for complete recovery of the extracted P, as was practised in the original procedure (Blanck, 1931), is not necessary with the described colorimetric procedure.
3. Preferably, the filtrates should be analyzed on the day of filtration. If necessary, the filtrates may be kept in closed flasks in a refrigerator for up to three days.

References

Blanck (1931), p. 175-181
Hofstee (1983), p. 74-75
Lab. for Soil and Crop Testing, Oosterbeek (1979)
John (1970)

14-4 PHOSPHATE RETENTION

(Procedure according to *Blakemore et al.*)

14-4.1 Principle

The sample is equilibrated with a phosphate solution and the proportion of phosphate withdrawn from the solution is determined. At the relatively low pH of the solution (≈ 4.6) phosphate retention is close to its maximum.

14-4.2 Apparatus

Reciprocating shaking machine
Centrifuge
Spectrophotometer (1 cm cuvette)

14-4.3 Reagents

Use *distilled water* throughout.

P-retention solution, 1000 mg/l P. Dissolve 8.80 g potassium dihydrogen phosphate and 32.8 g anhydrous sodium acetate or 54.4 g $NaAc.3H_2O$ in about a litre of water, add 23 ml glacial acetic acid and transfer to a 2 l volumetric flask. Make to volume with water. The pH should be 4.6 ± 0.1.

Nitric vanadomolybdate acid solution.

- Dissolve 0.8 g ammonium vanadate in 500 ml boiling water, cool and add 6 ml conc. HNO_3 (70%). Dilute to 1 l with water.
- Dissolve 16 g ammonium molybdate in water at 50°C, cool and dilute to 1 l with water.
- Dilute 100 ml conc. HNO_3 (70%) to 1 l with water.
- Transfer the diluted HNO_3 to a 5 l bottle or jar, add the vanadate solution and then the molybdate solution. Mix well.

Standard series. Of the P-retention solution (1000 mg/l P) pipette 0-10-20-30-40-50 ml into 50 ml volumetric flasks and make to volume with water. These solutions correspond to 100-80-60-40-20-0% P-retention respectively.

14-4.4 Procedure

1. Weigh 5 g air-dry fine earth (accuracy 0.1 g) into a 50 ml stoppered centrifuge tube or shaking bottle and add 25 ml P-retention solution with a pipette or dispenser.
2. Shake overnight (16 hrs.) at about 20°C.
3. Centrifuge (at 2000 rpm for about 15 minutes).
4. Add 19.0 ml nitric vanadomolybdate acid reagent into 30 ml tubes and by pipette add 1 ml aliquot of the (clear) supernatant solutions and the standard series. Homogenize.
5. After at least 30 minutes, but within 24 hours, read absorbance at 466 nm.

14-4.5 Calculation

Prepare a standard curve of % P-retention against absorbance. The P-retention of the samples are read from this curve and reported in %.

Note: Since the curve shows a decrease in absorbance with a decrease in P concentration (= increase in P absorption), the standard solution with the highest P concentration is plotted at the origin of the graph.

Reference: Blakemore et al. (1987), p. 44

15. ELEMENTAL ANALYSIS by X-RAY FLUORESCENCE SPECTROSCOPY

15-1 PRINCIPLE

The fine earth or the separated clay fraction is dried and ignited and then fused with lithium tetraborate. The formed bead can be analyzed by X-ray fluorescence spectroscopy for some 25 elements (in principle all elements except those below Na in the Periodic System).

15-2 APPARATUS

Ball grinder (tungsten carbide)
Freeze-dryer
Drying oven
Furnace
Centrifuge
Water bath
Milk shaker
Siphons
Reciprocating shaking machine
X-ray fluorescence spectrometer (Philips PW 1404)
High-frequency generator for inductive heating, or oven (at least 1200°C)
Porcelain crucibles 30 ml
Flat-bottom platinum crucible

15-3 REAGENTS

Acetate buffer solution, 1 M, pH 5. Dissolve 680 g $CH_3COONa.3H_2O$ in 4 l water. Adjust to pH 5 with approx. 250 ml glacial acetic acid (use pH-meter). Make to 5 l with water.

Hydrogen peroxide, 30%. Note: "Technical" grade H_2O_2 may contain phosphate as a stabilizer (up to 30 mg/l P). If phosphorus is an element to be determined, then *A.R.* grade should be used.

Sodium chloride saturated solution. Dissolve 375 g NaCl in 1 l warm water (70-80°C). Cool.

Sodium hydroxide solution, 1 M. Dissolve 40 g NaOH in 900 ml water and make to 1 l.

Lithium tetraborate. Powder A.R.

Barium acetate solution, 0.5 M (BaOAc). Dissolve 127.5 g $Ba(CH_3COO)_2$ in water and make to 1 l.

15-4 PROCEDURE FOR FINE EARTH

1. Weigh approx. 2.5 g of fine earth into the vessel of a tungsten carbide ball mill and grind for about 10 minutes.
2. Transfer to tared porcelain crucibles of 30 ml and dry overnight in oven at 105°C.
3. Proceed according to 15-5.3 Step 17.

15-5 PROCEDURE FOR CLAY FRACTION

15-5.1 Oxidation of organic matter

1. Weigh an amount of fine earth containing about 2.5 g of clay into a 500 ml beaker (high type).
   Note: If X-ray diffraction is done on the sample as well use a sample containing 3.5 to 4 g of clay and use a 1 l beaker.
2. Add 15 ml water and 15 ml H_2O_2 30%. Leave overnight. In case of excessive frothing add a little ethanol or place in a basin or sink partly filled with cold water. Keep beakers covered with a watch-glass as much as possible.

3. The next day, place beaker on hot water bath (80°C) and a few times add 5-10 ml increments of H_2O_2 30% (each time when effervescence has subsided) until decomposition of organic matter is completed: the supernatant is usually clear then.
4. Place beaker on hot plate and boil gently for about 1 hour to remove H_2O_2.
5. Remove beaker from hot plate and allow to cool.
6. Agitate suspension with a milk shaker for 2-3 minutes.
7. Return suspension to beaker and make volume to about 300 ml with water. Let suspension settle.
8. If no settling occurs add 5 ml saturated NaCl solution and stir. Leave to settle.
9. Siphon off and discard the clear supernatant solution.

Now, a distinction is made on basis of the presence or absence of calcium carbonate:

1. Calcareous soils ($pH\text{-}H_2O > 6.5$)
2. Non-calcareous soils ($pH\text{-}H_2O \leq 6.5$).

From the calcareous soils the carbonate is removed with acetate buffer (15-5.2).
If carbonate is absent proceed with 15-5.3 (Separation of clay).

15-5.2 Removal of carbonate*

1. Add approx. 100 ml acetate buffer pH 5 and place on hot water bath (80°C). Swirl occasionally. Keep beakers covered with a watch-glass as much as possible.
2. After effervescence has stopped, add increments of 5 ml glacial acetic acid at intervals of about an hour until effervescence does nor recur after addition of an increment.
3. Transfer suspension to a large centrifuge bottle (250 or 380 ml) and centrifuge-wash twice (or three times at high $CaCO_3$ content, i.e. >10%).
4. Wash sample back into its rinsed 500 ml beaker and continue with 15-5.3 (next section).

15-5.3 Separation of clay fraction

1. Make the volume of the suspension to about 300 ml with water.
2. Adjust the pH to 7-8 (indicator paper) with a few drops of NaOH 1 *M* (only in few cases HCl will be needed).
3. Add water until the top of the suspension is 11-12 cm above the bottom. Stir and leave.
4. After a settling time read from Table 15-1 siphon off the suspension at 9 cm depth into a 1 l beaker. *Note:* Siphon into a 2 l beaker when the sample for X-ray diffraction was included.
5. Repeat Steps 3 and 4. Siphon the second lot into same beaker as the first. Homogenize by stirring.
   Note: When X-ray diffraction is done also, at this stage take out a part of the suspension (about 1/5) and store in a polythene bottle. Proceed with this as described in Chapter 16.
6. Add 10 ml BaOAc 0.5 *M,* stir and leave suspension to settle.
7. Decant and discard clear supernatant solution and transfer sediment to a 250 or 380 ml centrifuge bottle.
8. Bring volume to about 200 ml with water and add 5 ml BaOAc 0.5 *M.*
9. Close the bottle and shake for about 15 minutes in shaking machine.
10. Centrifuge, and decant and discard clear supernatant solution.
11. Bring volume to 200 ml with water and shake to re-suspend the clay.
12. Repeat Steps 10 and 11 until peptization of the suspension is obtained.
13. Add 3 drops of BaOAc 0.5 *M* and homogenize.
14. Centrifuge and decant and discard clear supernatant solution.
15. Transfer sediment to round-bottom freeze-dryer flask and freeze-dry.
16. Transfer approx. 1 g of dry material to a tared porcelain crucible of 30 ml and dry overnight in an oven at 110°C.
17. Transfer crucibles to desiccator to cool and weigh (accuracy 0.001 g).
18. Place crucibles in furnace and heat at 900°C for 4 hours.
19. Cool the furnace and crucibles to about 100°C (furnace may be open) and transfer crucibles to desiccator. After cooling weigh crucible (accuracy 0.001 g). Use loss in weight to calculate the **"loss on ignition"**. Usually the material will remain loose during heating; if not, grind the sample gently in an agate mortar and dry in oven (110°C) for 1 hour.

