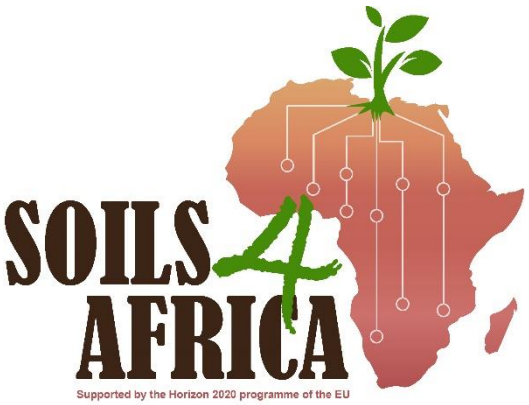

Guidance for the Laboratory Analysis

Project No. 869200

29 May 2021

Deliverable: Soils4Africa_D3.4_Guidance_LaboratoryAnalysis_v01

Version 1.0

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Project details

Project number	862900
Project acronym	Soils4Africa
Project name	Soil Information System for Africa
Starting date	01/06/2020
Duration In months	48
Call (part) identifier	H2020-SFS-2019-2
Topic	SFS-35-2019-2020 Sustainable Intensification in Africa

Document details

Work Package	3
Deliverable number	D3.4 Guidance for the laboratory analysis
Version	1
Filename	*Soils4Africa_D3.4_Guidance_laboratoryAnalysis_v01*
Type of deliverable	Report
Dissemination level	Public
Lead partners	ARC
Contributing partners	WUR, ICRAF,
Author	Garry Paterson
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Due date	31 May 2021
Submission date	29 May 2021

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Abbreviations

AfSIS	African Soil Information System
AgriLASA	Agricultural Laboratory Association of South Africa
ARC-SCW	Agricultural Research Council-Soil, Climate and Water, South Africa
DALRRD	Department of Agriculture, Land Reform and Rural Development (South Africa)
EC	European Commission
EU	European Union
LUCAS	Land Use and Coverage Area Frame Survey (EC)
GLOSOLAN	Global Soil Laboratory Network
GSP	Global Soil Partnership
ICRAF	International Centre for Research in Agroforesty, Nairobi, Kenya
ISRIC	International Soil Reference and Information Centre
JRC	Joint Research Centre – European Commission
LUCAS	Land Use and Coverage Area frame Survey
MIR	Mid-infrared spectroscopy
S4A	Soils4Africa
SANAS	South African National Accreditation System
SGS	SGS Hungary Ltd
WUR	Wageningen University & Research
WP	Work Package
SOP	Standard Operating Procedure

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1. Introduction

The soils of Africa are very diverse. From the arid sands of the Sahara, Kalahari and Namib deserts, to the alluvial soils along the Nile, the deeply weathered tropical Ferralsols, the dark clays of Ethiopian Highlands to Mediterranean-type soils at either end of the continent, it is important to know the characteristics and properties of these soils, especially where they are used for agriculture.

The main objective of the Soils4Africa project is to collect soil samples from 20 000 selected localities under agricultural land use across Africa. The main purpose is to obtain information on the distribution and level of variation of these soil properties, so that this knowledge can be used to utilize, protect and conserve the soils. Once the samples have been collected in the field, they will be transported to various regional hubs, where basic sample preparation will take place. The samples will then be transported to the delegated laboratory at ARC-Soil, Climate and Water in Pretoria, South Africa (ARC-SCW) for analysis.

Three different levels of analysis will be carried out, namely:

- Spectral analysis (mid infra-red or MIR, 4000-400 cm-1) on all 20 000 samples.
- Traditional "wet chemistry" analyses (as per LUCAS protocols) on a selected subset of between 2 000 and 3 000 samples for most wet chemical properties and more for properties that predict less well with spectroscopy (for example P, K) as specified in the Grant Agreement.
- Among the 20 000 locations, 250 "reference sites" will be selected where soil profiles will be excavated, described, classified, and sampled in more detail, including topsoil and subsoil horizons.

The wet chemistry analysis results will also be used as correlation data with the spectral data results.

This document supplies information on the types of analyses that will be performed, including protocols, equipment and any other critical information. This includes training requirements as well as the procedure to relate the wet chemistry with the spectroscopy results.

1.1 Soil sample import regulations

The South African Department of Agriculture, Land Reform and Rural Development (DALRRD), which regulates all aspects of agriculture in South Africa, has a legislative Requirement that all soil samples imported into South Africa must be accompanied by an approved certificate. This is in terms of the South African "Provisions of the Agricultural Pests Act", 1983 (Act No. 36 of 1983). However, there is only one permit required per year for the Soils4Africa project, and must be obtained at least 30 days before delivery of any samples. The cost of the certificate is US$20 and will be the responsibility of ARC in Pretoria.

1.2 Soil sample receiving and handling

It is anticipated that the soil samples will be received from the various hubs in batches at regular (or possibly irregular) intervals. This could be affected by delays in the fieldwork phase caused by the Covid-19 situation in various countries.

The official commencement date of the project was 01-06-2020 (Month 1). The approved schedule for the delivery and analysis of the samples (specified in the Grant Agreement) is as follows:

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Sample Delivery:

Month 24	25% of the 20 000 samples delivered
Month 28	50% of the 20 000 samples delivered
Month 32	75% of the 20 000 samples delivered
Month 36	100% of the 20 000 samples delivered

Analysis:

Month 28	25% of the 20 000 samples analyzed
Month 32	50% of the 20 000 samples analyzed
Month 36	75% of the 20 000 samples analyzed
Month 40	100% of the 20 000 samples analyzed

On receipt of each batch, the number of samples, and the registration number of each one, will be cross-checked with the reference list or other soil registration document provided by the respective hub coordinator, for correctness. Once this has been established, the samples will be processed for preparation and analysis.

The unique sample registration number will be used throughout the analysis phase, to ensure that all applicable soil analytical data are attached to the correct sample.

2. Spectroscopy

Principle

Diffuse reflectance spectroscopy involves illuminating samples with light and capturing diffuse reflected light in various ranges of the electromagnetic spectrum. These ranges include ***visible*** (390 – 780 nm), ***near infrared*** (NIR, 780 - 2500 nm) and the ***mid infrared*** range (MIR, 2500 – 25000 nm or 4000 – 400 cm^{-1}). The recorded spectrum bears the qualitative and quantitative chemical aspects relating to the mineral and organic composition of the sample. Soil properties measured in the laboratory using conventional analytical methods (reference analyses) can be calibrated to the spectral signatures. A spectral library is a calibration dataset containing both spectral and wet chemistry reference measurements of the same samples. A spectral calibration model for a soil property can be derived from this spectral library. The model can then be applied to a spectrum of a new sample to estimate the soil property of that sample.

Equipment

The Soils4Africa project will use a Bruker Alpha MIR spectrometer to measure all soil samples and investigate various soil parameters at the ARC lab. A subset of samples will be measured at ICRAF with a Bruker Tensor MIR spectrometer with a high throughput screening accessory. If budget allows, a subset of the samples will be measured with NIR equipment to align with the LUCAS soil spectral library. Samples will be finely ground prior to MIR spectral analysis with the standard equipment available at the ARC and ICRAF labs.

Procedure

Soil spectroscopy is a method that is now applied globally. Much of the knowledge gained in spectroscopy in Africa stems from the work by ICRAF, for example, in the AfSIS projects. Generally, organic and inorganic carbon, nitrogen, pH, exchangeable bases and soil texture give good prediction

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performance, while micronutrients are fairly well predicted except for Boron, Zinc and Sulphur, which are poor. Phosphorus (P) has remained difficult to predict. Table 1 below gives a summary of the accuracy of a subset of the AfSIS data.

Table 1. Prediction model performance summary for holdout set which is 30 percent of the calibration data set; n = 1,907. The samples are from the AfSIS1 set where samples were collected from 60 sentinel sites distributed in 19 countries.

Property	Unit	R^2	RMSE	RPD	RPIQ
Total C	% by weight	0.95	0.30	4.15	3.50
Acidified C	% by weight	0.95	0.28	4.28	3.53
m^3 Ca	mg/kg	0.94	788.46	3.82	1.73
Total N	% by weight	0.93	0.02	3.53	3.10
m^3 Mg	mg/kg	0.93	103.42	3.76	3.28
m^3 Al	mg/kg	0.92	127.31	3.43	4.57
pH	-	0.89	0.37	2.81	3.08
PSI	-	0.88	26.43	2.60	2.61
Exch. Bases	$cmol^+/kg$	0.88	6.70	2.70	1.66
Sand	% by volume	0.86	9.69	2.49	4.19
Clay	% by volume	0.86	9.07	2.47	4.30
Silt	% volume	0.80	4.42	**1.97**	2.63
Exch. Acidity	$cmol^-/kg$	0.74	0.29	**1.64**	1.32
m^3 Mn	mg/kg	0.72	54.80	**1.59**	1.89
m^3 B	mg/kg	0.72	0.90	**1.46**	0.24
m^3 Fe	mg/kg	0.66	45.34	**1.28**	1.55
m^3 Cu	mg/kg	**0.59**	1.27	**1.10**	1.52
m^3 Na	mg/kg	**0.55**	893.87	**0.99**	0.03
m^3 K	mg/kg	**0.52**	183.56	**0.88**	0.65
m^3 S	mg/kg	**0.51**	162.74	**0.86**	0.10
m^3 P	mg/kg	**0.49**	21.79	**0.77**	0.32
Elec. Cond.	dS/m	**0.35**	0.28	**0.66**	0.13
m^3 Zn	mg/kg	**0.25**	1.59	**0.50**	0.44

(Source: ICRAF)

RMSE = Root Mean Square Error

RPD = Ratio of Performance to Deviation (calculated as the ratio between the standard deviation of a variable and the standard deviation error of prediction of that variable by a given model)

RPIQ = Ratio of Performance to Interquartile Distance (calculated as the interquartile range of the observed values divided by the RMSE or prediction)

- Models with R^2 **<0.6** should generally not be used for prediction, however what is an acceptable level of accuracy depends on the application.
- Models with RPD values **<2** should also not generally be used.
- The larger the RPIQ value, the better prediction accuracy

For the properties where the prediction power of the spectral models is limited, as indicated with the guideline above (R^2<0.6, RPD<2), more samples will be analysed progressively with wet chemistry lab methods in an attempt to increase the predictive power of the spectral models.

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For lab spectral measurements in the Soils4Africa project, the Standard Operating Procedures of ICRAF[1] and or GLOSOLAN[2][1] will be used when harmonised. This will ensure that the resulting dataset can be used in conjunction with the African Soil Spectral Library of ICRAF and the Global Soil Spectral Calibration Library of GLOSOLAN.

The procedure includes:

- Subsample the air-dried 2 mm sieved soil sample for spectral analysis
- Finely grind the sample to specified size (less than 0.05 mm)
- Run quality checks on the Alpha spectrometer (measuring standards, controlling environmental conditions etc.)
- Load the sample in the steel sampling cup of the spectrometer
- Perform the measurements according to SOP specifications
- Perform quality check on results
- Store the spectrum in the database with the accompanying metadata
- Wet chemistry is performed on another sub-sample of the same original sample.

ICRAF SOP's can be found here (https://www.worldagroforestry.org/sd/landhealth/soil-plant-spectral-diagnostics-laboratory/sops)

3. Wet Chemistry

This set of analytical procedures addresses both physical and chemical soil properties that are to be determined. It was decided that, due to the time and costs involved, neither bulk density nor clay mineralogy would be included in the analysis package for the Soils4Africa project.

The specific parameters, as well as the methods that are used to do the analysis, have been selected to be compatible with the LUCAS initiative (Toth *et al.,* 2013).

The determinations include:

Physical

- Coarse fragment component (% soil material larger than 2 mm)
- Particle size (seven fractions)

Chemical

- pH (H_2O and $CaCl_2$)
- Electrical Conductivity (EC)
- Organic Carbon
- Carbonate Content
- Phosphorous content
- Phosphorous sorption
- Total Nitrogen content
- Cation Exchange Capacity (CEC) and Exchangeable Cations (Ca, Mg, Na, K)
- Micronutrients (Zn, Mn, Cu, Co, B)
- Heavy Metals (As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, V, Zn)
- Pesticide residues (multiple compounds)

[1] Method for analysing samples for spectral characteristics in Mid IR range using Alpha.pdf (worldagroforestry.org)
[2] http://www.fao.org/global-soil-partnership/glosolan/soil-analysis/dry-chemistry-spectroscopy/en/

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The LUCAS specifications regarding these parameters are given in Table 1 below.

Table 1a. Core parameters

Parameter	Unit	Decimals	Method/Standard
Basic soil parameters			
Coarse fragments	%	0	ISO 11464:2006
Particle size distribution (FAO, 2006)	-	-	ISO 13320:2009
Clay content < 0.002 mm	%	1	
Silt Content 0.002–0.063 mm	%	1	
Sand Content 0.063–2 mm	%	1	
pH in $CaCl_2$	-	1	ISO 10390:1994
pH in H_2O	-	2	ISO 10390:1994
Electrical conductivity (EC)	mS/m	2	ISO 11265:1994
Organic carbon (OC)	g/kg	1	ISO 10694:1995
Carbonate content ($CaCO_3$)	g/kg	0	ISO 10693:1995
Phosphorus (P) content	mg/kg	1	ISO 11263:1994
Total nitrogen (N) content	g/kg	1	ISO 11261:1995
Cation Exchange Capacity (CEC) and Exchangeable Cations (Ca, Mg, Na, K)	Cmol(+)/kg	1	ISO 11260:2018
Exchangeable Acidity	Cmol(+)/kg	1	
Oxalate extractable iron and aluminium	mg/g	1	Ross and Wang, 1993
Pesticide residues*	mg/kg	3	JRC-EU LUCAS 2018 SOPs, validation conform SANTE/12682/2019

*in the 250 reference sites and 50 "Hotspot" areas

Table 1b. Core parameters

Parameter	Unit	Decimals	
Heavy Metals			
Digestion of samples	-	-	ISO 11466: 1995 or equivalent*
From digested samples:			
Arsenic (As)	mg/kg	1	EPA Method 6020A:2007
Cadmium (Cd)	mg/kg	1	EPA Method 6010C:2007
Cobalt (Co)	mg/kg	1	EPA Method 6010C:2007
Chrome (Cr)	mg/kg	1	EPA Method 6010C:2007
Copper (Cu)	mg/kg	1	EPA Method 6010C:2007
Mercury (Hg)	mg/kg	1	EPA Method 6020A:2007
Nickel (Ni)	mg/kg	1	EPA Method 6010C:2007
Lead (Pb)	mg/kg	1	EPA Method 6010C:2007
Antimony (Sb)	mg/kg	1	EPA Method 6020A:2007
Vanadium (V)	mg/kg	1	EPA Method 6020A:2007
Zinc (Zn)	mg/kg	1	EPA Method 6010C:2007

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To provide a first assessment of soil pollution in Africa, all 20 000 samples will be analyzed for heavy metals using a smart combination of handheld XRF-scanner (if available within the budget or operational requirements of the project) and laboratory analysis (ICP). The steps and procedures of each determination are given below.

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3.1 Coarse Fragment Component

Principle

Soil samples are dried in drying room at temperature of 40 °C from the registration until the sample preparation. The samples are crushed and then sieved. The fraction of smaller than 2 mm is used for required analysis.

Equipment

- Balance, accurate to 0.1 g
- Sieve with 2 mm slots
- Crusher, rotary crusher
- Plastic trays

Procedure

- Place the soil samples (spread on plastic tray with proper identification) in drying room with a temperature not exceeding 40 °C.
- Based on experience the required time for drying process is 3-4 days.
- Weigh the mass of dried soil sample (m_1).
- Remove extraneous matter (e.g. stone, rests of plants, fragments of glass and rubbish).
- Crush the soil samples and then sieve. The aperture size of sieve applied is 2 mm. Weigh the mass of portion with particle size < 2 mm (m_2).
- The sample shall be homogenized after any separation sieving, crushing or milling operation has been carried out.

Calculation

Coarse fragment content is calculated as a difference between total mass of dried soil (m_1) and portion of soil with particle size smaller than 2 mm (m_2).

$$coarse\ \% = \frac{m_1 - m_2}{m_1} \times 100$$

where m_1 is the mass of the dried soil sample in g
m_2 is the mass of the portion with particle size < 2 mm in g

3.2 Particle size

The particle size of the soil samples will be determined by the pipette method, for seven fractions, as follows:

- Coarse sand 2.0 – 0.63 mm
- Medium sand 0.63 – 0.25 mm
- Fine sand 0.25-0.106 mm
- Very fine sand 0.106 – 0.05 mm
- Coarse silt 0.05 – 0.02 mm
- Fine silt 0.02 – 0.002 mm
- Clay <0.002 mm

From this determination, any other determination (e.g., sand, silt & clay) may be calculated.

See Section 35 of the Annexure: *"Handbook of Standard Soil Testing Methods for Advisory Purposes".*

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3.3 pH in $CaCl_2$ and in H_2O

Principle

The suspension of soil is made up by giving 5 times its volume of water for pH in H_2O and 0.01 mol/dm^3 solution of calcium chloride for pH in $CaCl_2$. The pH value of suspension is measured using a glass electrode connected to pH-meter.

Equipment

- pH-meter and glass-electrode
- Sample containers
- Spoon, 5 cm^3
- Dispensers, 30 cm^3

Reagents

- Water, EC < 0.2 mS/m and pH > 5.6
- Calcium chloride solution c = 0.01 mol/dm^3
- Buffer solutions to calibrate the pH-meter pH = 4.00 and pH = 10.00
- Buffer solutions to check the pH-meter pH = 2.00, pH = 7.00 and pH = 9.22

Procedure

- Take a test portion of 5 cm^3 of air-dried soil samples.
- Place the test portion into a container and add 25 cm^3 water or calcium chloride solution.
- Shake suspension vigorously for 5 minutes and leave it overnight.
- Measure this suspension within 24 h.
- Calibrate the pH-meter with buffer solutions of pH = 4.00 and pH = 10.00.
- Buffer solutions and soil suspensions are stored in the same room overnight, so that the difference in temperature is lower than 1 ºC.
- Shake the suspension just before the measurement then let it settle.
- Measure the pH in settled suspension. Read the pH value after stabilization and record it.

3.4 Electrical Conductivity

Principle

Air-dried soil is extracted with water at 20 °C ± 1 °C at an extraction ratio of 1:5 (m/V), to dissolve the electrolytes. The specific electrical conductivity of the filtered extract is measured, and the result is corrected to a temperature of 25 °C.

Equipment

- Conductivity meter
- Balance, accurate to 0.001 g
- Shaking machine
- Shaking bottles, 250 cm^3
- Filter paper

Reagents

- Water, electrical conductivity is not higher than 0.2 mS/m at 25 °C
- Potassium chloride solutions, 0.1 mol/l; 0.020 mol/l; 0.010 mol/l
-

Procedure

- Weigh 20.00 g of the laboratory sample into a shaking bottle.

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- Add 100 ml of water at a temperature of 20 °C ± 1 °C.
- Shake the bottle for 30 minutes in a shaking machine.
- Filter directly through a filter paper.
- Measure the electrical conductivity of the filtrates according to the instructions provided by the manufacturer of the conductivity meter with the temperature corrected to 25 °C.
- Perform the extraction with a blank sample. (The electrical conductivity of the blank sample shall not exceed 1 mS/m).

3.5 Organic Carbon

Principle

The carbon present in the soil is oxidized to carbon dioxide by heating the soil to 900 °C in a flow of oxygen-containing gas that is free from carbon dioxide. The amount of carbon dioxide released is then measured by a thermal conductivity detector in a CNS analyser. When the soil is heated to a temperature of 900 °C, any carbonates present are completely decomposed.

The determination of the organic carbon (OC) content is based on the calculation of the difference between the total carbon content and the inorganic carbon content (from the carbonate content determined according to ISO 10693:1995 (descriptions in section 3.2.7)) using the formula described in the standard.

Equipment

- Balance, accurate to 0.0001 g
- Elemental Analyzer

Reagents

1. Aspartic acid

Procedure

2. Determine the daily factor by running 250-300 mg aspartic acid for three times.
3. Weigh 0.5 g of the air-dried sample in a crucible. Carry out the analysis in accordance with the manufacturer's manual for the apparatus.
4. Based on the calibration and sample weight, the software of the instrument provides the total carbon content expressed in g/kg (TC). In case of results that are lower than the lower detection limit, the test shall be repeated with higher amount of sample (1 g). In case of results are higher than the upper detection limit, the test shall be repeated with lower amount of sample (0.25 g) and analysis repeated accordingly.

Calculation

Organic carbon content is a calculated amount from the difference of total and inorganic carbon content of the sample by formula below.

$$OC = TC - TIC$$

$$TIC = 0.12 \times c_{CaCO_3}$$

$$OC = \frac{TC - 0.12 \times c_{CaCO_3}}{dry\ matter\ \%} \times 100$$

where *OC* is the organic carbon content in the air-dried soil sample in g/kg
TC is the total carbon content measured in g/kg
TIC is the total inorganic carbon content in g/kg

C_{CaCO_3} is the carbonate content measured in g/kg

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3.6 Carbonate Content

Principle

Hydrochloric acid is added to the soil sample to decompose any carbonates present. The volume of the carbon dioxide produced is measured by using Scheibler apparatus and compared with the volume of carbon dioxide produced by pure calcium carbonate. The determination should be carried out in a temperature-controlled room.

Equipment

- Scheibler apparatus, adapted for carrying out determination of 10 samples simultaneously
- Balance, accurate to 0.001 g
- Reaction vessels, 250 cm^3 with wide neck
- Glass cups, about 10 cm^3, which can pass through the neck of the reaction vessel
- Watch glass

Reagents

- Hydrochloric acid c = 4 mol/dm^3
- Calcium carbonate

Procedure

- For a preliminary test, add some hydrochloric acid to a portion of the soil on a watch glass. The carbonate content of the sample can be estimated on the basis of the intensity and time of effervescence.
- Weigh a representative test portion of 1-10 g (m_1).
- Transfer this amount quantitatively into the reaction vessel and add 20 cm^3 of water.
- Also weigh the standard of 0.200 g calcium carbonate (m_2), transfer this amount quantitatively into the reaction vessel and add 20 cm^3 of water.
- For the blank determination, use reaction vessels containing 20 cm^3 of water.
- Fill the glass cups with hydrochloric acid and place this in the reaction vessel containing the test portion.
- Fill the burette with water using pump, close reaction vessel and equilibrate the level of water in tubes using the stopcocks. Close the stopcocks so to form a closed-system between burette and vessels.
- Carefully add the hydrochloric acid to soil. Start shaking and after 5 minutes read the volume of gas formed (V_1).
- Perform the test with standard samples and record volume (V_2). Also record the volume of blank determinations (V_3).

Calculation

$$c_{CaCO_3} = 1000 \times \frac{m_2 \times (V_1 - V_3)}{m_1 \times (V_2 - V_3)} \times \frac{100}{dry\ matter\ \%}$$

where m_1 is the mass of the sample in g
m_2 is the mass of the standard calcium carbonate in g
V_1 is the volume of the formed gas from the sample in ml
V_2 is the volume of the formed gas from the standard in ml
V_3 is the volume of the formed gas for the blank sample in ml

3.7 Phosphorous

Principle

Soil samples are treated with sodium hydrogen carbonate solution at pH = 8.5 to reduce the concentration of calcium, aluminium and iron (III) ions by precipitation of calcium carbonate and

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aluminium and iron (III) hydroxides and to release phosphate ions into solution. The clear extract is analysed for phosphorus by a spectrophotometric method involving the formation of an antimony-phosphate-molybdate complex reduced with ascorbic acid to form a deep-coloured, blue complex.

Equipment

- Balance, accurate to 0.001 g
- Shaker
- Shaking bottles, 500 cm^3
- pH meter
- Spectrophotometer and optical cells

Reagents

- Sodium hydroxide solution, 1 mol/dm^3
- Sodium hydrogen carbonate solution, 0.5 mol/dm^3; pH = 8.5
- Carbon, activated, phosphorus-free (descriptions see in section 4.1.8)
- Sulphuric acid, 5 mol/dm^3
- Potassium antimony (III) oxide tartrate solution, 0.5 g/dm^3
- Sulpho-molybdic reagent

Add cautiously 278 cm^3 ± 5 cm^3 concentrated sulphuric acid to 400 cm^3 water while stirring continuously. Cool to 50 °C. Add 49.08 g ± 0.01 g ammonium heptamolybdate tetrahydrate and stir until dissolved. Cool to 20 °C ± 5 °C and make up to the mark with water.

- Potassium antimony (III) oxide tartrate solution, 0.5 g/dm^3
- Colour reagent

Dissolve 1.0 g ± 0.01 g ascorbic acid in 525 cm^3 of water, then add 10 cm^3 dilute sulphomolybdic reagent, 15 cm^3 dilute sulphuric acid and 50 cm^3 potassium antimony (III) oxide tartrate solution. Mix well. (This reagent must be used within 30 min following of preparation.)

- Sodium thiosulphate solution, 12 g/dm^3
- Sodium metabisulphite solution, 200 g/dm^3
- Potassium dihydrogen phosphate standard stock solution (450 mg/dm^3 phosphorus), and standard solutions (0, 0.45, 2.25, 4.5 and 9.0 mg/dm^3 phosphorus)

Procedure

Extraction:

Weigh 2.5 g ± 0.01 g of pre-treated soil into a 250 cm^3 flask. Add 0.5 g phosphorus-free, activated carbon and 50 cm^3 ± 0.5 cm^3 extracting solution.

Stopper the flask and place it immediately on the shaker. Shake for exactly 30 min at 20 °C ± 1 °C. Once shaking ended, filter immediately (in 1 min) into a dry vessel of 100 cm^3 using phosphorus-free paper.

Prepare a blank by following the above procedure excluding soil.

Colour development:

Into a set of 50 cm^3 volumetric flasks, transfer 5.00 cm^3 of either blank solution or soil extract or standard solutions. Carefully add 0.5 cm^3 of 5 mol/dm^3 sulphuric acid solution to flasks and gently swirl to liberate carbon dioxide. Add 4.0 cm^3 sodium metabisulphite solution and 6.0 cm^3 sodium thiosulphate solution. Stopper the flask immediately, mix well and wait for 30 min. Then add 30 cm^3 of colour reagent, make up to the mark with water, stopper the flask and mix well. Wait for 60 min to allow the colour to develop.

Measurement:

Measurement shall be carried out at 880 nm by spectrophotometer.

Calculation

$$c_P = \frac{(c - c_{blank}) \times d}{dry\ matter\ \%} \times 100$$

where *c* is the calculated concentration of phosphorous of the extract in mg/l
d is the dilution factor of the soil (if required)

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c_{blank} is the concentration of phosphorous of blank in mg/l
c_P is the corrected concentration of phosphorous of oven dried soil in mg/kg

3.8 Nitrogen

Principle

The method is based on the Kjeldahl-digestion using titanium dioxide as catalyst. The following procedure specifies a method for the determination of the total nitrogen (ammonium-N, nitrate-N, nitrite-N and organic N) content of soil. Nitrogen in N-N linkages, N-O linkages and some heterocyclics (especially pyridines) is only partially determined.

Equipment

- Balance, accurate to 0.001 g
- Digestion tubes of nominal volume, 50-200 cm^3
- N-Analyzer Instrument

Reagents

- Salicylic acid/sulphuric acid

25 g of salicylic acid in 1 dm^3 of concentrated sulphuric acid

- Potassium sulphate catalyst mixture

200 g potassium sulphate mixed with 6 g copper sulphate pentahydrate and 6 g titanium dioxide

- Sodium thiosulphate pentahydrate
- Sodium hydroxide, 10 mol/dm^3
- Boric acid solution, 20 g/dm^3
- Mixed indicator

Dissolve 0.1 g bromocresol green and 0.02 g of methyl red in 100 cm^3 ethanol

- Sulphuric acid, 0.025 mol/dm^3

Procedure

- Place a test portion of air-dried soil sample of about 0.5 g (m) in a digestion flask. Add 10 cm^3 salicylic/sulphuric acid and swirl the flask until the acid is thoroughly mixed with the soil. Allow the mixture stand for overnight. Add 0.5 g of sodium thiosulphate and heat the mixture cautiously on the digestion stand until frothing is ceased.
- Then cool the flask, add 1.1 g of the catalyst mixture and heat on not higher than 400 °C for 1-2 h, until the mixture becomes clear.
- After digestion, allow the flask cool and add about 10 cm^3 of water slowly while shaking. Transfer the content into the distillation apparatus.
- Distillation is carried out by Kjeldhal system, which also includes automatic titration apparatus.
- At the beginning of each measurement cycle perform runs with blank tubes and record the amount of sulphuric acid consumed (V_0).
- Weigh 0.020 g ammonium sulphate into tubes, perform runs and record the amount of sulphuric acid (V_f).
- Carry out a blank test in which the same procedure is performed without soil. Notify the consumption of sulphuric acid in the blank test (V_{blank}) and in the tests of the soil samples (V).

Calculation

$$\frac{(V - V_{blank}) \times \frac{(V_f - V_0) \times 132}{0.02 \times 1000} \times \frac{2 \times 0.025}{m} \times 0.025 \times 14}{dry\ matter\ \%} \times 100$$

where V is the volume of the sulphuric acid used in the titration of the sample in ml
V_{blank} is the volume of the sulphuric acid used in the blank test in ml
V_f is the volume of the sulphuric acid used in the titration of the ammonium sulphate in ml
V_0 is the volume of the sulphuric acid used in the titration of the blank tube in ml

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m is the mass of the sample in g

3.9 Cation Exchange Capacity (CEC) and Exchangeable Cations

The ammonium acetate method is used to determine extractable cations Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Potassium (K^{+}) and Sodium (Na^{+}) in soils, reflecting the nutrient status.

See Section 8 of the Annexure: "Handbook of Standard Soil Testing Methods for Advisory Purposes".

3.10 Exchangeable Acidity

The procedure outlined by McLean (1965) with modifications set out below, was used. A 10 g soil sample was shaken with 70 cm^3 mol/litre KCl solution in a 100 cm^3 slopy neck plastic bottle on a reciprocating shaker at a minimum of 180 oscillations per minute for 1 hour. The suspension was filtered through Whatman No. 2V filter paper into a 500 cm^3 Erlenmeyer flask and washed with an additional 30 cm^3 1 mol/litre KCl solution. Total exchangeable acidity was determined on the KCl extract by titration with 0.1 mol/litre NaOH. Excess NaF was added to the titrated solution and the OH^- ions so released were titrated with 0.1 mol/litre HCl to determine exchangeable aluminium. In both titrations phenolphthalein was used as indicator.