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* Although the removal of carbonate is in principle an optional procedure (like in the particle-size analysis), in practice it is usually obligatory as calcium carbonate prohibits proper peptization of the suspension and thereby the proper separation of the clay. In contrast to the particle-size determination, here usually no dispersing agent may be added as this affects the chemical composition of the sample. If for some reason removal of carbonate is undesirable (it may also affect the chemical composition), then correction of the final results for added dispersing agent (e.g. sodium hexametaphosphate) can be considered.

20. Weigh 600 mg ignited sample and 2400 mg $Li_2B_4O_7$ into a special flat-bottom platinum crucible and make a bead at approx. 1200°C with a high-frequency heater or in an oven.
21. Analyze beads with X-ray fluorescence spectrometer against beads of standard mixtures according to apparatus instruction.

Table 15-1. Settling time after which the clay fraction (<2 μm) is siphoned off at 9 cm depth and the corresponding suspension temperature.

Temp °C	Hrs.	Mins.
19	7	7
20	6	57
21	6	47
22	6	37
23	6	28
24	6	19
25	6	10
26	6	2
27	5	55

Temp °C	Hrs.	Mins.
28	5	46
29	5	39
30	5	32
31	5	24
32	5	18
33	5	11
34	5	5
35	4	59

15-6 CALCULATIONS

The PW 1404 XRF spectrometer is programmed to determine the contents of the following elements: Major elements (expressed as oxides): Al, Fe, Si, Ca, Mg, K, Na, P, Ti, Mn. Minor elements (expressed as elements): Cu, Cr, Ni, Rb, Sr, Ba, Co, Ga, La, Nb, Pb, V, Zn, Zr.
The apparatus can be programmed to determine other elements.

With the present apparatus the lower limits of detection are in practice:

Major elements (as oxides): 0.01 - 0.03 %
Minor elements (as elements): 10 - 20 mg/kg

16. X-RAY DIFFRACTOMETRY

16-1 PRINCIPLE

The clay fraction is separated from the fine earth and deposited in an oriented fashion on porous ceramic plates to be analyzed on an X-ray diffractometer. Unoriented powder specimens of clay and other fractions are analyzed on the same apparatus or with a Guinier X-ray camera (photographs).

16-2 APPARATUS AND MATERIALS

Water bath
Drying oven
Furnace (with accurate temperature control)
Milk shaker
Siphons
Porous plate material (unglazed tile or *Diapor M8G*[*])
Suction apparatus (see Fig. 16-1)(Huting & Van Reeuwijk, 1986)
Vacuum pump
Spray-bottle
X-ray diffractometer (Philips PW 1820/1710)
Guinier X-ray camera (ENRAF Nonius FR 552)
JCPDS X-ray Diffraction File

16-3 REAGENTS

Acetate buffer solution, 1 M, pH 5. Dissolve 680 g $CH_3COONa.3H_2O$ in 4.5 l water.
Adjust to pH 5 with approx. 250 ml glacial acetic acid (use pH-meter). Dilute to 5 l.
Hydrogen peroxide, 30%.
Sodium chloride saturated solution. Dissolve 375 g NaCl in 1 l warm water (70-80°C). Cool.
Sodium hydroxide solution, 1 M. Dissolve 40 g NaOH in 900 ml water and make to 1 l.
Magnesium chloride solution, 0.5 M. Dissolve 102 g $MgCl_2.6H_2O$ in water and make to 1 l.
Glycerol/alcohol mixture 1:1. Dilute 100 ml glycerol with 100 ml ethanol 96%.
Potassium chloride solution, 1 M. Dissolve 76 g KCl in water and make to 1 l.
Formamide ($HCONH_2$), specific density 1.13 kg/l.

16-4 PROCEDURE

16-4.1 Preparation of clay suspension

(This procedure is virtually identical to the one given in Section 15-5 and leads to the same suspension as obtained in 15-5.3 Step 5.)

15-4.1.1 Oxidation of organic matter

1. Weigh an amount of fine earth containing about 1 g of clay into a 500 ml beaker (high type).
   Note: If X-ray fluorescence spectroscopy is done on the sample as well use a sample containing 3.5 to 4 g of clay and use a 1 l beaker.
2. Add 15 ml water and 15 ml H_2O_2 30%. Leave overnight. In case of excessive frothing add a little ethanol or place in a basin or sink partly filled with cold water. Keep beakers covered with a watch-glass as much as possible.
3. The next day, place beaker on hot water bath (80°C) and a few times add 5-10 ml increments of H_2O_2 30%

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[*] Manufactured by Schumacher Fabrik, Bietigheim/Württemberg, Germany.

(each time when effervescence has subsided) until decomposition of organic matter is completed: the supernatant is usually clear then.
4. Place beaker on hot plate and boil gently for about 1 hour to remove H_2O_2.
5. Remove beaker from hot plate and allow to cool.
6. Agitate suspension with a milk shaker for 2-3 minutes.
7. Return suspension to beaker and make volume to about 300 ml with water. Let suspension settle.
8. If no settling occurs add 5 ml saturated NaCl solution and stir. Leave to settle.
9. Siphon off and discard the clear supernatant solution.

Now, a distinction is made on basis of the presence or absence of calcium carbonate:

1. Calcareous soils ($pH\text{-}H_2O > 6.5$)
2. Non-calcareous soils ($pH\text{-}H_2O \leq 6.5$).

From the calcareous soils the carbonate is removed with acetate buffer (16-4.1.2).
If carbonate is absent proceed with 16-4.1.3 (Separation of clay).

16-4.1.2 Removal of carbonate

1. Add approx. 100 ml acetate buffer pH 5 and place on hot water bath (80°C). Swirl occasionally. Keep beakers covered with a watch-glass as much as possible.
2. After effervescence has stopped, add increments of 5 ml glacial acetic acid at intervals of about an hour until effervescence does nor recur after addition of an increment.
3. Transfer suspension to a large centrifuge bottle (250 or 380 ml) and centrifuge-wash twice (or three times at high $CaCO_3$ content, i.e. >10%).
4. Wash sample back into its rinsed 500 ml beaker and continue with 16-4.1.3 (next section).

16-4.1.3 Separation of clay fraction

1. Make volume of the suspension to 300 ml with water.
2. Adjust the pH to 7-8 (indicator paper) with a few drops of NaOH 1 *M* (only in few cases HCl will be needed).
3. Add water until the top of the suspension is 11-12 cm above the bottom. Stir and leave.
4. After a settling time indicated by Table 16-1 siphon off the suspension at 9 cm depth into a 1 l beaker.
5. Repeat Steps 3 and 4. Siphon the second lot into same beaker as the first. Homogenize by stirring.

Table 16-1. Settling time after which the clay fraction (<2 μm) is siphoned off at 9 cm depth and the corresponding suspension temperature.

Temp °C	Hrs.	Mins.
19	7	7
20	6	57
21	6	47
22	6	37
23	6	28
24	6	19
25	6	10
26	6	2
27	5	55

Temp °C	Hrs.	Mins.
28	5	46
29	5	39
30	5	32
31	5	24
32	5	18
33	5	11
34	5	5
35	4	59

16-4.2 Preparation and analysis of oriented clay specimen

16-4.2.1 General Run

1. Dilute suspension in a test tube with water until a fluorescent lamp of the laboratory lighting becomes just visible through it as a narrow bright line (rule of fist).
2. Place porous plate in the suction apparatus (see Fig. 16-1), wet the plate with water from a washing bottle, apply vacuum, and pass through approx. 5 ml suspension (containing about 10 mg of clay).
3. Similarly pass through about 5 ml $MgCl_2$ 1 *M* solution followed by 3 times 5 ml water.
4. Release vacuum, take specimen out of suction apparatus with a spatula.
5. Place specimen on a piece of filter paper and allow to air-dry overnight.
6. Run X-ray diffraction (*XRD*) between 3° and 42° 2Θ (= down to a spacing of 2.50 Å).

If this general diffractogram shows a reflection in the 11-15 Å range proceed with 16-4.2.2 (glycerol treatment). If the presence of halloysite is suspected (7.3 Å and/or 10.4 Å peak) carry out the formamide test (16-4.2.4).
Note: The 10.4 Å peak may also indicate the presence of palygorskite.

16-4.2.2 Glycerol treatment

1. Place Mg-saturated specimen on an upside-down petri-dish in a glass tray filled with a thin layer of a 1:1 glycerol/ethanol mixture. Spray the specimen with a 1:1 glycerol/ethanol mixture with a spray-bottle and place lid or cover on tray.
2. Place tray in drying-oven and heat overnight at 60-70°C.
3. Run *XRD* between 3° and 16° 2Θ (= down to 6.5 Å).

If not all 11-15 Å reflections have shifted to beyond 17 Å proceed with 16-4.2.3 (K-treatment).

16-4.2.3 Potassium treatment

1. Place the glycerol-treated specimen in the suction apparatus, apply vacuum and pass through approx. 5 ml of water to remove the glycerol.
2. Pass through 5 ml KCl 1 *M* solution followed by 3 times 5 ml water.
3. Release vacuum and place specimen on a piece of filter paper and allow to air-dry for a few hours.
4. Place specimen in drying oven and dry at 105°C for at least 2 hours.
5. Run *XRD* between 3° and 16° 2Θ.

Remark: In certain cases (e.g. to distinguish between low and high-charge types) it is useful to apply also other temperatures: air-dry, 250°C etc., and/or to run *XRD* of a glycerolated K-saturated specimen.