3.11 Oxalate Extractable Iron and Aluminium

Defined in Section 12.2 of the ISRIC "Procedures for Soil Analysis", attached as an Appendix.

3.12 Heavy Metals

These include Arsenic (As), Cadmium (Cd), Cobalt (Co), Chrome (Cr), Copper (Cu), Mercury (Hg), Nickel (Ni), Lead, (Pb), Antimony (Sb), Vanadium (V) and Zinc (Zn).

Principle

The soil samples are digested in an acidic medium in microwave digestion equipment and the resulting acidic digest is used for the determinations by an inductively coupled plasma-optical emission spectrometer (ICP-OES) or an inductively coupled plasma - mass spectrometer (ICP-MS) on the specific wavelengths or mass / charge (m / z) ratio for each element.

Equipment

- Microwave digestion equipment
- Polyethylene centrifuge tubes, 50 cm^3
- Balance, accurate to 0.001 g
- Inductively coupled plasma – optical emission spectrometer (ICP-OES)
- Inductively coupled plasma – mass spectrometer (ICP-MS)

Reagents

- Nitric acid 65%
- De-ionized water
- Standard stock solutions

Procedure

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- Weigh 0,800-0,900 g of each soil sample into the bombs belonging to the microwave digestion equipment to the nearest 0.1 g, add 1.0 ml of deionized water, 4.0 ml of cc. nitric acid (65%). The bombs are then sealed, and the samples are digested by a microwave destructor set according to the method.
- After the destruction of the samples, wash with deionized water to a final volume of 20.0 ml. Prepare a blank at the same time as the test. Blank sample: 5.0 ml nitric acid (65%) + 15.0 ml deionized water.
- Perform the mass calibration and check the solution over the measured mass range.
- Calibrate the instrument for the element to be tested, calibration blank and calibration standards as described by the manufacturer. For each calibration solution and sample, give the average of the three measurement results.
- Prepare the device for the measurement according to the manufacturer's instructions. First allow the device to stabilize for 30 minutes before measuring, especially the tuning solution by successive, mainly four - fold measurements (relative standard deviations ≤ 5%) to verify that the instrument is suitable for measurement. Calibrate the instrument for the element to be tested as described above.
- Flush the system with the blank solution before starting the analysis and measuring the samples. Spray the sample into the plasma until equilibrium is reached (about 30 seconds).
- Weigh back the calibration control sample and calibration blank solution every 10 samples. In case the sample concentration is outside the analytically relevant line range, dilute the sample and re-analyze.

Calculation

$$W\ (mg/kg) = \frac{(C_1 - \mathrm{Cb}_1) \times V_1 \times D}{m}$$

where,

C_1 - reading of the element content of the test solution from the calibration curve (mg/l)
Cb_1 - concentration of blank solution read from the calibration curve (mg/l)
V_1 - final volume of sample solution to be tested (ml)
m - mass of the measured sample (g)
D – dilution factor

3.13 Pesticide residues

Pesticide residues will be analysed in the soils from the 250 reference sites and 50 other, hotspot areas. These analyses will be conducted in Wageningen University & Research laboratories, in the Netherlands. WUR has an extensive analytical infrastructure and experience in the development and application of ultra-trace target and non-target analytical methods.

Different extraction and analytical methods will be used in each of these 300 soil samples to cover multiple synthetic active substances and their main metabolites. The list of analytes will be defined based on authorised pesticides, pesticide use and sales data, and (co)occurrence data of pesticide residues in soils and other environmental matrices from literature. Depending on the size of this list, a step-by-step approach may be used to shorten it to ~100 residues - the burden of validation and analytical quality control increases with the number of pesticides in a method.

Preference will be given to multi-residue methods, that involve a generic extraction and clean-up (typically QuEChERS), followed by analysis using liquid or gas chromatography combined with mass spectrometric detection (LC-MS/MS and GC-MS/MS). In addition, a single-residue method will be used to analyse glyphosate and its main metabolite AMPA, that due to their particular physical chemical properties are not amenable to generic multi-residue methods. The SOPs developed for the LUCAS 2018 topsoil samples will be used as default in African soil samples. See chemicals and reagents, equipment, procedure, and calculations of the following SOPs in the appendixes.

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a. SOP-A-1347: Soil - Pesticides - LC-MSMS
b. SOP –A-1348: Soil - Glyphosate and AMPA - LC-MSMS
c. SOP-A-1361: Soil – Multimethod Pesticides – GC-MSMS4. Laboratory Protocols

4. Laboratory Protocols

4.1 Health and Safety

The laboratory at ARC-SCW is subject to a number of Health & Safety conditions. Firstly, the South African Occupational Health and Safety Act (Act No. 85 of 1993) defines basic requirements and practices that are applicable to any workplace. This includes such aspects as fire prevention, access control, ventilation and a host of safe working conditions. Most important of these in a laboratory is the safe storage, handling and disposal of chemicals.

Secondly, the laboratory is subject to the ARC's own health and safety protocols, and there is a dedicated ARC health and safety practitioner, who performs regular inspections to ensure that the laboratory continually adheres to requirements of the Act.

Thirdly, there are a number of provisions made by the organization SANAS (South African National Accreditation System) in terms of health and safety, all of which have to be met before any laboratory can receive SANAS accreditation.

4.2 Training Requirements

The staff at the laboratory at ARC-SCW are experienced in most aspects of soil analysis, and it is anticipated that only limited training (mainly concerning perusal of analytical methods, as specified by LUCAS), will be required. If necessary, some analyses of existing samples from ARC's sample archive will be carried out to evaluate some of these procedures, as and when it is deemed necessary.

Training in spectroscopy will be required, as ARC has no prior experience in this area and one of the aims of the project is capacity building. A dedicated soil researcher (Mr Lebea Maribeng) has been identified and he will be supported by two technicians. As soon as the equipment is delivered, training will start. It will initially be provided by Bruker South Africa, but ICRAF have been contracted to provide continuous training and mentoring on aspects that include: sample preparation and equipment maintenance; analysis protocols using ICRAF SOPs; result quality and database structure.

4.3 Quality Control

Quality control, in the sense of soil analysis, is a vital component in ensuring that the results provided are of the highest possible standard, in terms both of procedures and accuracy.

For the preparations and the general laboratory environment, various aspects will be addressed, using the approved parameters of assessment. These include:

- Regular calibration of instruments prior to and during operation
- Reliability and repeatability of sample preparation procedures
- Status of gas and water supply
- Quality of chemicals, reagents and calibration blanks
- Calibration and maintenance of volumetric, weighing and other small apparatus

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- Environmental conditions (laboratory temperature and humidity).

The principle is that a selection of duplicate samples is provided to one or more external organizations where the same determinations are carried out. The results of this action will enable the laboratory in question to assess how successful its procedures are, and how well the results compare with the external organizations.

4.3.1 Proficiency Testing Schemes

The laboratory at ARC belongs to two quality control schemes. The first one is administered by AgriLASA (the Agricultural Laboratory Association of Southern Africa) and involves a series of reference soil samples being delivered to ARC on a quarterly basis. These samples are analyzed for a number of elements and the results are sent to AgriLASA. In this way, any laboratory can see how it compares to the overall average, as well as be informed where any outliers (results outside the accepted tolerance levels) occur, so that corrective measures can be taken. Approximately 70 laboratories in southern Africa belong to AgriLASA.

In addition, the ARC laboratory belongs to the WEPAL proficiency testing scheme, administered by the Wageningen University & Research, Netherlands. As is the case for AgriLASA, reference samples are provided several times per year and the results are supplied to WEPAL for quality assessment and feedback. This scheme involves several hundred laboratories from all over the world.

4.3.2 Internal Soils4Africa Quality Control

Selected soil samples will be sent to other Soils4Africa partners for quality control. These will include ICRAF (Kenya) for spectroscopy as well as SGS in Hungary and ISRIC (Netherlands) for wet chemistry analyses.

Firstly, subsets of all reference samples will be sent to ICRAF's Soil-Plant Spectral Diagnostics Laboratory for measurement on high-throughput FT-MIR, standard FT-MIR and FT-NIR spectrometers, both for quality control and to ensure that the new Soils4Africa spectra are compatible with the existing ICRAF/AfSIS calibration libraries.

Secondly, subsets of samples to be analysed with wet chemistry will be sent to SGS Hungary for quality control analysis, involving all of the parameters described in Section 3 of this Protocol Document.

It is also recommended to send 400 – 500 g samples from the reference sites to the US national soils laboratory for spectral and chemical analysis so that they can be incorporated into the Global Spectral Calibration Library and Estimation Service of the Global Soil Laboratory Network (GLOSOLAN) of the Global Soil Partnership (GSP), hosted by the Food and Agriculture Organisation (FAO).

4.4 Data Recording and Storage

All soil and related data obtained from the laboratory analysis phase will be stored in a format agreed with the leader of WP3 (Design of the SIS and methods for field and laboratory) and WP6 (Build Soil Information System & Capacity Building) to ensure the most effective and efficient means of data collection and transfer. A LIMS will be used to keep record of all aspects of administration and reporting.

The data will be stored in a central repository (for maximum accessibility to data users), as well as one or more separate back-up locations.

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4.5 Soil Sample Storage

All soil samples delivered to ARC, as well as any other samples that are collected during the course of the project (for example, subsoils that were mot budgeted for analysis), will be stored in a dedicated storage facility at ARC in Pretoria. This facility is a separate building, currently unutilized, which can be converted at minimal cost and effort, into a sample storage repository.

It is anticipated that up to 40 000 samples (approximately 20 000 topsoil samples as defined in the project proposal, as well as up to 20 000 subsoil samples, if collected) will be stored. These samples will also be available to researchers and others, on application, after the life of the project.

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5. Conclusion

The analysis phase of the soil samples from Soils4Africa, including all component processes, procedures and controls, has been comprehensively scheduled, as outlined in this document.

This includes:

1. Sample preparation
2. Sample recording
3. Analysis methods and protocols
4. Quality control of results
5. Data recording
6. Data storage and transfer
7. Soil sample storage

All of these aspects will be reported on at specified intervals, as required by the project plan and the deliverables included.

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This project has received funding from the
EU Horizon 2020 Research and Innovation Programme
under Grant Agreement 862900.

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Tóth, G., Jones, A., Montanarella, L. (eds.) 2013. LUCAS Topsoil Survey. Methodology, data and results. JRC Technical Reports. Luxembourg. Publications Office of the European Union, EUR26102 – Scientific and Technical Research series – ISSN 1831-9424 (online); ISBN 978-92-79-32542-7; doi: 10.2788/97922"

LIST OF ISO CODES

ISO 10390: Soil Quality – Determination of pH (2005)

ISO 10693: Soil Quality – Determination of carbonate content (1995)

ISO 10694: Soil quality — Determination of organic and total carbon after dry combustion (1995)

ISO 11261: Soil quality — Determination of total nitrogen — Modified Kjeldahl method (1995)

ISO 11263: Soil quality — Determination of phosphorus (1994)

ISO 11265: Soil quality — Determination of the specific electrical conductivity (1994)

ISO 11464: Soil quality — Pretreatment of samples for physico-chemical analysis (2006)

ISO 11466: Soil quality — Extraction of trace elements soluble in aqua regia (1995)

ISO 13320: Particle size analysis — Laser diffraction methods (2020)

This project has received funding from the
EU Horizon 2020 Research and Innovation Programme
under Grant Agreement 862900.

ANNEX

Annex 1: South African Handbook of standard soil testing methods for advisory purposes

Annex 2: ISRIC guidelines for soil analysis

This project has received funding from the
EU Horizon 2020 Research and Innovation Programme
under Grant Agreement 862900.

HANDBOOK OF STANDARD SOIL TESTING METHODS FOR ADVISORY PURPOSES

Compiled by

The Non-Affiliated Soil Analysis Work Committee

1990

ISBN 0-620-14800-4

Published and distributed by the

SOIL SCIENCE SOCIETY OF SOUTH AFRICA

P.O. Box 30030
Sunnyside 0132
Pretoria
Republic of South Africa

ACKNOWLEDGEMENTS

This handbook was compiled under the auspices of the Non-Affiliated Soil Analysis Working Committee which is greatly indebted to:

The Department of Agricultural Development
The Fertilizer Society of South Africa
RSA Universities
Co-operative, FSSA and other private laboratories.

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PREFACE

The importance of soil analysis as an aid in the determination of certain agricultural acitivities is recognised in all developed agricultural countries. All over the world different methods of analysis have been developed over the years for different situations.

Some of these methods are still valid and internationally recognised, while others have been changed for different reasons but are quite often still known under the original method name.

This phenomenon, together with the multiplication of methods to determine one specific element, e.g. phosphorus, has lead to a worldwide effort to standardise on and within methods. A well known example is the programme of the "International Soil Research Information Centre" (ISRIC) in Wageningen.

Since its inception The Fertilizer Society of South Africa (FSSA) was committed to the standardisation of soil analysis methods. This meant rationalisation in terms of the number of methods as well as the number of laboratories. The first success in this direction was achieved in 1963 when the soil analysis laboratories of the fertilizer industry standardised their methods. During the subsequent 20 years several other laboratories adopted the same methods.

Early in the seventies the then Department of Agricultural Technical Services' Fuls Report addressed the necessity to co-ordinate and standardise soil analysis methods. As a result the Department appointed a committee for the co-ordination of soil and plant analysis services for fertilization purposes, with the Soil and Irrigation Research Institute (SIRI) as convener. One of the tasks of this committee was to promote the standardisation of soil analysis methods.

This committee played a leading role for more than a decade in efforts to promote standardisation, to refine methods and to test these methods. The committee was also involved in finding and providing solutions to analytical problems. As early as 1975 a "Handbook of standard methods for soil testing" was compiled by the Department.

Another important goal achieved was the development of the ammonium-bicarbonate-fluoride - EDTA method (Ambic method) to determine phosphorus and other nutrients. The aim with this method was to establish a standard method to provide valid results for a wide range of soils. However, as a result of the high autonomy of individual laboratories within the Department, the proposed reference method could not be enforced and co-operation was voluntary.

In order to investigate this and other analytical service related aspects, a departmental committee was appointed in 1982 with the then Director of the SIRI, Dr M.C.F. du Plessis as convener.

As a result of this investigation an Inter-Chief Directorate Working Group for Soil Fertility, Plant Nutrition and Analytical Services (SFPNA) was appointed in 1986 with, as one of its tasks, to pay attention to the problem of standardisation. This Working Group replaced the co-ordinating committee among others.

The SFPNA Working Group with its three area co-ordinating task teams, each for a defined geographical area, made good progress. Detailed descriptions of all current soil analysis methods were decided on as a first phase in order to compile standard methods. This task was undertaken by officers of the SIRI and in mid-1987 a first approximation on the description of soil extraction methods was completed.

In the meantime, the FSSA and its member companies appointed a soil analysis working committee which independently of the Department, promoted standardisation among some private laboratories. The publication "Soil analysis - Manual of Methods" was published in 1974 and has since been revised several times.

Changes were made in 1980 and in 1984 in an attempt to achieve overall standardisation for all 30 (now 40) of the country's laboratories. These new methods were recommended by the then Department of Agricultural Technical Services and were to be followed by all its laboratories. Despite valiant efforts this attempt unfortunately met with little success. Many laboratories then tended to follow methods of their own choice, resulting, at one time, in some ten different methods for the extraction of phosphorus. A further complication was that several varieties of some of the methods ensued.

By 1985 it was realised that the different organisations rendering analytical services could not continue their attempts in isolation and officials of the SIRI were invited by the FSSA to participate in discussions on this matter. Subsequently a Non-Affiliated Soil Analysis Working Committee was established, represented by experts from all sectors involved, to promote standardisation of analytical methods on a broad front.

At that stage the Department was well advanced in describing its soil extraction methods, while private laboratories started with a similar action.

A highlight in standardising on soil analytical methods was the first Soil Analysis Symposium in August 1987, organised under the joint auspices of the Department and the FSSA. The first approximation of the Department was used as basis for this co-ordinated action to standardise on soil extraction methods. All participating labora-

tories had the opportunity to discuss the proposed methods and to help decide on the most feasible standard methods.

A follow-up Soil Analysis Symposium was held during 1988 to finally standardise methods compiled by the Non-Affiliated Soil Analysis Working Committee in co-operation with the SIRI, the Departmental Working Group for Soil Fertility, Plant Nutrition and Analytical Services and other participating laboratories. At the Symposium it was decided that the handbook of standard methods would be published under the auspices of the Soil Science Society of South Africa.

The methods described in this handbook represent those methods currently in use in the Republic of South Africa. Some methods have been modified, either to suit local conditions or to improve reproducibility.

Though primarily intended for fertilizer advisory purposes, several other methods, in fairly general use in the country and requiring standardisation, have been included in this text.

It is hoped that in using these methods, the minimum of deviation and modification will occur in future. Some modifications will no doubt be necessary and sensible, but these should only be made after comparison with the methods included in this text, which should be regarded as "standard". Such modifications should preferably only be made after acceptable comparative work has been published.

This is the basis against which the performance of laboratories participating in the control scheme of the FSSA, currently administered by the Department of Soil Science and Plant Nutrition of the University of Pretoria, will be evaluated.

It is furthermore hoped that this handbook will find wider application in educational institutions and in all laboratories undertaking soil analysis.

Members of the Non-Affiliated Soil Analysis Working Committee 1990

CONTENTS

1 SOIL PREPARATION

1.1 Introduction

Samples destined for analysis must either be dried in an oven not exceeding 40 °C or air-dried, protected from direct sunlight, to prevent fixation or release of compounds. After drying, the sample is crushed carefully to pass a 2 mm stainless steel sieve and thoroughly mixed. Stones should not be crushed. Soil samples must be ground to pass a 1 mm stainless steel sieve if small masses (<5 g) of soil are to be analysed or if volume based methods of analysis are to be used.

For the Resin-P method, the soil must be crushed to pass a 0,15 mm sieve. **This preparation is not applicable for particle size analysis. See section 35.4.**

1.2 Apparatus

Pestle and mortar, porcelain or agate
Sieves, stainless steel, 2 ; 1 and 0,15 mm
Mixing container with lid
Trays; stainless steel
Drying ovens (forced draught)
Mechanical crusher

1.3 Procedure

* Spread the soil sample evenly over the surface of a stainless steel tray and prevent contamination by dust, fertilizer dust, cigarette ash, etc.
* Dry the sample at room temperature, protected from direct sunlight or in an oven at a maximum temperature of 40 °C
* Screen the total sample through a 2 mm sieve
* Crush the remaining material on the 2 mm sieve, using a suitable mortar and pestle, until all the soil passes the 2 mm sieve
* Do not pulverise the soil or crush any stones
* Mix the sample thoroughly in the mixing container by turning end over end several times
* Transfer the mixed sample (maximum 2 kg) to suitably marked containers
* Fill each container only to 75 % of its capacity, thus allowing for thorough mixing immediately before analysis
* Depending on the type of analysis required, a sample of the treated soil may be pulverised either to pass a 1 mm or 0,15 mm sieve

2 pH (KCl)

2.1 Introduction

$pH = -\log_{10} (aH^+)$. This method indicates the activity of hydrogen ions in a soil suspension in 1 mol dm^{-3} KCl. Potassium chloride is used to mask variation in salt concentration resulting from fertilizer residues, irrigation water and microbial decomposition of organic material. A stable reading is obtained by using 1 mol dm^{-3} KCl. Hydrogen ion activity in 1 mol dm^{-3} KCl may be as much as 1 or 2 pH units lower or higher than that measured in water, using the same soil/water ratio. Also, if bulk density is not taken into account, considerable error in measured pH may result where soils are tested in scooped quantities and not on a mass basis.

2.2 Apparatus

Balance, accurate to 0,1 g
Beakers, 50 cm^3 capacity
Measuring cylinders or automatic dispenser, 25 cm^3
Glass rods
pH meter, readings reproducible to 0,05 pH units
A combined glass-calomel electrode system or separate glass and calomel electrodes

2.3 Reagents

Potassium chloride, 1 mol dm^{-3}: Dissolve 74,5 g KCl (AR) in 1 dm^3 de-ionised water
Buffer solutions: Use commercially available buffer solutions, pH=4,0 and 7,0 or 8,0

2.4 Procedure

* The pH meter is calibrated at a given constant temperature with commercially available standard buffer solutions
* Re-calibrate hourly to compensate for drift
* Place 10 g dried soil (≤ 2 mm) in a glass beaker
* Add 25 cm^3 KCl solution (1 mol dm^{-3})
* Stir the contents rapidly for 5 seconds with a glass rod
* Stir again after 50 minutes and allow to stand for 10 minutes
* Determine pH with a calibrated pH meter with the electrodes positioned in the supernatant

* Results are reported as pH (KCl)

2.5 References

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3 pH(H_2O)

3.1 Introduction

This procedure determines the pH of a soil in a 1:2,5 soil/water ratio suspension on a mass basis. By definition pH is the negative logarithm to base 10 of the H^+ ion activity. Due to the possible presence of soluble cations with a greater affinity for adsorption on exchange sites on the soil, adsorbed H^+ ions will be displaced from such sites, leading to a lowering of pH. Carbon dioxide will also lower the pH of calcareous soils and care must be taken to exclude CO_2.

3.2 Apparatus

Balance accurate to 0,1 g
Beakers, 50 cm^3 capacity
Measuring cylinders or automatic dispenser, 25 cm^3
Glass rods
pH meter, readings reproducible to 0,05 pH units
A combined glass-calomel electrode system or separate glass and calomel electrodes

3.3 Reagents

Buffer solutions: Use commercially available buffer solutions, pH=4,0 ; 7,0 and 8,0

3.4 Procedure

* The pH meter is calibrated at a given constant temperature with commercially available standard buffer solutions
* Re-calibrate hourly to compensate for drift
* Place 10 g dried soil (≤2 mm) in a glass beaker
* Add 25 cm^3 de-ionised water
* Stir the contents rapidly for 5 seconds with a glass rod
* Stir again after 50 minutes and allow to stand for 10 minutes
* Determine pH after 30 seconds with the electrodes positioned in the supernatant. Results are reported as pH(H_2O)

3.5 References

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4 ELECTRICAL CONDUCTIVITY AND WATER SOLUBLE CATIONS OF THE SATURATION EXTRACT

4.1 Introduction

Electrical conductivity (EC) of the saturation extract is indicative of the total dissolved salts in the extract and therefore of soluble salts in the soil. The EC values are used to classify the salt hazard of brackish soils and to estimate the leaching requirements of brackish soils for reclamation purposes. EC values can be used to predict crop reduction as a result of high salt concentrations.

Sodium adsorption ratio values are used to characterise brackish soil with regard to the reaction between sodium and calcium plus magnesium in the saturation extract. The sodium adsorption ratio (SAR) value is used to determine whether a high sodium content is likely to be physically detrimental to a soil.

4.2 Apparatus

Conductivity cell with a known cell constant of ± 1 cm^{-1}
Conductivity bridge
Buchner funnels, 100 mm in diameter or Richards funnels
Whatman no 50 filter paper for Buchner or Richards funnels
Suitable test tubes for receiving filtrate
Spatulas
Suction flasks, 300 cm^3 capacity
Vacuum system
Flame spectrophotometer
Burette
Plastic or porcelain dishes

4.3 Reagents

Ammonia buffer, pH 10: Dissolve 67,5 g ammonium chloride in 200 cm^3 de-ionised water. Add 570 cm^3 concentrated ammonia solution and dilute to 1 dm^3 with de-ionised water

Sodium hydroxide, pH 12: Dissolve 200 g sodium hydroxide in 400 cm^3 de-ionised water and dilute to 1 dm^3

EDTA solution, 0,01 mol dm^{-3}: Prepare from commercially available standard solution. Standardise against standard solutions of calcium and magnesium respectively

Potassium cyanide, 1% solution: Dissolve 1 g KCN in 100 cm^3 de-ionised water

Hydroxylamine solution, 5% : Dissolve 5 g hydroxylamine hydrochloride in 100 cm^3 de-ionised water

Triethanolamine (TEA): Dilute 1:1 with de-ionised water

Indicator, Ca: Mix together in a mortar 0,2 g calcein, 0,12 g thymolphthalein and 20 g potassium chloride (AR)

Indicator, Ca and Mg: Dissolve 0,5 g methyl red in 300 cm^3 ethyl alcohol and make up to 500 cm^3 with de-ionised water

Dissolve 0,2 g Eriochrome Black T in 50 cm^3 ethyl alcohol. Stable for 3 weeks

4.4 Procedure

4.4.1 Preparation of the saturated soil paste and saturation extract

By hand:

A 250 g air-dry soil sample is placed in a suitable container and moistened with de-ionised water while mixing with a spatula. Consolidate the mixture from time to time by tapping the container on the work bench. Test for the properties of a saturated paste and add more de-ionised water if necessary. Allow to stand for at least an hour and test whether it still has saturation properties. If left overnight cover the container. Special care should be taken to ensure that water does not collect and that the paste does not dry out too much. Add more de-ionised water if required. If too much water was added, repeat procedure. Note the total volume of water added (**w**).

Properties of a saturated paste

* In a saturated soil paste all the pores are filled with water
* It has the following characteristics: The surface is shiny; the paste flows slightly when the container is tilted; free water does not collect when a small trench is drawn on the surface and it does not cling to the spatula (with the exception of clayey soil).

By capillary saturation:

Based on the method of Longenecker and Lyerly (1964), sample holders are prepared from Whatman no 50 filter paper, 180 mm diameter. A 250 g air-dry soil sample is transferred to each filter paper holder, which is then placed on sand (about 40 mm thick) in a plastic container with de-ionised water. The level of water is controlled to saturate the bottom 10 mm of sand (Fig. 4.1). The

sample is allowed to absorb water for 24 hours. The sample is then emptied into a plastic dish and carefully mixed to ensure even distribution of soluble salts. Before extraction of moisture, determine mass of soil and absorbed moisture. Soils high in sodium or clay do not saturate satisfactorily with this method and the hand method should be used.

Preparation of saturation extract

* Filter the soil paste by suction through Whatman no 50 paper on a Buchner or Richards funnel
* Collect filtrate in a test tube placed under the funnel in the suction flask
* Repeat filtration if the solution is not clear
* Store filtrate in a plastic bottle with a drop of toluene added as a bacteriostat

4.4.2 Determination

Determination of EC of the saturation extract

* Calibrate the conductivity cell with 0,01 mol dm^{-3} KCl solution. This solution has an electrical conductivity of 141,18 mS m^{-1} at 25 °C
* Rinse the conductivity cell with saturation extract
* Determine the conductivity of the saturation extract and calculate the electrical resistance from this value
* Temperature control is necessary because conductance increases with temperature. Conductivity of the saturation extract is expressed in mS m^{-1}

Determination of water soluble cations in the saturation extract

Calcium

Take 5 cm^3 saturation extract and dilute to 100 cm^3
Pipette a 20 cm^3 aliquot of the diluted saturation extract in a 500 cm^3 Erlenmeyer flask, add 2 cm^3 sodium hydroxide solution, 1 cm^3 1% KCN solution, 1 cm^3 hydroxylamine solution, 1 cm^3 TEA and calcium indicator. Titrate with 0,01 mol dm^{-3} EDTA. The end point is indicated by a change of colour from pink-green to pink. Record the volume EDTA titrated (**a** cm^3).

Magnesium plus calcium

As for calcium but use ammonia buffer solution (10 cm^3) instead of NaOH. Use 1,5 cm^3 methyl red and 0,5 cm^3 Eriochrome Black T as indicator. Titrate with

0,01 mol dm^{-3} EDTA from purple to green. Record the volume EDTA titrated (**b** cm^3).

Sodium and potassium

Sodium and potassium are determined by flame emission spectroscopy against standard solutions prepared with de-ionised water.

4.5 Calculations

Standardisation of EDTA

Standardise the EDTA solution against standard solutions of calcium and magnesium respectively

$$\text{Concentration of EDTA (mol dm}^{-3}) = \frac{\text{Volume of Ca/Mg standard (cm}^3) \times \text{Concentration of Ca/Mg standard (mol dm}^{-3})}{\text{Volume of EDTA (cm}^3)}$$

Calcium

$$\text{mg kg}^{-1}\text{ Ca in soil} = \frac{\mathbf{b} \times \mathbf{a} \times 40{,}08 \times \mathbf{w} \times 1\,000}{20 \times 250} \times 20$$

$$\text{c mol (+) kg}^{-1}\text{ Ca in soil} = \frac{\text{mg kg}^{-1}\text{ Ca in soil}}{20{,}04 \times 10}$$

$$\text{mg dm}^{-3}\text{ Ca in saturation extract} = \frac{\mathbf{b} \times \mathbf{a} \times 40{,}08 \times 1\,000}{\mathbf{w}} \times 20$$

$$\text{m mol (+) dm}^{-3}\text{ Ca in saturation extract} = \frac{\text{mg dm}^{-3}\text{ Ca in saturation extract}}{20{,}04}$$

Magnesium

$$\text{mg kg}^{-1}\text{ Mg in soil} = \frac{(\mathbf{c} - \mathbf{b}) \times \mathbf{a} \times 24{,}31 \times \mathbf{w} \times 1\,000}{20 \times 250} \times 20$$

$$\text{c mol (+) kg}^{-1}\text{ Mg in soil} = \frac{\text{mg kg}^{-1}\text{ Mg in soil}}{12{,}15 \times 10}$$

$$\text{mg dm}^{-3}\text{ Mg in saturation extract} = \frac{(\mathbf{c} - \mathbf{b}) \times \mathbf{a} \times 24{,}31 \times 1\,000}{\mathbf{w}} \times 20$$

$$\text{m mol (+) dm}^{-3} = \frac{\text{mg dm}^{-3}\text{ Mg in saturation extract}}{12{,}15}$$

Potassium and sodium

Let concentration of K/Na be **k** mg dm^{-3} as read from the calibration curve

$$\text{mg kg}^{-1}\text{ Na/K in soil} = \frac{\mathbf{k} \times \mathbf{w}}{250} \times 20$$

$$\text{m mol (+) dm}^{-3}\text{ Na in saturation extract} = \frac{\mathbf{k} \times 20}{22{,}99}$$

$$\text{c mol (+) kg}^{-1}\text{ Na in soil} = \frac{\text{mg kg}^{-1}\text{ Na in soil}}{22{,}99 \times 10}$$

$$\text{c mol (+) kg K}^{-1}\text{ in soil} = \frac{\text{mg kg}^{-1}\text{ K in soil}}{39{,}1 \times 10}$$