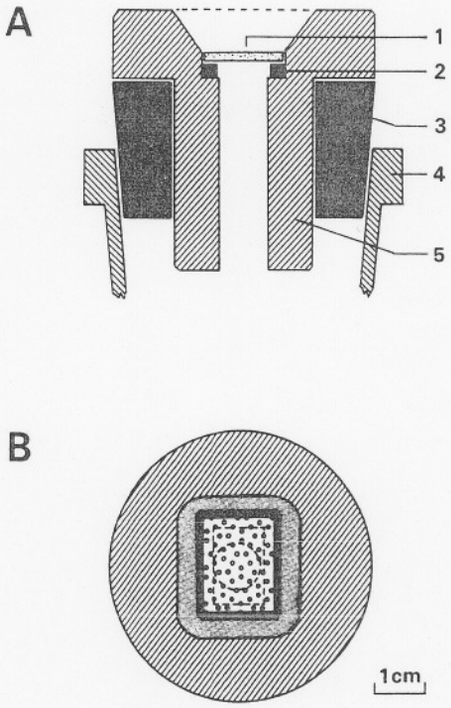
16-4.2.4 Formamide test for halloysite

Intercalation of formamide in the interlayer of halloysite is rapid whereas that in kaolinite is sluggish. Upon intercalation the basal spacing of halloysite will shift to 10.4 Å. Subsequent heating at 100°C makes all kandites collapse to 7 Å allowing a distinction from mica/illite and palygorskite.

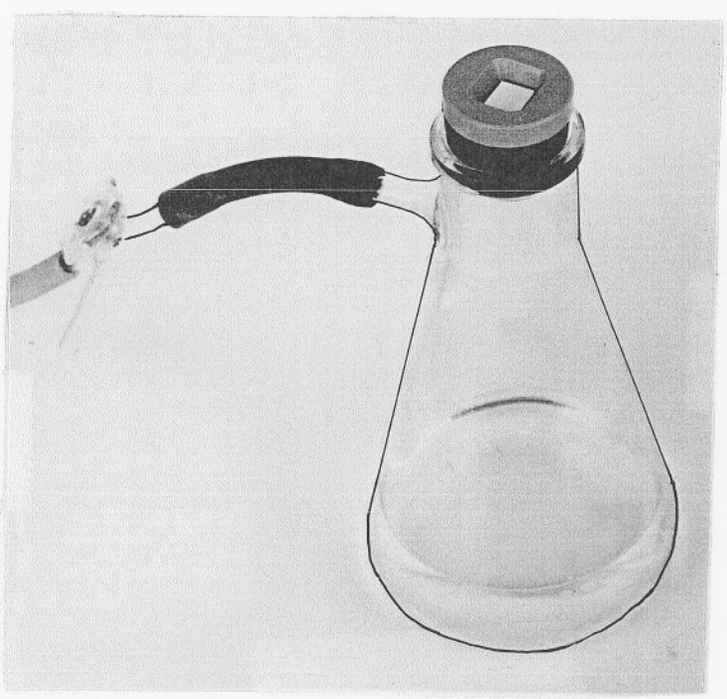
1. Make Mg-saturated specimen as indicated for *General Run* (16-4.2.1) or wash glycerol-treated specimen as indicated in 16-4.2.3 Step 1 (if no K-treatment is applied).
2. If no *General Run* is made, run *XRD* between 3° and 16° 2Θ.
3. Spray the specimen with formamide with a spray-bottle.
4. Allow to dry for 20-30 minutes (in any case no longer than 1 hr.) and run *XRD* between 3° and 16° 2Θ.
5. Heat the specimen in drying oven at 100°C for 10-15 minutes and re-run *XRD*.

Reference:

Churchman et al. (1983)



A. Vertical cross-section. 1. Porous plate.
2. Rubber or neoprene washer.
3. Perforated rubber stopper. 4. Rim of vacuum flask.
5. Stem. B. View from above.



Complete unit connected to vacuum line.

Fig. 16-1. Suction apparatus for the preparation of porous-plate clay specimens (Huting and Van Reeuwijk, 1986).

16-4.3 Analysis of unoriented powder sample on diffractometer

The procedure is the same for all size fractions. The clay powder can be obtained by drying the clay suspension in an oven or by freeze-drying. Then carefully powder the clay and/or the other fractions in an agate mortar and fill the sample holder with powder instead of with the porous plate. Run specimen in the diffractometer between 3° and 42° 2Θ.

16-4.4 Analysis of unoriented powder sample with the Guinier camera

About 10-25 mg powder of any size fraction obtained as described above in 16-4.3 is mixed with about the same volume of stop-cock grease or glycerol (smectite expansion!) and smeared onto the sample grid of the Guinier camera. Place grid in camera and make X-ray photograph.

16-5 INTERPRETATION

The X-ray diffractograms produced by the Philips PW 1820/1710 assembly show the *d*-values (spacings) in Å printed above all reflections of some significance. The *d*-value of weak reflections can be obtained directly with a special ruler or indirectly with the 2Θ scale at the bottom of the diffractogram. Identification of the minerals is done with the help of the JCPDS Diffraction Data File.
The Guinier photos are interpreted with a special ruler and an illuminated table and using the JCPDS File.

Reference

JCPDS Diffraction Data File (1974 or later editions).

17. SPECIFIC SURFACE AREA

17-1 PRINCIPLE

The sample is saturated with ethylene glycol monoethyl ether (EGME), after which the excess is removed by vacuum suction. Under correct conditions a monomolecular layer of EGME will be left behind on the soil surface. The mass of this layer is a measure for the surface area.

17-2 APPARATUS

Vacuum pump, electrical (<0.05 bar). Preferably with automatic on-off switch
Vacuum desiccators with extra perforated plate and bent air-inlet
Vacuum erlenmeyer flask 1 l with rubber stopper, plastic tube and funnel (for EGME trap)
Vacuum erlenmeyer flask 2 l with rubber stopper (for air-inlet)
Manometer, 2-way stopcocks, 3-way stopcocks
Glass weighing bottles, 40 mm diameter, 25 mm high
Analytical balance
Petri dishes, 80 mm diameter
Pipette 2 ml, or adjustable pipette

17-3 REAGENTS

Ethylene glycol monoethyl ether (EGME) (= 2-ethoxyethanol)
Phosphor pentoxide
Calcium chloride, anhydrous, pellets 2-5 mm.

17-4 APPARATUS ASSEMBLY (see Fig. 17-1)

EGME-trap

Perforate rubber stopper of a 1 l vacuum erlenmeyer flask and push a tightly fitting plastic tube through the perforation. Make a number of 2-3 cm incisions in bevelled edge of a small plastic funnel (small enough to pass the opening of the flask) and fit this upside-down in the plastic tube. The funnel must just touch the bottom of the flask. Fill the flask with $CaCl_2$ pellets up to a few centimetres below the outlet and fit stopper.

Air-inlet

Perforate rubber stopper of a 2 l vacuum erlenmeyer flask and push a tightly fitting tube through the perforation down to a few centimetres above bottom of flask (An even larger vessel or flask, if available, is preferred). The tube is fitted with a stopcock (stopcock 1) to open or close the inlet. Cover the bottom with a 1-2 cm layer of P_2O_5.

Vacuum desiccator

Place a number of petri-dishes on the bottom of the desiccator as well as on the perforated plate (8 dishes fit into a desiccator of 30 cm diameter). Place a second perforated plate on the uppermost dishes.

The assembly

Place manometer in between two 3-way stopcocks. Connect two vacuum desiccators, with one (stopcock 2) of the two 3-way stopcocks. Of the other 3-way stopcock (stopcock 3) connect one end to the outlet of the air-inlet flask and the other to the plastic tube of the EGME-trap. Connect the glass outlet of the EGME-trap to the vacuum pump (with stopcock 4 in this connection).
Note: The assembly can readily be extended with more vacuum desiccators.

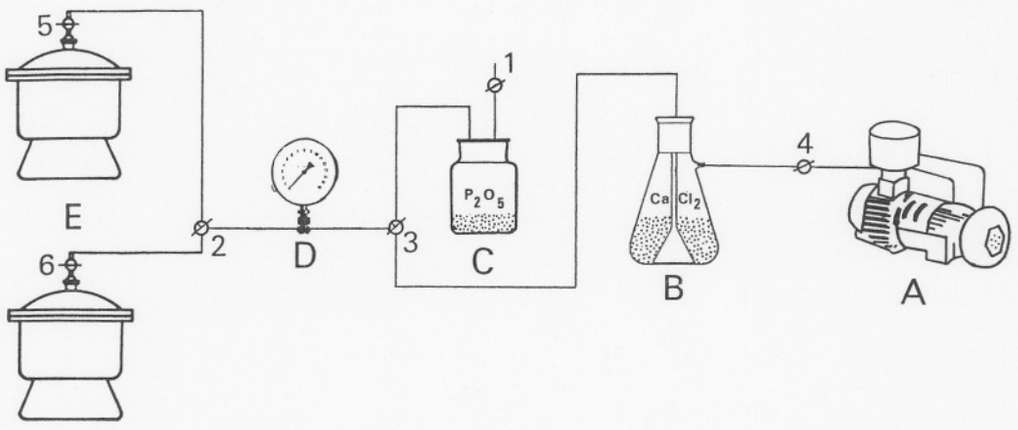


Fig. 17-1. Schematic assembly of apparatus for the determination of specific surface area with *EGME*. A. vacuum pump; B. *EGME*-trap; C. air-inlet; D. manometer; E. desiccators.