Where: **a** = Concentration of EDTA (mol dm^{-3})
b = Volume (cm^3) of EDTA used in Ca titration
c = Volume (cm^3) of EDTA used in Mg + Ca titration
w = Volume (cm^3) of water absorbed by 250 g soil

Calculation of saturation percentage

$$\text{\% Saturation} = \frac{\mathbf{w} \times 100}{250}$$

Calculation of Sodium Adsorption Ratio

$$\text{SAR} = \frac{\text{Na}}{\sqrt{\frac{\text{Ca} + \text{Mg}}{2}}}$$

Where Ca, Mg and Na are expressed as m mol (+) dm^{-3}

4.6 References

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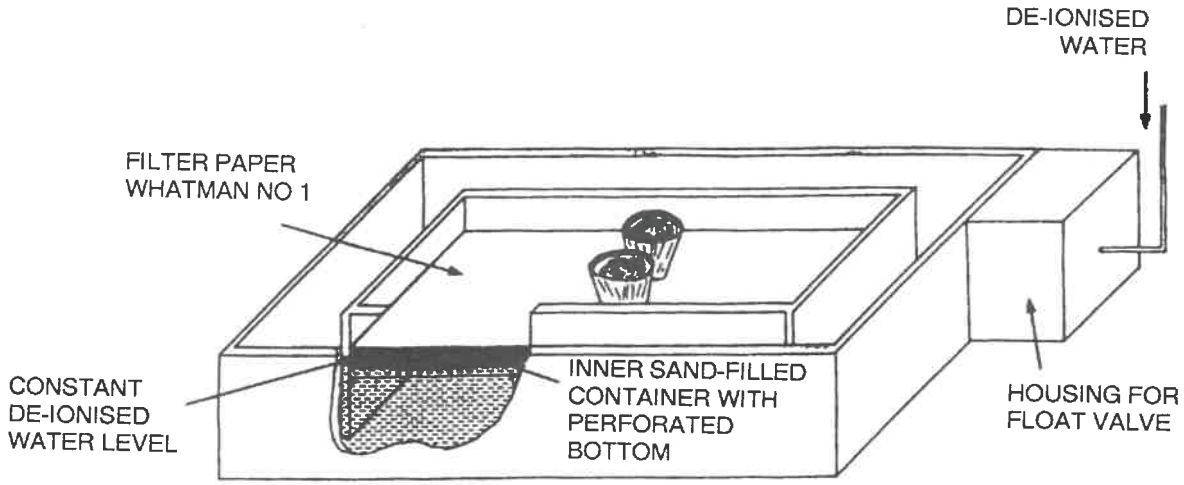

Figure 4.1 Construction of capillary saturation table

5 ELECTRICAL RESISTANCE OF SOIL PASTE

5.1 Introduction

The electrical resistance of a saturated soil paste is a function of the salt concentration of the soil and is inversely proportional to the salt concentration. The electrical resistance can therefore be considered to be an index of the salt hazard of a soil. It is, however, not a reliable guide to predict reduction in crop yield, because the salt content of sub-surface water rather than that of the soil as a whole, is the determining factor.

5.2 Apparatus

US Bureau of Soils standard electrode cup
Resistance bridge

5.3 Procedure

* Sufficient soil to fill the electrode cup is placed in a suitable container and moistened with de-ionised water while stirring with a spatula until a homogeneous mixture is obtained
* Consolidate the mixture from time to time by tapping the container on the work bench
* Test for the properties of a saturated paste (see 4.4.1) and add more water if necessary
* After an hour test whether the paste still has saturation properties
* Allow sample to stand for 4 hours
* Determine the electrical resistance of the paste in ohms with a resistance bridge corrected for a temperature of 25 °C
* It must be taken into account that the determination described by the US Salinity Laboratory corrects the resistance to a temperature of 15,5 °C (60 °F)

5.4 Reference

UNITED STATES SALINITY LABORATORY STAFF, 1954. Diagnosis and improvement of saline and alkali soils. USDA Handbook no. 60, 91. U.S. Govern. Printing Office, Washington D.C.

6 EXTRACTABLE ACIDITY: KCl (1 mol dm^{-3}) ON A MASS BASIS

6.1 Introduction

Extractable acidity is a fairly arbitrary quantity composed of usually four types of acidity. The first is H ions obtained from the hydrolysis of exchangeable Al^{3+}. The second is from the hydrolysis of partially hydrolysed and non-exchangeable Al. The third type is from weakly acidic groups, mostly on organic matter and the fourth is exchangeable H.

These reactions in a solution containing an excess of OH^- ions may be as follow:

$$Al^{3+} + 3OH^- \longrightarrow Al(OH)_3 \quad (1)$$

$$yOH^- + Al_x(OH)_{3x-y} \longrightarrow Al_x(OH)_{3x} \quad (2)$$

$$RCOOH + OH^- \longrightarrow RCOO^- + HOH \quad (3)$$

$$H^+ + OH^- \longrightarrow HOH \quad (4)$$

In soils with pH above 5,5 reactions (2) and (3) are the most important, with reaction (1) featuring below pH 5,5. Reaction (4) occurs below pH 4.

Using a salt such as KCl with negligible buffering properties, exchangeable H and Al can be replaced, rendering it possible to determine total exchangeable acid and by addition of NaF, the contribution made by Al can be determined.

KCl extraction thus relates to neutral and salt exchangeable acidity.

$$KCl \longrightarrow K^+ + Cl^-$$

$$K^+ + \text{adsorbed } H^+ \text{ and } Al^{3+} \longrightarrow H^+ + Al^{3+} + K^+ \text{ (adsorbed)}$$

$$H^+ + NaOH \longrightarrow Na^+ + HOH \quad (1)$$

$$Al^{3+} + 3NaOH \longrightarrow 3Na^+ + Al(OH)_3 \quad (2)$$

$$Al(OH)_3 + 6Na\,F \longrightarrow AlF_6^{3-} + 3OH^- + 6Na^+ \quad (3)$$

$$3OH^- + 3HCl \longrightarrow 3Cl^- + 3HOH \quad (4)$$

6.2 Apparatus

Balance accurate to 0,01 g
Extracting bottles, screw cap or stoppered, 100 cm^3 capacity
Filter paper, Whatman no 2V or equivalent
Burette, 10 cm^3 semi-micro or digital
Reciprocating shaker
Erlenmeyer flasks 500 cm^3

6.3 Reagents

Potassium chloride, 1 mol dm^{-3}: Dissolve 74,5 g potassium chloride in 1 dm^3 de-ionised water

Sodium hydroxide, 0,1 mol dm^{-3}: Prepared from commercially available standard solutions

Hydrochloric acid, 0,1 mol dm^{-3}: Prepared from commercially available standard solutions

Sodium fluoride, 1 mol dm^{-3}: Dissolve 41 g sodium fluoride in 1 dm^3 de-ionised water, store in a plastic bottle

Phenolphthalein: Dissolve 0,1 g phenolphthalein in 100 cm^3 commercial grade ethanol

6.4 Procedure

* A 10 g sample of soil is shaken horizontally with 70 cm^3 1 mol dm^{-3} KCl in a 100 cm^3 slopy neck bottle at 180 oscillations per minute for 1 hour
* Immediately filter through Whatman no 2V paper into a 500 cm^3 Erlenmeyer flask. Wash contents of paper with 30 cm^3 KCl solution (3 portions) to a total volume of about 100 cm^3. Total extractable acidity is determined in the KCl extract by titration with 0,1 mol dm^{-3} NaOH and phenolphthalein as indicator (5 to 8 drops). Do not over-titrate to a deep pink
* Add 1 drop of 0,1 mol dm^{-3} HCl to remove pink colour of the indicator and add 10 cm^3 NaF solution. While stirring the solution, titrate liberated alkalinity with 0,1 mol dm^{-3} HCl. A few extra drops of indicator may be necessary. The end point is indicated when colour does not return after 2 minutes. Exchangeable aluminium is determined by NaF addition
* It is recommended that extractions be performed at a temperature of 20 ± 2 °C.

6.5 Calculations

$$\text{cmol (+) kg}^{-1}\text{ KCl acidity} = \frac{\text{cm}^3\text{ NaOH} \times \mathbf{M} \times 100}{\text{mass of soil (10 g)}}$$

$$\text{cmol (+) kg}^{-1}\text{ exchangeable Al} = \frac{\text{cm}^3\text{ HCl} \times \mathbf{M} \times 100}{\text{mass of soil (10 g)}}$$

where **M** = concentration of the NaOH or HCl (mol dm^{-3})

cmol (+) kg^{-1} H = KCl acidity - KCl exchangeable Al

6.6 Reference

THOMAS, G.W., 1982. Exchangeable cations. In Methods of soil analysis. Part 2, 159-165. Am. Soc. Agron. Madison, Wis.

7 EXTRACTABLE ACIDITY : KCl (1 mol dm^{-3}) ON A VOLUME BASIS

7.1 Introduction

Extractable acidity is a fairly arbitrary quantity composed of usually four types of acidity. The first is H ions obtained from the hydrolysis of exchangeable Al^{3+}. The second is from the hydrolysis of partially hydrolysed and non-exchangeable Al. The third type is from weakly acidic groups, mostly on organic matter and the fourth is exchangeable H.

These reactions in a solution containing an excess of OH^- ions may be as follow:

$$Al^{3+} + 30H^- \longrightarrow Al(OH)_3 \quad (1)$$
$$yOH^- + Al_x(OH)_{3x-y} \longrightarrow Al_x(OH)_{3x} \quad (2)$$
$$RCOOH + OH^- \longrightarrow RCOO^- + HOH \quad (3)$$
$$H^+ + OH^- \longrightarrow HOH \quad (4)$$

In soils with pH above 5,5 reactions (2) and (3) are the most important, with reaction (1) featuring below pH 5,5. Reaction (4) occurs below pH 4.

Using a salt such as KCl with negligible buffering properties, exchangeable H and Al can be replaced, rendering it possible to determine total exchangeable acid and by addition of NaF, the contribution made by Al can be determined.

KCl extraction thus relates to neutral and salt exchangeable acidity.

$$KCl \longrightarrow K^+ + Cl^-$$
$$K^+ + \text{adsorbed } H^+ \text{ and } Al^{3+} \longrightarrow H^+ + Al^{3+} + K^+ \text{ (adsorbed)}$$
$$H^+ + NaOH \longrightarrow Na^+ + HOH \quad (1)$$
$$Al^{3+} + 3NaOH \longrightarrow 3Na^+ + Al(OH)_3 \quad (2)$$
$$Al(OH)_3 + 6Na\,F \longrightarrow AlF_6^{3-} + 3OH^- + 6Na^+ \quad (3)$$
$$3OH^- + 3HCl \longrightarrow 3Cl^- + 3HOH \quad (4)$$

7.2 Apparatus

2,5 cm^3 scoop
Extracting bottles, screw cap or stoppered, 100 cm^3 capacity
Filter paper, Whatman no 2V or equivalent
Burette, 10 cm^3 semi-micro or digital
Stirrer

7.3 Reagents

NaOH stock solution, 0,05 mol dm^{-3}: Dissolve 2 g NaOH (AR) in 1 dm^3 de-ionised water, store in a plastic container

NaOH standard, 0,01 mol dm^{-3}: Dilute 1 part stock solution with four parts of de-ionised water. Standardise against potassium hydrogen phthalate (AR), using phenolphthalein as indicator. Store solution in a plastic container fitted with a CO_2 trap

KCl solution: Dissolve 74,55 g KCl (AR) in 1 dm^3 de-ionised water

Superfloc (optional): One g Superfloc 127 or 100 (Cyanamid) is dissolved in 1 dm^3 de-ionised water. To facilitate dissolution of Superfloc, the solution must be stirred for about three hours

7.4 Procedure

* Scoop out 2,5 cm^3 ≤ 2 mm soil sample and transfer to an extraction bottle
* Add 25 cm^3 1 mol dm^{-3} KCl and optionally four drops Superfloc
* Stir for 10 minutes at 400 rpm
* Filter solution into a 150 cm^3 capacity Erlenmeyer flask
* Take a 10 cm^3 aliquot, add 10 cm^3 de-ionised water
* Titrate with 0,01 mol dm^{-3} NaOH with phenolphthalein as indicator
* Include a 10 cm^3 KCl blank

7.5 Calculation

Extractable acidity:

$$\text{cmol (+) } dm^{-3} \text{ soil} = \frac{cm^3 \text{ NaOH (sample)} - cm^3 \text{ NaOH (blank)} \times \mathbf{f} \times 100}{(cm^3) \text{ sample volume}}$$

where **f** = concentration of NaOH (mol dm^{-3})

7.6 Reference

THOMAS, G.W., 1982. Exchangeable acidity. In A.L. Page (ed.). Methods of soil analysis. Part 2, 159-165. Am. Soc. Agron. Madison, Wis.

8 EXTRACTABLE CATIONS: AMMONIUM ACETATE(1 mol dm^{-3}, pH 7)

8.1 Introduction

This method is used to determine extractable cations Ca^{2+} , Mg^{2+}, K^{+} and Na^{+} in soils, reflecting the nutrient status.
The method does not give accurate results with respect to the exchangeable plus water soluble cation status.
The amount of extractable potassium may increase on drying of soils. However, soil samples can be extracted in a moist state.
As the rate of extraction is a function of temperature, extraction must be performed at 20 ± 2 °C (including the extractant solution).

8.2 Apparatus

Balance to measure accurately to 0,05 g
Extraction bottles, 100 cm^3 capacity with stoppers
Reciprocating shaker, 180 oscillations per minute
Funnels and funnel racks
Whatman no 40 filter paper
Volumetric flasks and pipettes
Atomic absorption spectrophotometer
Flame spectrophotometer

8.3 Reagents

NH_4OAc solution, 1 mol dm^{-3}, pH 7: Dilute 57 cm^3 glacial acetic acid (99,5% AR) with de-ionised water to a volume of 500 cm^3. Add 69 cm^3 concentrated ammonia solution to the diluted solution of acetic acid. Mix well and dilute to about 900 cm^3 with de-ionised water. Adjust pH to 7 by adding acetic acid or ammonia solution. Make up to 1 dm^3 with de-ionised water
Standard solutions (1 000 mg dm^{-3}) : Prepare K, Ca, Mg and Na standards with NH_4OAc solution

8.4 Procedure

8.4.1 Extraction

* Place 5 ± 0,05 g air-dry, ≤ 2 mm soil in a 100 cm^3 extraction bottle
* Add 50 cm^3 NH_4OAc solution cooled to 20 ± 2 °C to the soil in the extraction bottle and shake horizontally on a reciprocating shaker at 180 oscillations per minute for 30 minutes

* Rapidly filter extract through a Buchner funnel, with suction
* Collect filtrate but discard first few drops
* Refilter if extract is not clear
* The filtrate containing K, Na, Ca and Mg should not be stored for longer than 24 hours unless refrigerated or treated to prevent bacterial growth (a drop of toluene may be added)

8.4.2 Analysis

The elements K, Ca, Mg and Na in the filtrate can be determined by either flame emission or atomic absorption spectroscopy where applicable.

8.5 Calculations

$$\text{Ammonium acetate extractable cations} = \frac{\mathbf{b} \times 50}{5} \text{ mg kg}^{-1}$$

where **b** =mg dm^{-3} of Ca, Mg, Na or K in the extract.

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THOMAS, G.W., 1982. Exchangeable acidity. In A.L. Page (ed.). Methods of soil analysis. Part 2, 159-161. Am. Soc. Agron. Madison, Wis.

9 EXTRACTABLE CATIONS AND ACIDITY : KCl (1 mol dm^{-3}) ON A VOLUME BASIS

9.1 Introduction

A potassium chloride solution was first used by Hunter (1974) to displace part of the adsorbed and soluble Ca^{2+}, Mg^{2+}, Na^{+}, H^{+} and Al^{3+} present in the soil. The cations determined are referred to as extractable Ca, Mg, Na and acidity.

Separation of calcium from interfering ions is achieved by dialysis. The dialysed calcium is detected colorimetrically at 570 nm using cresolphthalein complexone in a buffered alkaline medium.

Magnesium hydroxide is precipitated in an alkaline medium and the Magnesium Blue dye is absorbed in the presence of a wetting agent (Brij-35) and suspending material (PVA). The intensity of the developed blue complex is measured at 630 nm.

9.2 Apparatus

Scoop, 2,5 cm^3 capacity
Sample cups
Multiple stirrers
Whatman no 1 filter paper
Continuous flow analysers

9.3 Reagents

Sodium hydroxide: Prepare an approximately 1 mol dm^{-3} sodium hydroxide (AR) solution, by dissolving 400 g NaOH in 10 dm^{-3} de-ionised water
Magnesium Blue stock solution: Dissolve 0,2 g Magnesium Blue in 200 cm^3 N,N-dimethylformamide in a 1 dm^3 volumetric flask. Allow to stand for 2 days before making up to the mark with de-ionised water. Filter before use
Magnesium Blue working solution: Mix 250 cm^3 of the filtered stock solution with 150 cm^3 N,N-dimethylformamide in a 1 dm^3 volumetric flask. Dilute to the mark with de-ionised water
Polyvinyl alcohol (PVA): Dissolve 3 g PVA (AR) in 500 cm^3 hot de-ionised water. Stir continuously. After cooling, transfer solution to a 1 dm^3 volumetric flask. Make up to the mark with de-ionised water
Magnesium standard, 1 000 mg dm^{-3} Mg: From commercially available sources, make up a standard solution in 1 mol dm^{-3} KCl

Phosphate buffer: Dissolve 150 g potassium dihydrogen phosphate in 800 cm^3 de-ionised water. Add 1 cm^3 Brij-35 (30%) and make up to the mark with de-ionised water (1 dm^3). Filter if necessary

Cresolphthalein complexone stock solution: Dissolve 0,125 g o-cresolphthalein in 400 cm^3 de-ionised water. Make up to the mark with de-ionised water (500 cm^3)

Cresolphthalein complexone-8-hydroxy-quinoline solution (CPC): To 20 cm^3 concentrated hydrochloric acid and 200 cm^3 de-ionised water add 2,5 g 8-hydroxy-quinoline in a 1 dm^3 volumetric flask. Allow to dissolve. Add 100 cm^3 cresolphthalein solution and 1 cm^3 Brij-35. Make up to the mark with de-ionised water

2-Amino-2-methyl-1-propanol: Dissolve 37,5 g 2-amino-2-methyl-1-propanol in de-ionised water in a 500 cm^3 volumetric flask. Make up to the mark with de-ionised water. If reagent has solidified, heat flask in warm water prior to pipetting. Prepare a fresh solution every second day

Calcium standard, 1 000 mg dm^{-3} Ca: From commercially available sources, make up standard solution in 1 mol dm^{-3} KCl

Potassium chloride, 1 mol dm^{-3}: Dissolve 745 g KCl (AR) in 10 dm^3 de-ionised water

9.4 Procedure

9.4.1 Extraction (at 20 ± 2 °C)

* Scoop 2,5 cm^3 dry soil into a sample cup
* Add 25 cm^3 1 mol dm^{-3} KCl to the soil sample
* Stir at 400 rpm for 10 minutes on a multiple stirrer
* Filter through Whatman no 1 filter paper into a clean cup

9.4.2 Determinations

Calcium

* Set up manifolds and complete systems as shown in Fig. 9.1 (low Ca) and 9.2 (high Ca) respectively
* Standards must be prepared as follow in 1,0 mol dm^{-3} KCl:

Low Ca: 5 to 100 mg dm^{-3} Ca
High Ca: 25 to 350 mg dm^{-3} Ca

Magnesium

* Set up manifolds and complete systems as shown in Fig. 9.3 (low Mg) and 9.4 (high Mg) respectively.

Standards are prepared as follow in 1,0 mol dm^{-3} KCl:

Low Mg : 5 to 45 mg dm^{-3} Mg
High Mg: 7,5 to 250 mg dm^{-3} Mg

Extractable Acidity

As described in 7.4

Sodium

Sodium in the extract can be determined with a flame photometer or by atomic absorption spectroscopy

9.5 Calculation

2,5 cm^3 soil is extracted with 25 cm^3 1 mol dm^{-3} KCl
Let concentration of calcium/magnesium be **c** mg dm^{-3} as read from the calibration curve

$$\text{mg dm}^{-3}\text{ Ca/Mg in soil} = \frac{\mathbf{c} \times 25}{2{,}5\ (\text{cm}^3)}$$

9.6 References

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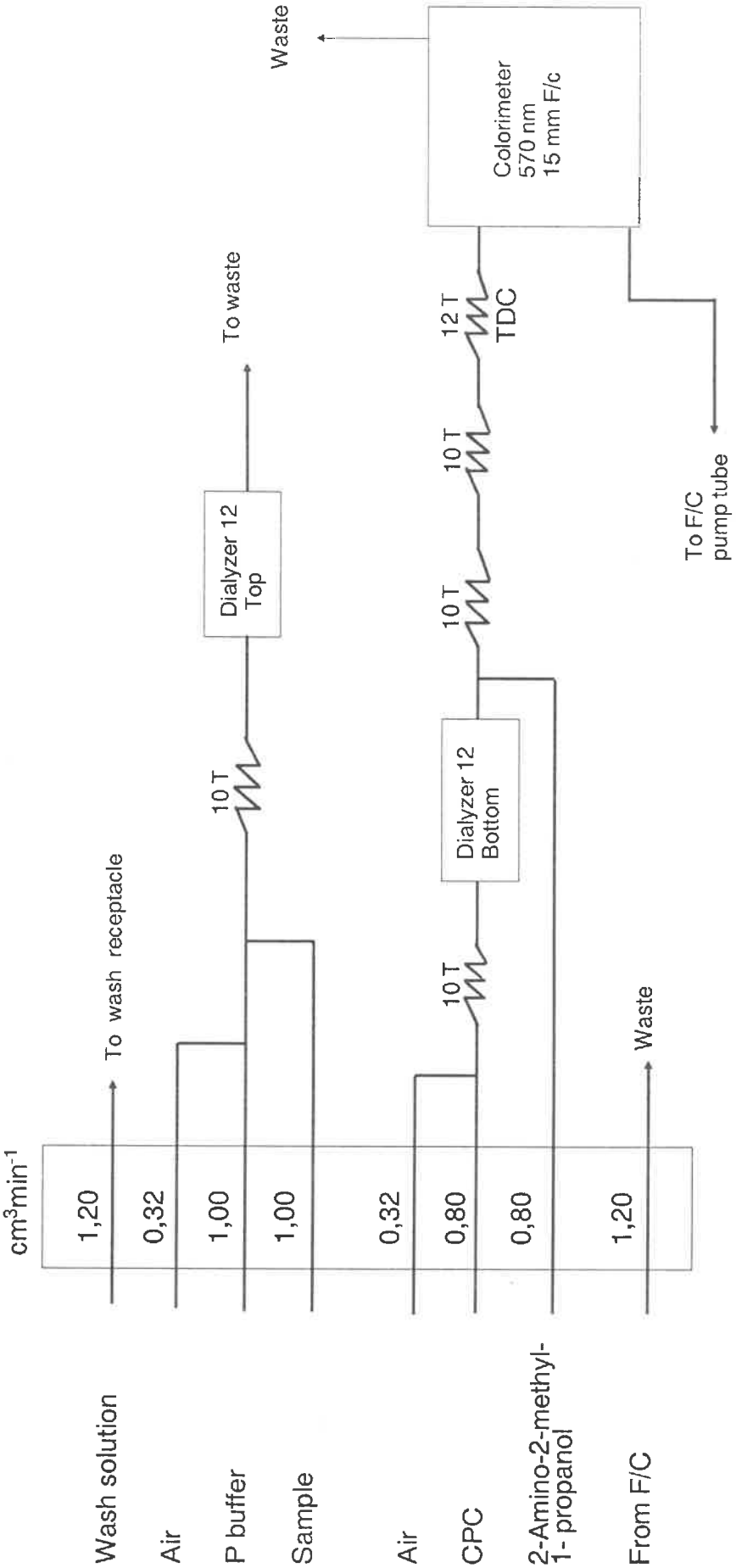

Figure 9.1: Flow system for Ca (Low)

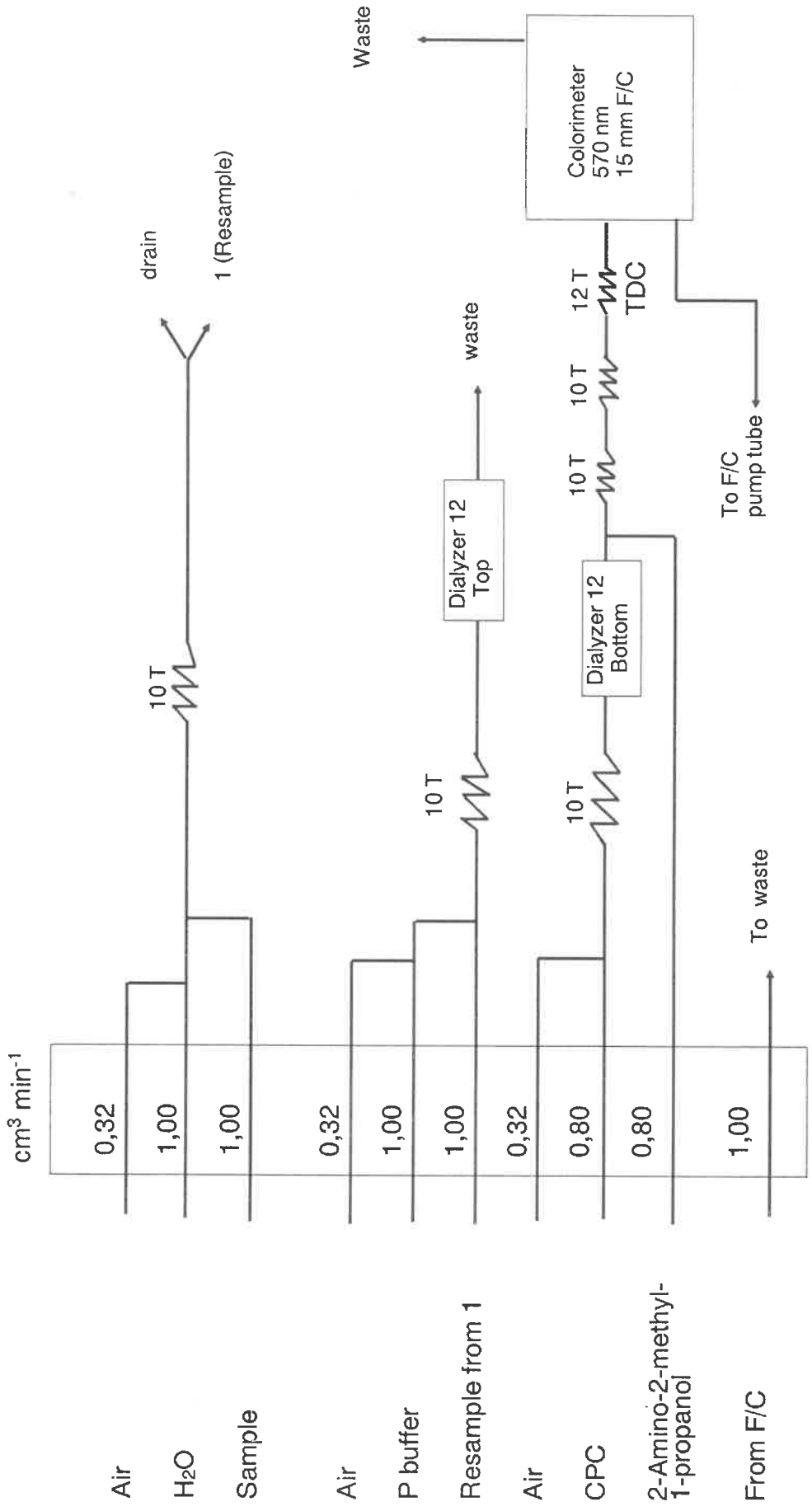

Figure 9.2: Flow system for Ca (High)

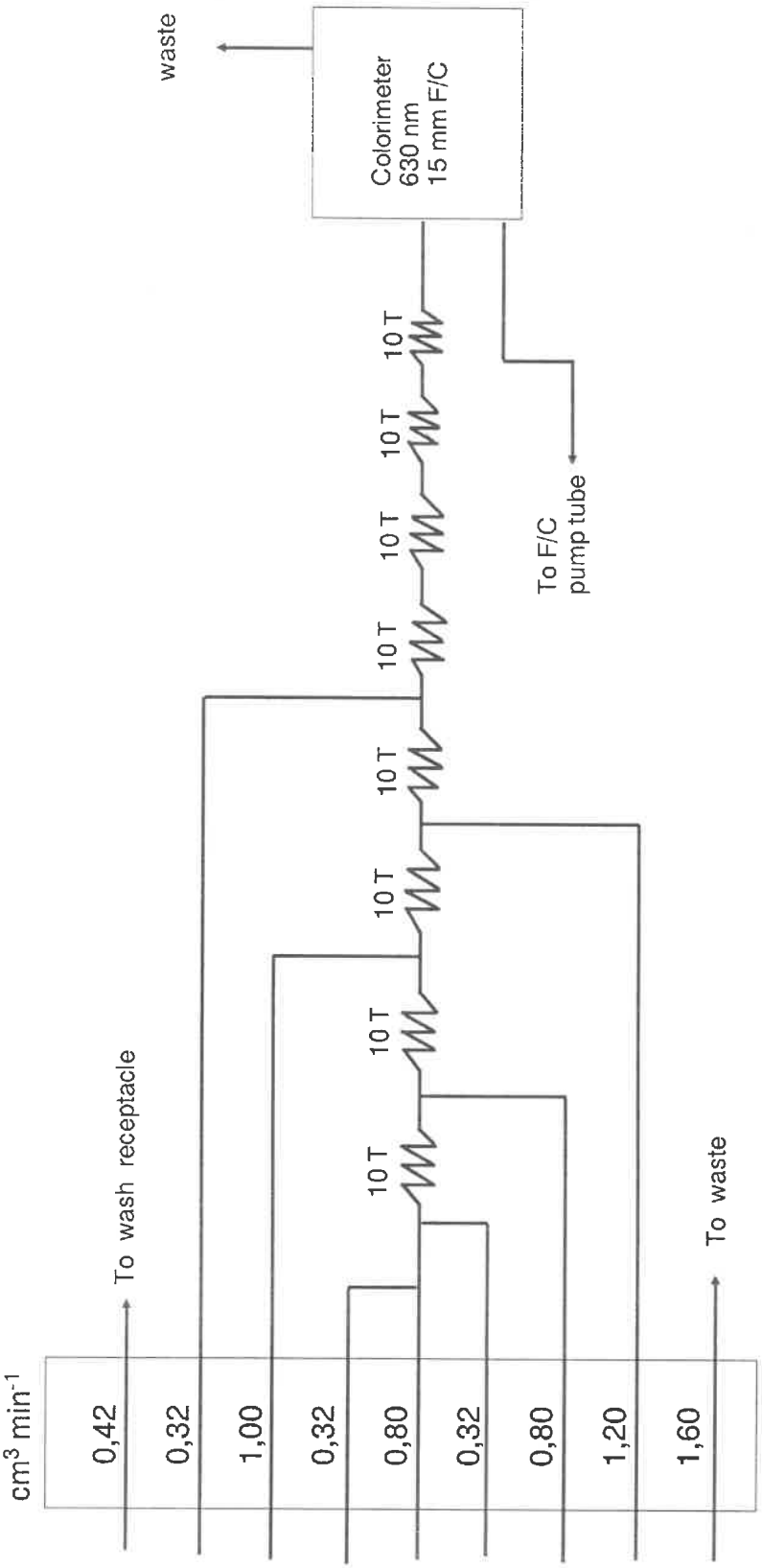

Figure 9.3: Flow system for Mg (Low)