17-5 PROCEDURE

17-5.1 Safety precautions

While working with P_2O_5 the use of safety glasses, gloves and a filter mask is recommended.

17-5.2 Drying of samples

1. Cover the bottom of the petri-dishes with a thin layer of P_2O_5.
2. Mark weighing bottles and lids. Tare.
3. Weigh approx. 3.5 g of air-dry fine earth into a weighing bottle and place in vacuum desiccator (without lids. Include a reference sample.
   Note: Plastic weighing bottles are unsuitable because of electrostatic attraction of soil particles.
4. Switch 3-way stopcock no. 3 in position connecting pump with desiccators (and closing off P_2O_5 air-inlet).
5. Open desiccator stopcocks 5 and 6 and apply vacuum. Dry for 48 hours (e.g. during a week-end).
6. Release vacuum as follows:
   1) Close desiccator stopcocks 5 and 6
   2) Close stopcock 4
   3) Switch stopcock 3 in position connecting P_2O_5 air-inlet with desiccator (and closing off *EGME*-trap)
   4) Open stopcock 1 of air-inlet and then carefully stopcock 5 of desiccator.
7. After release of vacuum, close stopcock 1 of air-inlet, open desiccator and immediately place lids on weighing bottles.
8. Release vacuum of second desiccator not until samples of the first have been saturated with *EGME* (described next).

17-5.3 Saturation with *EGME*

1. Weigh samples on analytical balance (accuracy 0.001 g). Do not return bottles to desiccator.
2. Carefully remove P_2O_5 from petri-dishes and discard in safe way.
3. Fill petri-dishes with anhydrous $CaCl_2$ and re-assemble desiccator.
4. Remove lid from weighing bottle and with a 2 ml pipette drop *EGME* on sample until this is just saturated (this usually takes 1.5-2 ml). Place lid on weighing bottle. One by one, treat all samples of desiccator likewise.

5. Remove lids and place bottles back into re-assembled desiccator. Close desiccator.
6. Now release vacuum of second desiccator and treat this as described in steps 1 through 4 above.
7. Switch stopcocks in position for vacuum (see 17-5.2 steps 4 and 5) and apply vacuum.
8. Leave desiccators under vacuum for about 10 days.

17-5.4 Constant weight

1. Release vacuum as indicated in 17-5.2 steps 6 and 7.
2. Place lids on weighing bottles and weigh bottles on analytical balance.
3. Remove lids and place bottles back in desiccator. Apply vacuum.
4. Repeat steps 1 through 3 every day until the difference between the two last weighings is less than 10 mg.
5. Continue this procedure but close desiccator stopcock one hour after vacuum was applied (so that a state of *EGME* equilibrium may be reached). Leave until the next day.
6. Release vacuum as indicated above, weigh the bottles and place back in desiccator.
7. Repeat steps 5 and 6 until constant weight. This is achieved when the deviation between three consecutive daily weighings is less than 1 mg per day.
8. The mean of the two lowest of these readings is used for the calculation.

17-6 CALCULATIONS

First calculate:

$$\text{Retention of } EGME: \quad R \text{ (mg/g soil)} = \frac{E-P}{P-T} \times 1000$$

where

E = weight of *EGME*-treated sample + bottle in gram
P = weight of P_2O_5 treated sample + bottle in gram
T = weight bottle in gram (tare)

then:

$$\text{Specific surface area:} \quad S \text{ (m}^2\text{/g soil)} = \frac{R}{0.286}$$

where

0.286 = weight in milligram of a 1 m^2 monomolecular layer of *EGME*.

Also:

$$\text{Specific surface area of clay fraction:} \quad S_{clay} \text{ (m}^2\text{/g clay)} = S \times \frac{100}{C}$$

where

C = clay content in %.

REFERENCES

Heilman et al. (1965)
USDA, SCS (1982) p. 90

18. SOIL WATER RETENTION CURVE (pF-curve)*

18-1 PRINCIPLE

The water content is determined of soil samples that have been equilibrated with water at various suction (tension) values. For low suction values undisturbed core samples are equilibrated on a silt and kaolin bath respectively, for high suction values disturbed samples are equilibrated in pressure plate extractors. The bulk density is calculated from the core sample weight.

Two slightly different procedures are described. The pathways for the low-suction range are identical but differ for the high-suction range. When *fine earth* is used as disturbed sample then ***Procedure A*** is followed. Sometimes such a separate sample is not available and then a (sub)sample has to be taken from the core sample after completion of the low-suction range. In this case ***Procedure B*** is followed.

18-2 APPARATUS

Silt bath with hanging water column (= water manometer)
Kaolin bath with hanging water and mercury column (= mercury manometer). Both baths connected to water-jet pump.
Linen or nylon cloth (e.g. of a shirt)
Flat basin or tray with cover
5-bar** pressure plate extractor (Soil Moisture Equipment Corp.)
15-bar pressure plate extractor (ditto)
Pressure source (compressor or cylinder) with necessary control manifolds
Steel sample rings with bevelled edge and flat caps, diameter 5 cm, content 100 ml.

18-3 PROCEDURE A (when disturbed sample is available)

18-3.1 Undisturbed core samples (pF 0 - 2.7)

1. Uncap ring containing the core sample, if necessary carefully cut off excess soil with a knife, and fix a piece of cloth like a cap to one side of the ring with an elastic.
2. Place ring in basin (cloth downward) of which the bottom is covered with about 1 cm water.
3. Place cover on basin and allow to soak for 1 to 2 weeks (light textured soils will be saturated quicker than heavy soils).
4. Take ring carefully out of basin, wipe off any water hanging under the cloth and weigh (accuracy 0.01 g) (***Weight A***). This gives the water content at pF 0 (moisture tension = -1 cm water head or 0.001 bar suction).
   Note 1: This pF value is relatively inaccurate since the moisture tension ranges from +1 cm water at the bottom of the ring to -4 cm at the top of the ring.
   Note 2: Record any irregularity of the samples such as cracks, holes, swelling, or incomplete filling of the ring.
5. Place ring on silt bath which has been set at a moisture tension of -10 cm water head (0.01 bar, pF 1.0). Leave for about a week (place cover on silt bath!).
6. Take ring carefully off the silt bath (gently wipe off any adhering silt) and weigh. (***Weight B***).
7. Repeat Steps 5 and 6 at moisture tensions of -31.6 cm water (0.03 bar, pF 1.5), and -100 cm water (0.1 bar, pF 2.0). (***Weights C*** *and* ***D***).
8. Repeat Steps 5 and 6 using the kaolin bath at moisture tensions of -200 cm water (0.2 bar, pF 2.3) and -500 cm water (0.5 bar, pF 2.7). (***Weights E*** *and* ***F***).
9. Transfer ring (with sample and cloth, but without elastic) to drying oven and dry for at least 72 hours at 105°C. *Note:* Elastics produce a nauseating smell when heated at 105°C. They must therefore be kept outside the oven on a labelled place in the same sequence as the rings in the oven so that they can be weighed together with their original sample ring.

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* pF is an obsolete but still used term. It may be defined as the logarithm of the moisture *suction* or as the logarithm of the negative moisture *tension*, both in cm head of water. For instance, pF 2 corresponds with a *suction* of 100 cm or a *tension* of -100 cm head of water (≈0.1 bar or 10 kPa).

** Bar is an obsolete but still used unit of pressure. In the present procedure the following relationship is used: 1 bar = 100 kPa = 1000 cm water head.

10. Weigh the ring (with sample, cloth and elastic). (***Weight G***).
11. Remove sample and cloth (and elastic) from the ring, clean ring and cloth and discard sample.
12. Weigh ring, cloth and elastic. (Tare: ***weight T***).

Remark: Ring samples may also be equilibrated in a 5-bar plate extractor instead of on silt and kaolin baths. A longer equilibration time is then usually needed because of less adequate contact between sample and plate. This may be improved by a thin layer of kaolin on the plate.

18-3.2 Disturbed samples (pF 3.4 and 4.2)

The moisture content at pF 3.4 (2.5 bar suction) is determined with the 5-bar pressure plate extractor and at 15 bar with the 15-bar extractor. The procedure is the same for both:

1. To saturate the porous extractor plates submerge them in water in a basin for 24 hours.
2. Place saturated plate on the table and place rubber rings (5 cm diameter, 1 cm high) on plate; each plate can take 12 rings.
3. Fill the ring with air-dry fine earth with a spoon (about 25 g).
4. Add water drop-wise until the sample is just saturated.
5. With the back of a spoon slightly compress the sample to ensure good contact between soil particles and/or aggregates. *Do not puddle!* If necessary add a few more drops of water. Make a situation sketch to identify samples or label the rings.
6. Install plate in lowermost position in extractor and continue with the next plate.
7. After placing the last plate, close the extractor, leave for 6 hours and apply pressure according to instruction. Leave for one week. The applied suction or pressure needs to be inspected (and readjusted) once or twice a day.

   Note: Inspect the outlets of the porous plates. If they continue to bubble after a few hours, the plate is probably defective and should be replaced by another.
8. Release pressure and open the extractor.
9. Transfer sample with a spoon to a tared moisture tin, weigh immediately (accuracy 0.01 g) (calculate **net moist weights** for 2.5 bar: ***H***, for 15 bar: ***K***) then place in drying oven and dry overnight at 105°C.
10. Weigh again (calculate **net dry weights** for 2.5 bar: ***I***, for 15 bar: ***L***).