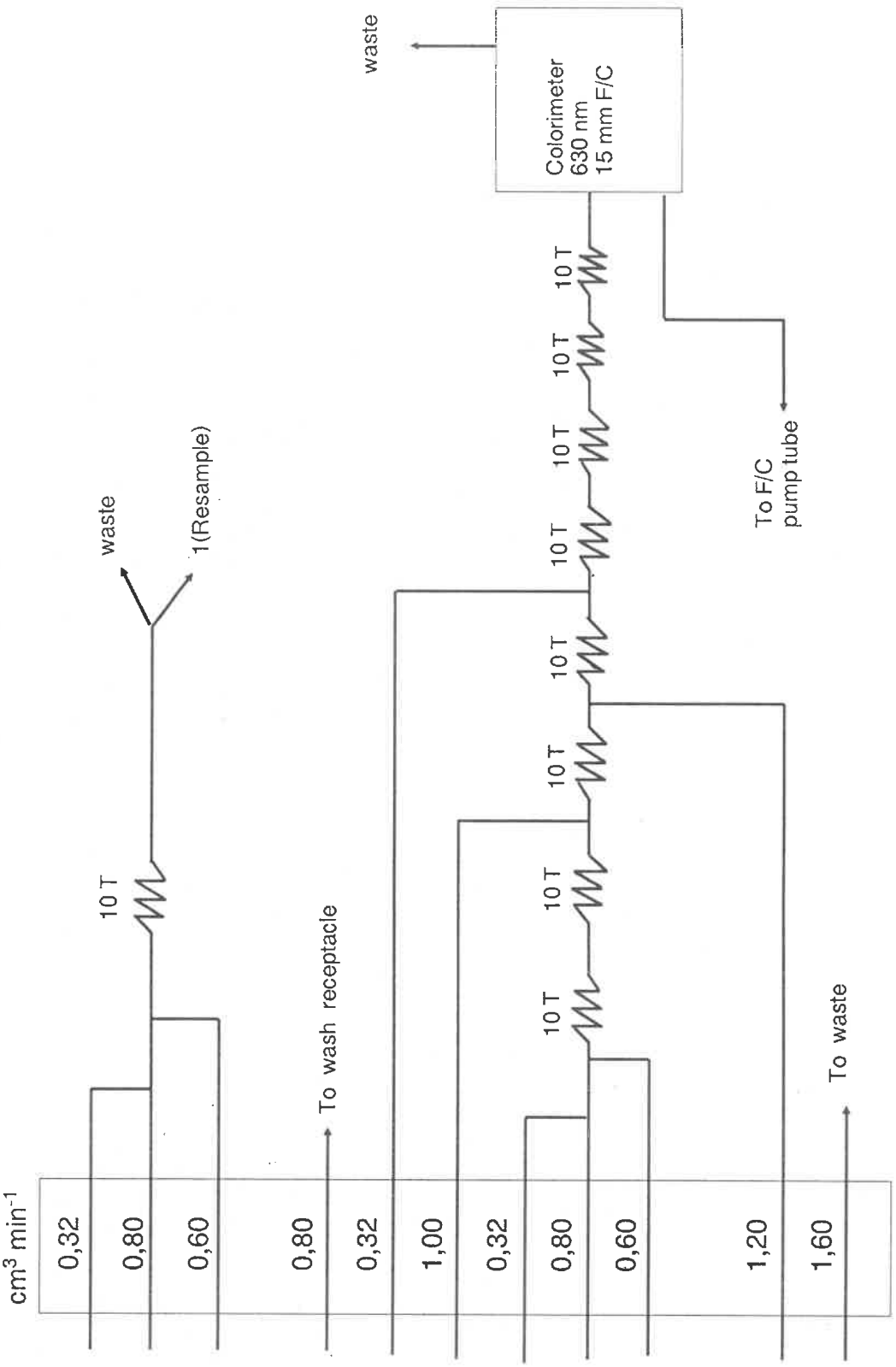

Figure 9.4: Flow system for Mg (High)

10 EXTRACTABLE CATIONS AND ACIDITY: KCl (1 mol dm^{-3}) ON A MASS BASIS

10.1 Introduction

A potassium chloride solution (Hunter, 1974) is used to replace part of the adsorbed and soluble Ca^{2+}, Mg^{2+}, Na^{+}, H^{+} and Al^{3+} present in the soil. The cations determined are referred to as extractable Ca, Mg, Na and acidity.

Separation of calcium from interfering ions is achieved by dialysis. The dialysed calcium is detected colorimetrically at 570 nm using cresolphthalein complexone in a buffered alkaline medium.

Magnesium hydroxide is precipitated in an alkaline medium and the Magnesium Blue dye is absorbed in the presence of a wetting agent (Brij) and suspending material (PVA). The intensity of the developed blue complex is measured at 630 nm.

10.2 Apparatus

Balance, to measure accurately to 0,01 g
Slopy, plastic extraction bottles, 100 cm^3 capacity and stoppers
Reciprocating shaker set at 180 oscillations per minute
Whatman no 2 filter paper
Funnels
Continuous flow analyser

10.3 Reagents

Potassium chloride, 1 mol dm^{-3} : Dissolve 745 g KCl (AR) in 10 dm^3 de-ionised water

Phosphate buffer: Dissolve 150 g potassium dihydrogen phosphate in 800 cm^3 de-ionised water. Add 1 cm^3 Brij-35 (30%) and make up to the mark with de-ionised water(1 dm^3). Filter if necessary

Cresolphthalein complexone stock solution: Dissolve 0,125 g o-cresolphthalein in 400 cm^3 de-ionised water. Make up to the mark with de-ionised water (500 cm^3). Store in refrigerator

Cresolphathalein complexone-8-hydroxy-quinoline solution (CPC): To 20 cm^3 concentrated hydrochloric acid add 200 cm^3 de-ionised water and 2,5 g 8- hydroxy-quinoline in a 1 dm^3 volumetric flask. Allow to dissolve. Add 100 cm^3 cresolphthalein solution and 1 cm^3 Brij-35. Make up to the mark with de-ionised water

2-Amino-2-methyl-1-propanol: Dissolve 37,5 g 2-amino-2-methyl-1-propanol in de-ionised water in a 500 cm^3 volumetric flask. Make up to the mark with de-ionised water. If reagent has solidified, heat flask in warm water prior to pipetting. Prepare a fresh solution every second day

Calcium, Magnesium and Sodium standards, 1 000 mg dm^{-3} Ca, Mg and Na: From commercially available sources, make up standard solutions in 1 mol dm^{-3} KCl

Sodium hydroxide: Prepare an approximately 1 mol dm^{-3} sodium hydroxide (AR) solution, by dissolving 400 g NaOH in 10 dm^{-3} de-ionised water

Magnesium Blue stock solution: Dissolve 0,2 g Magnesium Blue in 200 cm^3 N,N-dimethylformamide in a 1 dm^3 volumetric flask. Allow to stand for 2 days before making up to the mark with de-ionised water. Filter before use

Magnesium Blue working solution: Mix 250 cm^3 of the filtered stock solution with 150 cm^3 N,N-dimethylformamide in a 1 dm^3 volumetric flask. Dilute to the mark with de-ionised water

Polyvinyl alcohol (PVA): Dissolve 3 g PVA (AR) in 500 cm^3 hot de-ionised water. Stir continuously. After cooling, transfer solution to a 1 dm^3 volumetric flask and add 1 cm^3 Brij 35. Make up to the mark with de-ionised water

10.4 Procedure

10.4.1 Extraction (at 20 ± 2 °C)

Place 5 g soil in a 100 cm^3 slopy, plastic extraction bottle
Add 50 cm^3 1 mol dm^3 KCl to the sample
Shake horizontally for 30 minutes on a reciprocating shaker at 180 oscillations per minute
Filter immediately through Whatman no 2 filter paper.

10.4.2 Determinations

Calcium

Set up manifolds and complete systems as shown in Fig. 10.1 (low Ca) and 10.2 (high Ca) respectively.
Standards are prepared from the stock as follow with 1 mol dm^{-3} KCl solution:

Low Ca: 5 to 100 mg dm^{-3} Ca
High Ca: 25 to 350 mg dm^{-3} Ca

Magnesium

Set up manifolds and complete systems as shown in Fig. 10.3 (low Mg) and 10.4 (high Mg) respectively.
Standards are prepared in 1,0 mol dm^{-3} KCl from the stock solution as follow:

Low Mg: 5 to 45 mg dm^{-3} Mg
High Mg: 7,5 to 250 mg dm^{-3} Mg

Sodium

Sodium is determined with a flame photometer

Standards ranging from 0 to 100 mg dm^{-3} Na are prepared from the stock with 1 mol dm^{-3} KCl solution

Extractable Acidity

As described under extractable acidity in 7.4

10.5 Calculation

5 g soil is extracted with 50 cm^3 1 mol dm^{-3} KCl
Let concentration of calcium/magnesium be **c** mg dm^{-3} read from the calibration curve

$$\text{mg kg}^{-1}\ \text{Ca/Mg in soil} = \frac{\mathbf{c} \times 50}{5\ (\text{g})}$$

10.6 References

ANALYTICAL METHODS USED IN THE SOIL SCIENCE LABORATORIES AT CEDARA. 1986.

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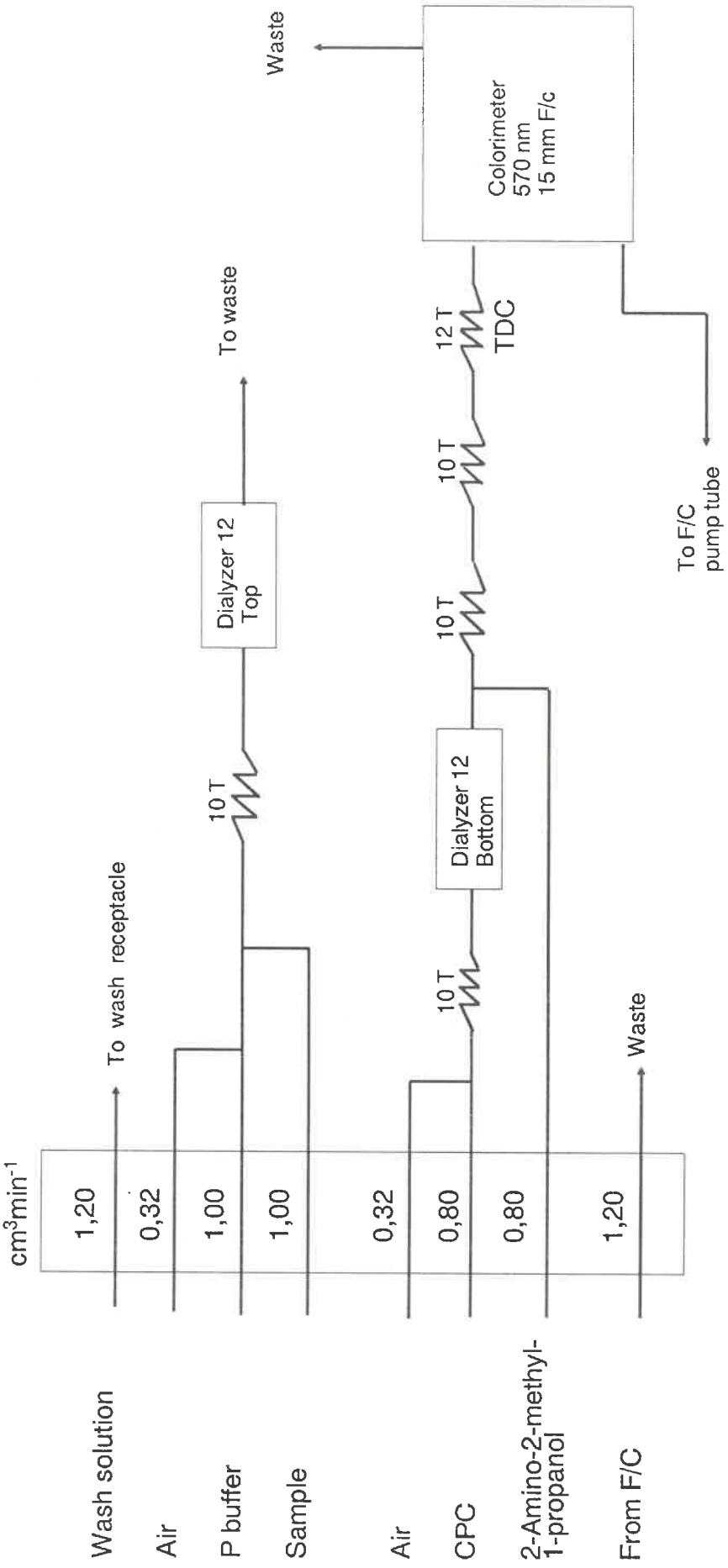

Figure 10.1: Flow system for Ca (Low)