18-3.3 Calculations

First calculate:

Dry core-sample weight:	$S = G - T$
Moisture weight at 2.5 bar (pF 3.4):	$M = H - I$
Moisture weight at 15 bar (pF 4.2):	$N = K - L$

Then the *moisture content* (in wt%, w/w) at the various pF values:

pF 0.0 (1 cm or 0.001 bar or 0.1 kPa)	$= \frac{A-G}{S} \times 100\%$
pF 1.0 (10 cm or 0.01 bar or 1 kPa)	$= \frac{B-G}{S} \times 100\%$
pF 1.5 (31.6 cm or 0.03 bar or 3.2 kPa)	$= \frac{C-G}{S} \times 100\%$
pF 2.0 (100 cm or 0.1 bar or 10 kPa)	$= \frac{D-G}{S} \times 100\%$
pF 2.3 (200 cm or 0.2 bar or 20 kPa)	$= \frac{E-G}{S} \times 100\%$
pF 2.7 (500 cm or 0.5 bar or 50 kPa)	$= \frac{F-G}{S} \times 100\%$
pF 3.4 (2.5 bar or 250 kPa)	$= \frac{M}{I} \times 100\%$
pF 4.2 (15 bar or 1.5Mpa)	$= \frac{N}{L} \times 100\%$

The *bulk density* is obtained by:

$$\text{Bulk density (kg/litre)} = \frac{S}{\text{ring volume}} = \frac{S}{100}$$

Note: In case of incomplete filling of the ring (see Note 2 in Section 18-3.1 Step 4), make a correction for the ring volume (1 mm height of ring corresponds with a volume of 2 cm^3).

Conventionally, in pF curves the moisture content of the soil is expressed in *volume* % (w/v) rather than in *weight* % (w/w). To convert *wt%* to *vol%* use equation:

$$\text{Moisture content (vol \%)} = \text{Moisture content (wt \%)} \times \text{bulk density}$$

"Available moisture" is an arbitrary parameter that can be derived from the pF curve. It may be defined as the quantity of water available in the soil between the "field capacity" and the "wilting point". The former is an arbitrary point on the pF curve between pF 2.0 and 2.5 (often, 2.2 is taken). For the wilting point usually pF 4.2 is taken.

The *moisture content at 1/3 bar* (≈ pF 2.5) can be read from the pF-curve.

18-4 PROCEDURE B (when disturbed or fine earth sample is *not* available)

18-4.1 Undisturbed core samples (pF 0 - 2.7)

Down to Step 9 this procedure is identical to that in 18-3.1.

1. Uncap ring containing the core sample, if necessary carefully cut off excess soil with a knife, and fix a piece of cloth like a cap to one side of the ring with an elastic.
2. Place ring in basin (cloth downward) of which the bottom is covered with about 1 cm water.
3. Place cover on basin and allow to soak for 1 to 2 weeks (light textured soils will be saturated quicker than heavy soils).
4. Take ring carefully out of basin, wipe off any water hanging under the cloth and weigh (accuracy 0.01 g) (***Weight A***). This gives the water content at pF 0 (moisture tension = -1 cm water head or 0.001 bar suction).
   Note 1: This pF value is relatively inaccurate since the moisture tension ranges from +1 cm water at the bottom of the ring to -4 cm at the top of the ring.
   Note 2: Record any irregularity of the samples such as cracks, holes, swelling, or incomplete filling of the ring.
5. Place ring on silt bath which has been set at a moisture tension of -10 cm water head (0.01 bar, pF 1.0). Leave for about a week (place cover on silt bath!).
6. Take ring carefully off the silt bath (gently wipe off any adhering silt) and weigh. (***Weight B***).
7. Repeat Steps 5 and 6 at moisture tensions of -31.6 cm water (0.03 bar, pF 1.5), and -100 cm water (0.1 bar; pF 2.0). (***Weights C and D***).
8. Repeat Steps 5 and 6 using the kaolin bath at moisture tensions of -200 cm water (pF 2.3) and -500 cm water (0.5 bar, pF 2.7). (***Weights E and F***).
9. Take out two subsamples from the ring with a tea-spoon (subsample size approx. 1/6 of whole sample) for pF 3.4 and 4.2 determinations (see 18-4.2).
10. Weigh ring (with remaining sample and cloth). (***Weight P***).
11. Transfer ring (with sample and cloth) to drying oven and dry for at least 72 hours at 105°C.
    Note: Elastics produce a nauseating smell when heated at 105°C. They must therefore be kept outside the oven on a labelled place on in the same sequence as the rings in the oven so that they can be weighed together with their original sample ring.
12. Weigh ring (with sample, cloth and elastic). (***Weight Q***).
13. Remove sample and cloth (and elastic) from the ring, clean ring and cloth and discard sample.
14. Weigh ring, cloth and elastic. (Tare: ***weight T***).

Remark: Ring samples may also be equilibrated in a 5-bar plate extractor instead of on silt and kaolin baths. A longer equilibration time is then usually needed because of less adequate contact between sample and plate. This may be improved by a thin layer of kaolin on the plate.

18-4.2 Disturbed samples (pF 3.4 and 4.2)

Except for Step 3 this procedure is identical to that in 18-3.2.
The moisture content at pF 3.4 (2.5 bar suction) is determined with the 5-bar pressure plate extractor and at 15 bar with the 15-bar extractor. The procedure is the same for both:

1. To saturate the porous extractor plates submerge them in water in a basin for 24 hours.
2. Place saturated plate on the table and place rubber rings (5 cm diameter, 1 cm high) on plate; each plate can take 12 rings.
3. Fill the ring with about 25 g material taken from ring sample (≈ 1/6 of ring sample) after this has completed its suction range.
4. Add water drop-wise until the sample is just saturated.
5. With the back of a spoon slightly compress the sample to ensure good contact between soil particles and/or aggregates. *Do not puddle!* If necessary add a few more drops of water. Make a situation sketch to identify samples or label the rings.
6. Install plate in lowermost position in extractor and continue with the next plate.
7. After placing the last plate, close the extractor, leave for 6 hours and apply pressure according to instruction. Leave for one week. The applied suction or pressure needs to be inspected (and readjusted) once or twice a day.
   Note: Inspect the outlets of the porous plates. If they continue to bubble after a few hours, the plate is probably defective and should be replaced by another.
8. Release pressure and open the extractor.
9. Transfer sample with a spoon to a tared moisture tin, weigh immediately (accuracy 0.01 g) (calculate **net moist weights** for 2.5 bar: ***H***, for 15 bar: ***K***) then place in drying oven and dry overnight at 105°C.
10. Weigh again (calculate **net dry weights** for 2.5 bar: ***I***, for 15 bar: ***L***).

18-4.3 Calculations

The calculation is identical to that given in 18-3.3. However, ***G,*** the gross dry sample weight, has to be calculated first as it could not be determined in a direct way because of the removal of subsamples:

$$G = T + \frac{Q-T}{P-T} \times (F-T)$$

Then calculate:

Dry-core sample weight:	$S = G - T$
Moisture weight at 2.5 bar (pF 3.4):	$M = H - I$
Moisture weight at 15 bar (pF 4.2):	$N = K - L$

The *moisture content* (in wt%) at the various pF values is obtained by:

pF 0.0 (1 cm or 0.001 bar or 0.1 kPa)	$= \frac{A-G}{S} \times 100\%$
pF 1.0 (10 cm or 0.01 bar or 1 kPa)	$= \frac{B-G}{S} \times 100\%$
pF 1.5 (31.6 cm or 0.03 bar or 3.2 kPa)	$= \frac{C-G}{S} \times 100\%$
pF 2.0 (100 cm or 0.1 bar or 10 kPa)	$= \frac{D-G}{S} \times 100\%$
pF 2.3 (200 cm or 0.2 bar or 20 kPa)	$= \frac{E-G}{S} \times 100\%$
pF 2.7 (500 cm or 0.5 bar or 50 kPa)	$= \frac{F-G}{S} \times 100\%$
pF 3.4 (2.5 bar or 250 kPa)	$= \frac{M}{I} \times 100\%$
pF 4.2 (15 bar or 1.5Mpa)	$= \frac{N}{L} \times 100\%$

The *bulk density* is obtained by:

$$\text{Bulk density (kg/litre)} = \frac{S}{\text{ring volume}} = \frac{S}{100}$$

Note: In case of incomplete filling of the ring (see Note 2 in Section 18-4.1 Step 4), make a correction for the ring volume (1 mm height of ring corresponds with a volume of 2 cm^3).

Conventionally, in pF curves the moisture content of the soil is expressed in *volume* % (w/v) rather than in *weight* % (w/w). To convert *wt%* to *vol%* use equation:

$$\text{Moisture content (vol\%)} = \text{Moisture content (wt\%)} \times \text{bulk density}$$

"Available moisture" is an arbitrary parameter that can be derived from the pF curve. It may be defined as the quantity of water available in the soil between the "field capacity" and the "wilting point". The former is an arbitrary point on the pF curve between pF 2.0 and 2.5 (often, 2.2 is taken). For the wilting point usually pF 4.2 is taken.

The *moisture content at 1/3 bar* (≈ pF 2.5) can be read from the pF-curve.

REFERENCES

Blake and Hartge, *in:* Klute (1986), p. 363
Klute, *in:* Klute (1986) p. 635
USDA, SCS (1972, 1982)

19. MINERALOGICAL ANALYSIS OF THE SAND FRACTION

19-1 PRINCIPLE

After removal of cementing and coating materials the sand is separated from the clay and silt by wet sieving. From the sand, the fraction 50-420 µm is separated by dry sieving. This fraction is divided into a *heavy* and a *light* fraction with the aid of a high density liquid: a solution of sodium polytungstate* with a specific density of 2.85 kg/dm^3. Of the *heavy fraction* a microscopic slide is made, the *light fraction* is selectively stained for microscopic identification of feldspars and quartz.

19-2 SEPARATION OF SAND FRACTION

19-2.1 Apparatus

Water bath
Set of sieves, including bottom
Small 50 µm sieve (diameter approx. 8 cm)
Drying oven
Evaporating dishes
Separatory funnels
Areometer (hydrometer) with range of 2.50 - 3.00 kg dm^{-3}.

19-2.2 Reagents

Hydrogen peroxide, 30%.
Hydrochloric acid, 1 M. Add 87 ml conc. HCl (37%) to about 800 ml water in a 1 l graduated beaker. Make to 1 l with water.
Deferration buffer solution, 0.3 M sodium citrate and 0.1 M sodium bicarbonate. Dissolve 88 g Na-citrate.2H_2O and 8.4 g $NaHCO_3$ in water and make to 1 l.
Sodium dithionite, powder.
Sodium chloride solution, 1 M. Dissolve 58.5 g NaCl in 1 l of water.
Sodium chloride, saturated solution. Dissolve 375 g NaCl in 1 l warm water (70-80°C). Cool.
Sodium polytungstate solution (SPT), specific density = 2.85 kg/dm^3. Dissolve 830 g of $3Na_2WO_4.9WO_3.2H_2O$ powder** in 160 ml water and, with the help of an areometer, adjust the specific density of this solution to 2.85 kg/dm^3. To increase the density, either add more *SPT* powder to the solution or evaporate water from it. To decrease the density, add water.

19-2.3 Procedure

19-2.3.1 Oxidation of organic matter

1. Weigh out into a 1 l beaker 15 to 25 g of fine earth containing an estimated amount of 5 g of sand in the fraction 50-420 µm.
2. Add 15 ml water and 15 ml H_2O_2 30% Cover beaker with watch-glass. In case of strong frothing place beaker in basin with cold water. In addition, frothing can be tempered by "anti foam" or a few drops of ethanol.
3. Let stand overnight.
4. The next day, place beaker on hot water bath (80°C) and regularly add 5-10 ml increments of H_2O_2 30% (each time when effervescence has subsided) until decomposition of organic matter is completed: usually the supernatant is clear then.

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* The use of bromoform for this purpose is discouraged because of its highly toxic vapour.

** Supplier: SOMETU, Falkenried 4, Berlin, Germany.

7. Remove beaker from hot plate and allow to cool.
8. Add about 600 ml water, stir and let stand for about 5 minutes. Decant and discard the supernatant suspension (retaining the sand fraction). Repeat this at least two more times until a (nearly) clear supernatant is obtained.

Now, a distinction is made on basis of the presence or absence of calcium carbonate:

1. Calcareous soils: $pH\text{-}H_2O > 6.5$
2. Non-calcareous soils: $pH\text{-}H_2O \leq 6.5$

In case carbonate is present this is removed by a treatment with HCl 1 *M* (19-2.3.2). If carbonate is absent proceed with separation of the sand fraction (19-2.3.3).

19-2.3.2 Removal of carbonate

1. Add 100 ml HCl 1 *M* and place beaker on boiling water bath. Cover beaker with watch-glass, swirl occasionally. After effervescence has stopped, add increments of 25 ml HCl until effervescence does not recur after addition of new acid. Allow to cool.
   Note: The relatively harsh treatment with HCl is used here for convenience. Chemical attack of sand-size minerals to be studied is usually insignificant. Should unwanted dissolution be suspected in a particular case then removal of carbonates must be done with the mildly acid Na-acetate buffer (1 *M*, pH 5, see Chapter 16).
2. Add about 500 ml water, stir and let stand for about 5 minutes. Decant and discard the supernatant suspension.
3. Repeat Step 2 two more times. Proceed with separation of sand (19-2.3.3).

19-2.3.3 Wet separation of the sand fraction (fraction >50 μm)

1. Transfer the residue obtained above to a 50 μm sieve with a wash bottle. Wash residue on the sieve using a hard brush or a wide (3 cm) rubber policeman until the wash-water passing through the sieve is clear.
2. Wash the sand fraction remaining on the sieve into a 400 ml beaker.

Remark: Instead of carrying out above procedure, the sand fraction obtained during the particle-size determination may be used. In that case, start with: Removal of carbonate (19-2.3.2) followed by Deferration (19-2.3.4) (unless one or both of these pretreatments have already been performed).

19-2.3.4 Deferration

1. To the sand fraction obtained after the wet separation add 100 ml buffer solution.
2. Heat on water bath to about 75°C (do *not* exceed 80°C as elemental sulphur will then precipitate).
3. Add approx. 0.5 g sodium dithionite and stir constantly for about a minute and then occasionally for 5 minutes.
4. Repeat Step 3 two more times.
5. Allow sand to settle and decant.
6. For samples containing more than 5% extractable Fe_2O_3, repeat the procedure once or twice: a brownish or reddish colour of the sample may indicate still incomplete deferration.
7. Wash once more with 100 ml 1 *M* NaCl.
8. Add 100 ml water and re-disperse sediment. Repeat Steps 5 and 8 twice and transfer the residue into a porcelain dish and dry on water bath and in oven (105°C).

19-2.3.5 Dry separation of sand fraction (50-420 μm)

Transfer the dried deferrated sand to the top sieve of a set of sieves with sizes: 420 μm, 50 μm, and bottom and sieve by hand (or machine) for several minutes. The material collected on the 50 μm sieve (fraction 50-420 μm) is used for the separation of heavy minerals.

Note: If a 420 μm sieve is not available, a 500 μm sieve can be used. The boundaries of the fraction used have not been standardized but have evolved from a combination of practical experience and convenience.

Remark: For quantification purposes the sand may be divided into a number of fractions with sieves, e.g. 50-105 μm, 105-210 μm, 210-420 μm.

19-2.3.6 Separation into a heavy and a light fraction

1. Transfer the sand fraction (50-420 μm, or alternatively, 50-500 μm) into a separatory funnel filled with the *SPT* liquid.
2. To prevent evaporation stopper the separatory funnel.
3. The mixture of liquid and sand is stirred every 30 minutes during a period of 4 hours.

a. Heavy fraction

4. Release the heavy fraction into a tared evaporating dish.
5. Wash at least 5 times with water from a wash bottle. The washings must be carefully decanted into a large storage bottle.
6. The washed heavy fraction is dried on a water bath and then for about an hour in an oven (105°C). Weigh dish with sample. (Subtract tare: **net weight heavy fraction = *H*.**)

b. Light fraction

7. Filter the light fraction with a funnel and a coarse filter, collect the solution in a storage bottle.
   Note: This solution is the original *SPT* liquid and should be kept separate from the washings in the large storage bottle.
8. Wash the light fraction in the filter paper 4 or 5 times with approx. 5 ml portions of water from a wash bottle (also rinse stirring rod) and then wash into a tared evaporating dish.
9. Collect the washings and transfer to the large storage bottle mentioned in Step 5.
10. Decant water from the light fraction, dry on water bath and then for about an hour in oven (105°C). Weigh dish with sample. (Subtract tare: **net weight light fraction = *L*.**)
    Note: Alternative for Steps 8 and 10: after washing the light fraction on the filter, dry filter with sample and tap out the sample into a dish for weighing.
11. For recovery of *SPT,* transfer solution from storage bottle to beaker and evaporate to (almost) dryness on a water bath.

19-3 PREPARATION OF THE HEAVY-MINERAL MOUNT

19-3.1 Apparatus

Hot plate
Petrological microscope
Microscopic slides and cover slips
Mounting needle

19-3.2 Reagents

Canada balsam for optical microscopy.
Xylene.
Ethanol 96%.

19-3.3 Procedure

1. Clean microscopic slide with alcohol.
2. Place on a hot plate (120-130°C) and add a few drops of Canada balsam in the centre.
3. Bubbles are removed from the balsam by pricking with a mounting needle. The heavy-mineral grains are transferred to the centre of the balsam and dispersed by stirring with the mounting needle.
4. The balsam is left for a few minutes until it has "cured". This is the case when after a needle inserted into the balsam is withdrawn, the balsam adhering is hard and shiny and no longer sticky.
5. Place a clean cover-slip, heated on the hot plate, over the grains. Try to remove possible air-bubbles by very gently pressing on the cover-slip with the mounting needle.
6. Remove the slide from the hot plate and, after cooling, remove excess balsam with xylene.
7. The slide can now be used for mineral identification and counting with a petrological microscope (see 19-5.1).

19-4 STAINING THE LIGHT FRACTION FOR MINERAL ESTIMATION

19-4.1 Principle

All feldspars are stained by hemateine (reaction with Al), whereas K-feldspars are stained with Na-Co-nitrite (reaction with K), both after activating the surface with HF fumes. Quartz grains remain unstained. The stained grains are counted under the petrological or binocular microscope.

19-4.2 Apparatus

Etching assembly, consisting of a plastic container of approx. 1 l with wide cap (e.g. a chemical bottle). Attach to the underside of the cap a plastic rod or tube with a platform-like support at the end so that when the cap is placed on the container this platform is situated about 3 cm above the bottom of the container. The platform should be sufficiently large to hold a flat plastic dish of approx. 2 cm diameter and an edge of ½ to 1 cm high (e.g. cap of a centrifuge tube or of a sample vial). A model is shown in Fig. 19-1.
Nickel crucibles with round bottom, diameter approx. 5 cm
Porcelain crucible
Plastic watch-glasses
Electrical furnace
Water bath in fume-cupboard
Safety glasses and gloves

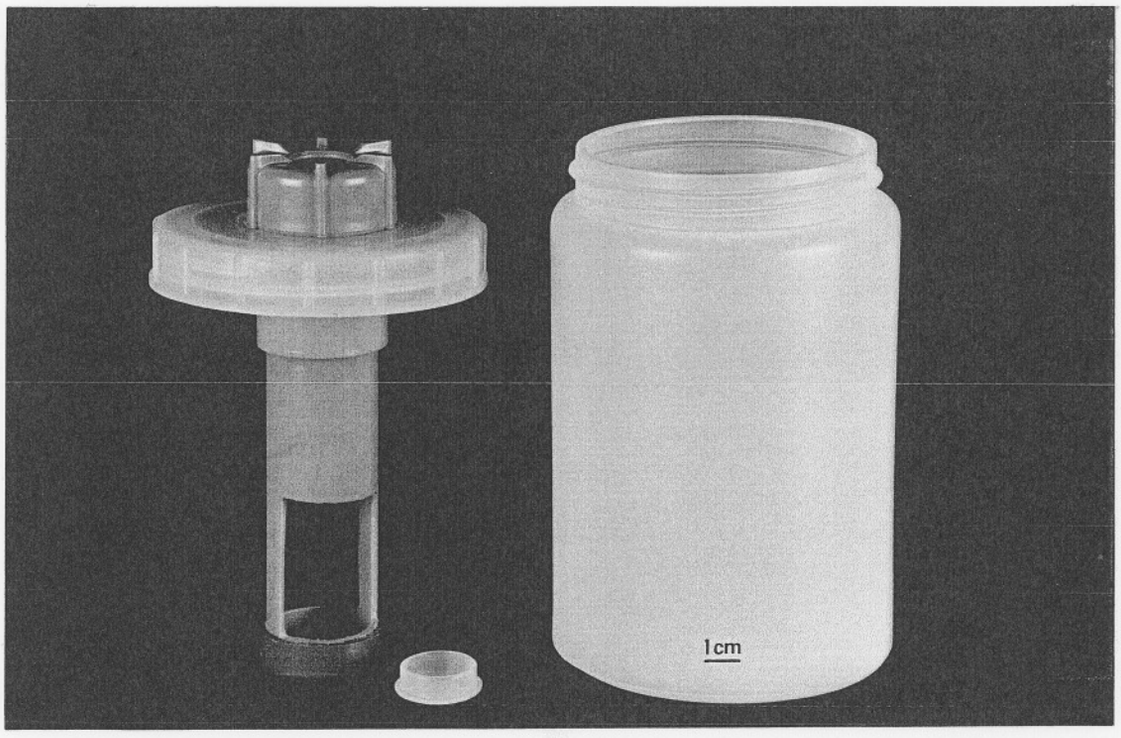

Fig. 19-1. Etching assembly.

19-4.3 Procedures

19-4.3.1 Etching

19-4.3.1.1 Reagents

Hydrofluoric acid, concentrated, 48%.
Acetone.

19-4.3.1.2 Procedure

1. Add approx. 3 ml HF to the 1 l plastic container. ***Warning:*** wear safety glasses and gloves!
2. Place container on boiling water bath in fume-cupboard. Cover opening with plastic watch-glass. After 5 minutes the container will be filled with HF fumes.
3. Spread a small amount of the light sand fraction over the bottom of the plastic dish. This is facilitated by adding a little acetone. Dry for 1 minute at 105°C.
4. Place the dish carefully on the platform under the container-lid, remove cover from container opening and place lid on the container thereby bringing the sample in the HF fumes.
   Note: The lid may be screwed on a little, but this is not necessary. ***Warning****: do not tighten* the lid!
5. After 1 minute, the lid with the sample is removed and the sample is washed and decanted 2 times with a little water and then twice with acetone (use crucible tongs to remove plastic dish).
6. After drying for 1 minute in an oven at 105°C, the etching is repeated during 2 minutes.
7. Transfer sample to porcelain crucible and place in furnace which has a temperature of 400°C.
8. Heat for 5 minutes to fix fluoride coating.
9. Allow to cool and divide sample with a small brush over two Ni crucibles.

19-4.3.2 Staining with hemateine (for all feldspars)

19-4.3.2.1 Reagents

Hemateine solution. Dissolve 50 mg hemateine in 100 ml ethanol 96%.
Acetate buffer solution, pH≈4.8. Dissolve 20 g CH_3COONa (or 33 g $CH_3COONa.3H_2O$) in about 100 ml water, add 6 ml glacial acetic acid and dilute to 200 ml with water.
Ethanol 96%.

19-4.3.2.2 Procedure

1. To an etched sample in a Ni crucible (see 19-4.3.1.2) add successively: 10 drops of the hemateine solution and 5 drops of the buffer solution.
2. Swirl crucible for 2 to 3 minutes and then allow to stand for 5 minutes.
3. Wash and decant 4 or 5 times with small increments of ethanol from a wash bottle.
4. Dry for a few minutes in oven (105°C). The feldspar grains now show a purple to bluish stain.
5. Bring (part of) the sample evenly onto a slide and carry out counting procedure (Section 19-5).

Remark: Experience has shown that the blue colour is not always stable and may fade after a few days. Therefore, counting should be done as soon as possible, at least within a few days.

19-4.3.3 Staining with Na-Co-nitrite (for K-feldspars)

19-4.3.3.1 Reagents

Na-Co-nitrite solution. Dissolve 1 g $Na_3Co(NO_2)_6$ in 4 ml water.
Note: This chemical is also known as *sodiumhexanitrocobaltate(III).*
Ethanol 96%.

19-4.3.3.2 Procedure

1. To an etched sample in a Ni crucible (see 19-4.3.1.2) add a few drops of Na-Co-nitrite solution until sample is completely submerged. Allow to stand for 1 minute.
3. Wash and decant twice with water and then with two increments of ethanol.
3. Dry for a few minutes in oven (105°C). The K-feldspars now show a yellow stain.
4. Bring (part of) the sample evenly onto a slide and carry out counting procedure (Section 19-5).

19-5 COUNTING PROCEDURE

19-5.1 Microscopy

Counting grains can be done in various ways. *Ribbon counting* is preferred to other techniques such as *line counting* and *point counting* as it has less bias towards counting larger grain sizes.
The *ribbon* technique can be done as follows: Select the width of the ribbon according to the diameter of the largest visible grain, e.g. from the 20th to the 30th mark of the eyepiece micrometer scale. From an arbitrary starting point slowly move the specimen with the mechanical stage perpendicular to the micrometer scale and count the grains whose centres cross this scale between the fixed marks. Lay out several ribbons systematically across the sample and identify and count at least 200 grains.

For identification and counting the *heavy mineral fraction* a petrographic microscope with a mechanical stage is needed; for counting stained grains of the *light mineral fraction* a petrographic microscope can be used also but a binocular microscope with a mechanical stage and incident light is preferred.

19-5.2 Calculations

1. The *weight fractions* of the heavy and light minerals (%, w/w) are calculated from the weights of the fractions obtained after separation (see 19-2.3.6):

$$\text{Heavy fraction (wt\%)} = \frac{H}{H+L} \times 100$$

$$\text{Light fraction (wt\%)} = \frac{L}{H+L} \times 100$$

where
H = weight heavy fraction
L = weight light fraction, both in gram.

2. Estimations by counting are *volume* estimations rather than *weight* estimations. Therefore, the amount of individual heavy mineral species are reported in *vol%* (v/v) of the *heavy fraction:*

$$\text{Heavy mineral species (vol\%):}\quad V_m = \frac{\text{number of counted species grains}}{\text{total number of counted grains}} \times 100$$

3. If desired, the *percentage by volume* (v/v) can be converted to *percentage by weight* (w/w) with:

$$W_m = \frac{V_m \times G_m}{\sum (V_i \times G_i)} \times 100$$

where
W_m = wt% (w/w) of mineral species m
V_m = vol% (v/v) of mineral species m
G_m = specific density of mineral species m
V_i = vol% (v/v) of all mineral species taken one (individual) at a time
G_i = specific density of all mineral species taken one at a time

4. In contrast to the heavy fraction where the specific density of the minerals may vary widely, the range of specific density of the minerals of the light fraction, quartz and feldspars, is rather narrow (2.54 - 2.76 kg/dm^3) so that, considering other inaccuracies and bias inherent in the technique, the estimations by counting (vol%, v/v) may in this case be taken to represent weight percentages (wt%, w/w) as well:

$$\text{Quartz (wt\%)} = \frac{\text{number of unstained grains}}{\text{total number of counted grains}} \times 100$$

$$\text{Feldspars (wt\%)} = \frac{\text{number of blue grains}}{\text{total number of counted grains}} \times 100 \quad (= a)$$

$$\text{K-Feldspars (wt\%)} = \frac{\text{number of yellow grains}}{\text{total number of counted grains}} \times 100 \quad (= b)$$

$$\text{Plagioclases (wt\%)} = a - b$$

5. Above calculated contents are percentages of the heavy and light fractions respectively. The percentage by weight (w/w) of each mineral species of the *whole sand fraction* (50-420 µm) is obtained by:

$$P_m \text{ (wt\%)} = W_m \times \frac{(H, L)}{H + L}$$

where:

P_m = wt% of mineral species m in whole sand fraction
W_m = wt% of mineral species m in heavy or light fraction
(H, L) = either weight $\boldsymbol{H}$ of heavy fraction, or weight $\boldsymbol{L}$ of light fraction in gram
H = weight $\boldsymbol{H}$ of heavy fraction in gram
L = weight $\boldsymbol{L}$ of light fraction in gram

Remark: Among other components that may be encountered in the light fraction are notably muscovite and volcanic glass. These may also be stained to some extent but can in most cases easily be distinguished: micas are thin and flaky, glass is isotropic and contains vesicles.

REFERENCES

Van der Plas (1962, 1966)
Brewer (1964)
Galehouse (1969)
Savage (1988)
Gregory and Johnston (1987)

20. OPTICAL DENSITY OF OXALATE EXTRACT (ODOE)

20-1 PRINCIPLE

The sample is percolated with an acid ammonium oxalate solution. The optical density of the extract is measured at 430 nm wavelength. ODOE is used in the characterisation of Podzols.

20-2 APPARATUS

Mechanical extractor* (Holmgren et al., 1977. See Fig. 9-2 on p. 9-5).
Spectrophotometer

20-3 REAGENTS

(Sufficient for some 90 extractions)

Acid ammonium oxalate solution, 0.2 M in oxalate, pH 3. Dissolve 81 g $(COONH_4)_2.H_2O$ and 54 g $(COOH)_2.2H_2O$ in 4.5 l water and make to 5 l. Prepare 0.5 l of two separate 0.2 *M* solutions of NH_4-oxalate (28 g/l) and oxalic acid (25 g/l) and add some of either solution to the mixture until the pH is 3. Store in polypropylene bottle.

Alternative way of preparation:
Solution A (ammonium oxalate): Dissolve 142 g of $(COONH_4)_2.H_2O$ in 5 l water. *Solution B* (oxalic acid): dissolve 126 g of $(COOH)_2.2H_2O$ in 5 l water. Mix 4 parts of solution *A* with 3 parts of solution *B*. Adjust the pH of the acid oxalate solution by adding either solution *A* (base) or *B* (acid).

20-4 PROCEDURE

1. "Close" the bottom of the sample (syringe) tube with approx. 1 g of filter pulp. Compress with a plunger.
2. Weigh 0.500 g fine earth into the sample tube. If necessary, level sample to even thickness with a spatula. Include a control sample and two blanks in the batch.
3. Place the sample tube in the upper disc of the extractor and with a rubber tubing (length approx. 2.2 cm) connect an extraction syringe. The plunger of this syringe is inserted in a slot of the stationary (bottom) disc of the extractor.
4. Add 15.0 ml (dispenser or pipette) acid ammonium oxalate extractant to the sample tube (while rinsing the wall of the tube). In case of hydrophobic behaviour (organic samples) some swirling may be necessary for effective wetting. Allow sample to stand for at least 30 minutes.
5. Set extractor for for 30-min extraction rate and extract until the extractant surface level is at 0.5 to 1 cm above sample. Stop extractor.
6. Place reservoir tube on top of sample tube and add 35.0 ml (dispenser or pipette) of acid ammonium oxalate extractant to reservoir tube.
7. Cover extractor with a black plastic bag to exclude light (see Remark 2). Set the extractor rate at 12-hrs extraction rate and start extractor.
8. After extraction, pull plunger of syringe down without removing it from syringe tube. Remove syringe from extractor leaving the rubber tubing on sample tube.
9. Press extract into a 50ml or 100 ml polypropylene tube (capped tablet tube, polycon)
10. "Zero" the spectrophotometer with acid ammonium oxalate reagent blank at 430 nm wavelength.
11. Read optical density (absorbance) of extract to the nearest 0.000.

Remark 1: Spodic materials should have an ODOE ≥ 0.25.

Remark 2: We have data that indicate that in this extract the contents of Al, Fe, and Si are generally lower than those obtained with the shaking procedure (Section 12-2). Therefore, it is recommended **not** to use the here described percolation procedure as a substitute for the shaking procedure for the determination of oxalate-extractable Al, Fe, and Si (see also Remark 2, p. 12-6).

REFERENCE

USDA, NRCS, NSSC (1996) p. 253-256.

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* Manufactured by Mavco Industries Inc. , 5300 N. 57th Str., Lincoln, NE 68507, USA.

21. MELANIC INDEX

21-1 PRINCIPLE

The sample is shaken with a 0.5 *M* NaOH solution and the absorbance of the extract is measured at 450 and 520 nm wavelength respectively. The ratio of the two absorbances is the "melanic index". This index can be used to differentiate *melanic* from *fulvic* Andisols.

21-2 APPARATUS

Reciprocating shaking machine
Centrifuge
Spectrophotometer

21-3 REAGENTS

(Sufficient for up to 40 samples)

Sodium hydroxide, 0.5 M. Dissolve 20 g of NaOH pellets in about 900 ml water in a 1 l volumetric flask. Cool and make to 1 l with water.

Sodium hydroxide, 0.1 M. Dissolve 4 g of NaOH pellets in about 900 ml water in a 1 l volumetric flask and make to 1 l.

"Superfloc" solution, 0.1%. Dissolve 50 mg superfloc* in 50 ml water (stir overnight in the dark)

Note: Store in the dark. This solution can be kept for about a week.

21-4 PROCEDURE

1. Weigh out into a 50 ml centrifuge tube: 0.5 g of air-dry fine earth (accuracy 0.01 g) containing > 5% organic carbon (wt/wt).
2. Add 25 ml of the 0.5 *M* NaOH solution and stopper the tube.
3. Shake for 60 minutes at room temperature (20–30°C; frequency approx. 125 strokes/min.; amplitude approx. 1 - 1.25 cm)** overnight.
4. Add one drop of superfloc solution and centrifuge for 10 minutes at 4000 rpm.
   N.B. The supernatants should be clear. In dark-coloured extracts this is not always easy to judge. In case the extract is not clear, centrifuge longer or use superspeed accessory.
5. Pipette into a 50 ml erlenmeyer or test tube 20 ml of the 0.1% NaOH solution and 1 ml of the supernatant solution if organic C content of sample ≤10%, or 0.5 ml of the supernatant if organic C content >10%. Homogenize.
7. "Zero" the spectrophotometer with the blank 0.5 *M* NaOH solution.
8. Measure absorbance of the test solutions at 450 nm and 520 nm wavelength respectively.

21-5 CALCULATION

$$\text{Melanic Index (MI)} = \frac{\text{Absorbance at 450 nm}}{\text{Absorbance at 520 nm}}$$

Remark: When $MI \leq 1.65$, Andisols are classified as *"melanic"*.

REFERENCE

Honna, T., S. Yamamoto, and K. Matsui (1988)

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* e.g., Cyanamid Superfloc N-100; Floerger Kemflock FA 20H.

**The original paper by Honna et al. (1988) does not state these shaking details. Although these are not expected to influence the results significantly, to the author's knowledge no data on this possible effect has been reported and until then some standardization seems to be in order.

APPENDIX 1. Approximate data on concentrated acids and ammonia.

	% (w/w)	Density (kg/l)	Molarity	ml required to make 1 litre solution of 1 mol(I)/l*
Acetic acid (glacial)	99	1.05	17.4	58
Hydrochloric acid	37	1.18	11.6	87
Hydrofluoric acid	48	1.15	27.6	36
Nitric acid	70	1.42	15.7	63
Perchloric acid	70	1.66	11.6	86
Phosphoric acid	85	1.69	14.7	23
Sulphuric acid	96	1.84	17.8	28
Ammonium hydroxide	25	0.90	14.3	71

*Previously called: "1 *N*(ormal) solution"

APPENDIX 2. Atomic weight of selected elements.

Element	Symbol	Atomic weight	Element	Symbol	Atomic weight
Aluminium	Al	26.98	Magnesium	Mg	24.31
Antimony	Sb	121.75	Manganese	Mn	54.94
Barium	Ba	137.34	Mercury	Hg	200.59
Boron	B	10.81	Molybdenum	Mo	95.94
Bromine	Br	79.91	Nickel	Ni	58.71
Cadmium	Cd	112.40	Nitrogen	N	14.01
Calcium	Ca	40.08	Oxygen	O	16.00
Carbon	C	12.01	Phosphorus	P	30.97
Cesium	Cs	132.91	Platinum	Pt	195.01
Chlorine	Cl	35.45	Potassium	K	39.10
Chromium	Cr	52.00	Rubidium	Rb	85.47
Cobalt	Co	58.93	Selenium	Se	78.96
Copper	Cu	63.55	Silicon	Si	28.09
Fluorine	F	19.00	Silver	Ag	107.87
Gold	Au	196.97	Sodium	Na	22.99
Hydrogen	H	1.01	Strontium	Sr	87.62
Iodine	I	126.90	Sulphur	S	32.06
Iron	Fe	55.85	Tin	Sn	118.69
Lanthanum	La	138.91	Titanium	Ti	47.90
Lead	Pb	207.19	Vanadium	V	50.94
Lithium	Li	6.94	Zinc	Zn	65.37

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