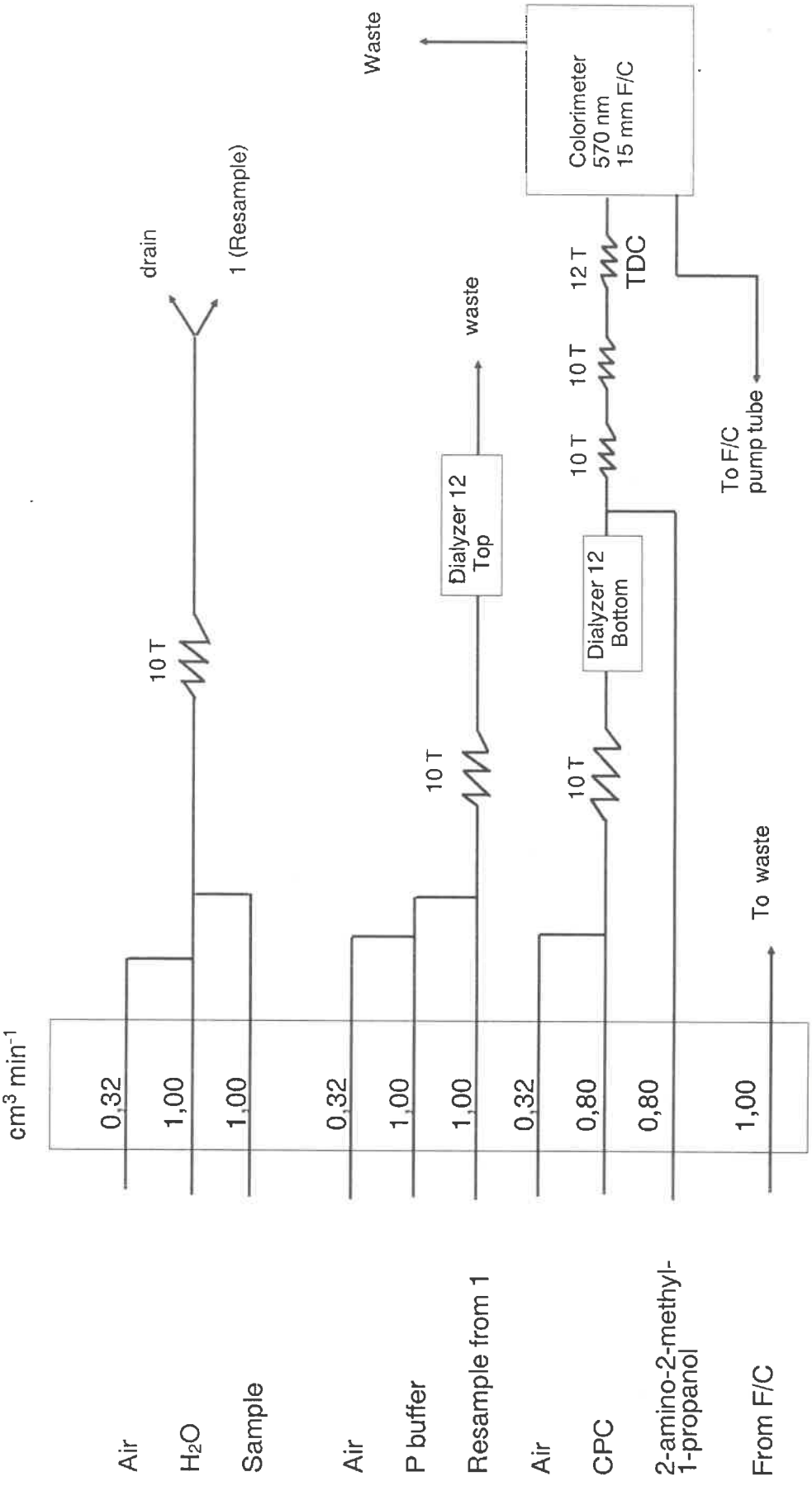

Figure 10.2: Flow system for Ca (High)

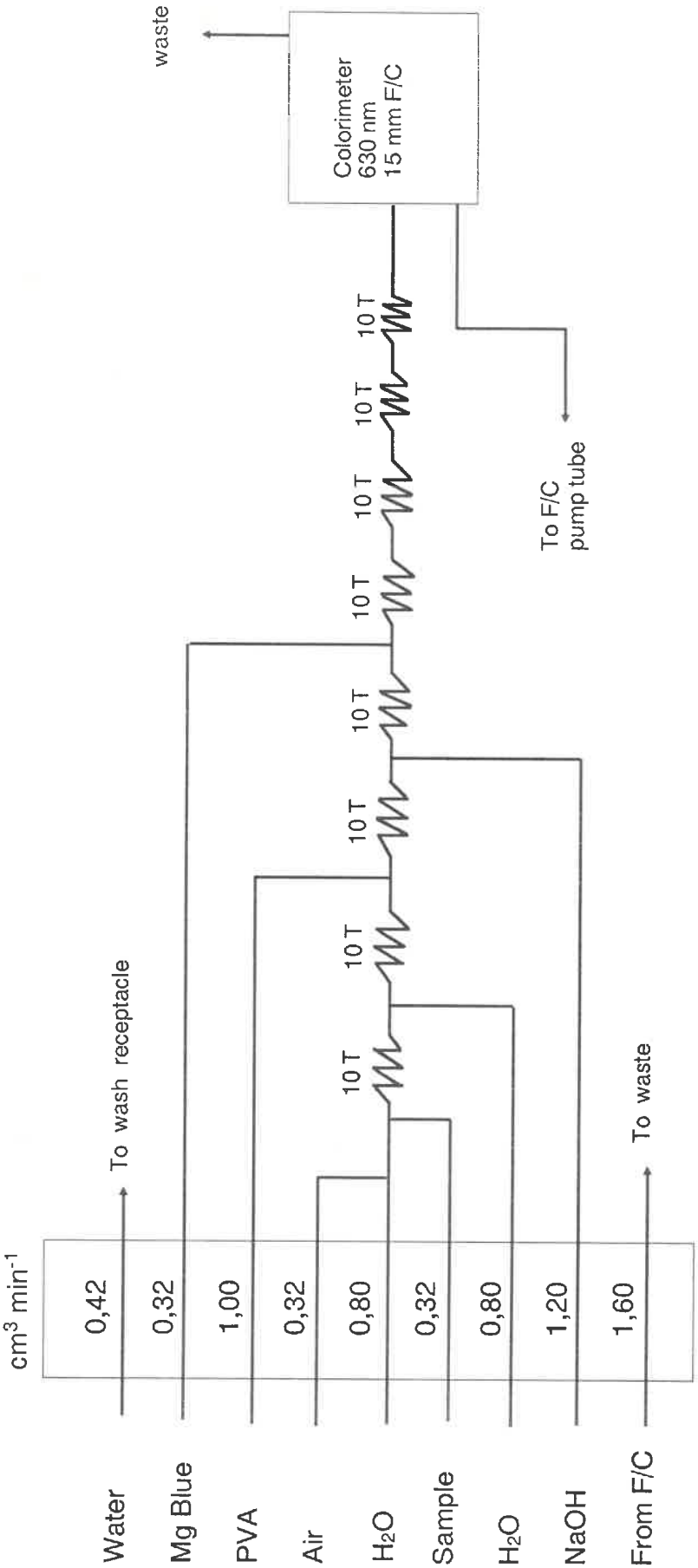

Figure 10.3: Flow system for Mg (Low)

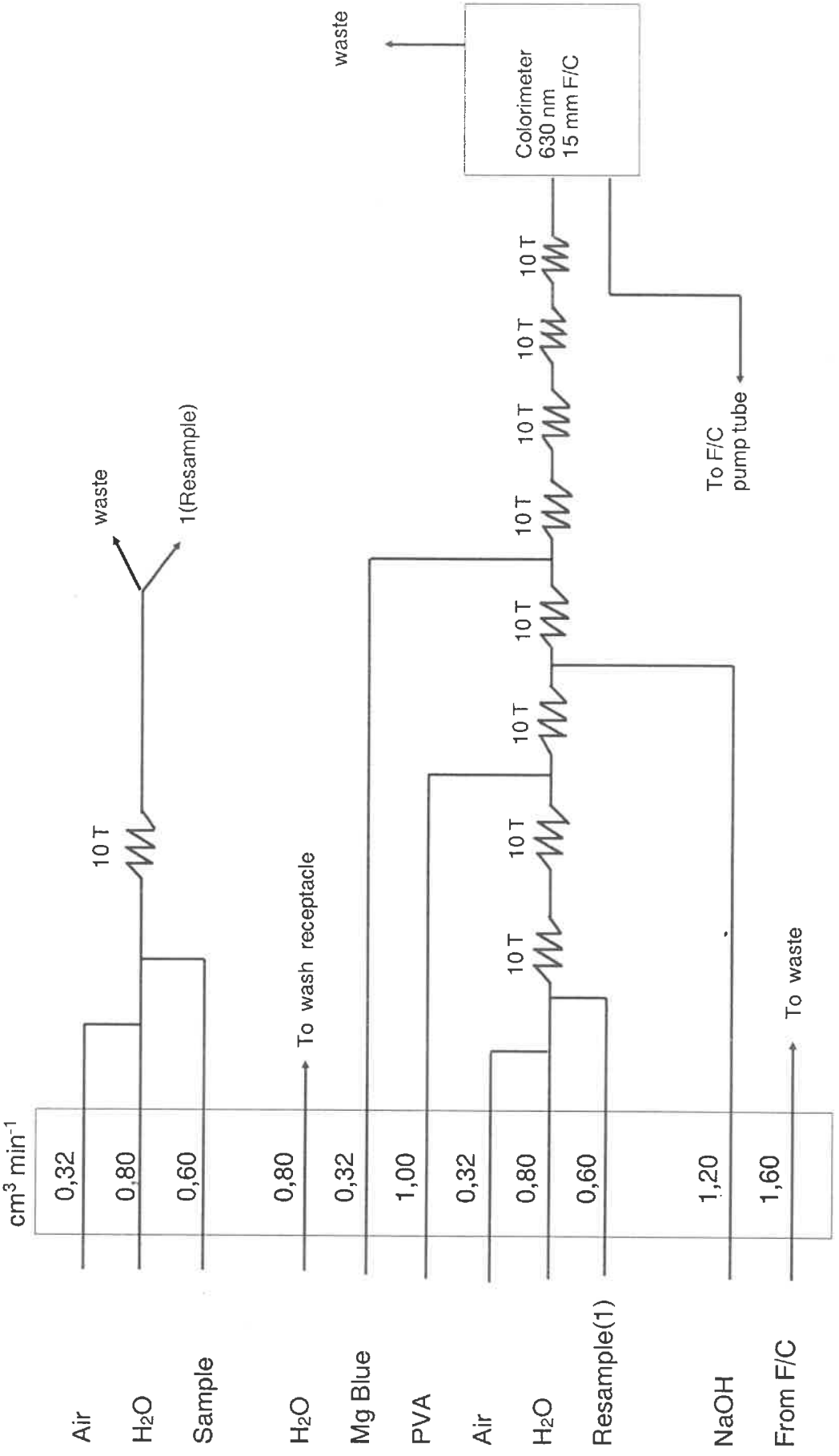

Figure 10.4: Flow system for Mg (High)

11 CATION EXCHANGE CAPACITY (CEC) AND EXCHANGEABLE CATIONS: LiCl (0,5 mol dm^{-3})

11.1 Introduction

Lithium chloride (0,5 mol dm^{-3}) serves as extractant for exchangeable and soluble cations, and simultaneously saturates the exchange complex of the soil with Li^+. The adsorbed Li^+ is subsequently displaced from the soil with calcium. The displaced Li^+ acts as an index of cation exchange capacity of the soil. Soluble cations are determined separately in soils containing significant quantities of soluble salts. These are subtracted from the LiCl extractable cations to obtain exchangeable cations.

For soils with an electrical resistance of less than 460 ohms, the exchangeable cations are estimated by subtracting the cations in the saturation extract from the total extractable cations. In soils containing lime or gypsum or those with a very high salt content, not all the water soluble salts are dissolved in the saturation extract. In these cases the figure for total exchangeable cations is higher than the CEC.

11.2 Apparatus

Beakers, 800 cm^3 capacity
Buchner funnels
Whatman no 40 filter paper
Glass rods
Volumetric flasks, 500 cm^3 capacity
Waterbath (80 - 90 °C)
Continuous flow analyser (e.g. AutoAnalyzer) fitted with a flame photometer

11.3 Reagents

Ethyl alcohol: Commercial grade
Lithium chloride, 0,5 mol dm^{-3}: Dissolve 424 g LiCl (AR) in about 5 dm^3 de-ionised water. Pour into a 20 dm^3 polythene container. Dilute to the 20 dm^3 mark with de-ionised water
Calcium nitrate, 0,25 mol dm^{-3}: Dissolve 590 g $Ca(NO_3)_2$ (AR) in about 2 dm^3 de-ionised water in a 10 dm^3 container. After dissolving, make up to 10 dm^3
Sodium chloride, 1 mol dm^{-3}: Dissolve 29,23 g NaCl (AR), dried at 105 °C, in de-ionised water in a 500 cm^3 volumetric flask. Make up to volume with de-ionised water

Potassium chloride, 1 mol dm^{-3}: Dissolve 37,29 g KCl (AR), dried at 105 °C, in 200 cm^3 de-ionised water in a 500 cm^3 volumetric flask. Make up to volume with de-ionised water

Calcium chloride, 0,5 mol dm^{-3}: Dissolve 25,02 g $CaCO_3$ (AR), dried at 105 °C, in 300 cm^3 2 mol dm^{-3} HCl, in a 500 cm^3 volumetric flask. After complete dissolution of the $CaCO_3$, make up to the mark with de-ionised water

NOTE: It is recommended that the $CaCO_3$ is first moistened with de-ionised water before adding the acid. Addition of 25 cm^3 aliquots of acid, until all $CaCO_3$ is converted to $CaCl_2$, is recommended

Magnesium chloride, 0,5 mol dm^{-3}: Dissolve 6,09 g pure magnesium ribbon in 300 cm^3 2 mol dm^{-3} HCl, in a 500 cm^3 volumetric flask. Add acid in 25 cm^3 aliquots. After dissolution of Mg ribbon, make up to the mark with de-ionised water

Lithium chloride, 0,1 mol dm^{-3}: Dissolve 4,3255 g LiCl (98% pure) in 1 dm^3 0,25 mol dm^{-3} calcium nitrate solution

11.4 Procedure

11.4.1 Extraction (at 20 ± 2 °C)

* Transfer 25 g soil (≤ 2 mm, air-dry or of known moisture content) to a 800 cm^3 beaker
* Add 150 cm^3 LiCl-solution and stir contents
* Allow to stand overnight (20 °C)
* Transfer soil and contents to a Buchner funnel fitted with Whatman no 40 filter paper
* Filter with suction
* Rinse beaker and soil with 50 cm^3 portions of LiCl solution until about 450 cm^3 leachate has been collected
* Each added portion of solution must drain completely
* Prevent soil from cracking due to excessive drying especially soils with a high clay content
* Transfer leachate quantitatively to a 500 cm^3 volumetric flask and make up to the mark with LiCl solution. The extracted cations are determined with a suitable method in this solution
* Wash the soil on the Buchner funnel with about 150 cm^3 ethyl alcohol in three to four portions
* Allow each portion to drain away completely before adding the next portion. Do not allow the soil to crack

* Transfer soil and filter paper to a 800 cm^3 beaker. Add 500 cm^3 0,25 mol dm^{-3} $Ca(NO_3)_2$
* Heat on a waterbath at 80 - 90 °C. Stir intermittently to break up clods (especially in clayey soils)
* Filter after 30 minutes through Whatman no 40 paper, using a Buchner funnel
* When filtration is complete, determine CEC in terms of the Li content of the calcium nitrate extract

11.4.2 Determination

Calcium and magnesium

Determination of Ca and Mg is carried out colorimetrically on a continuous flow analyser with the manifold set up as shown in Fig. 11.1, 11.2, 11.3 and 11.4

Preparation of Standards

To a 1 dm^3 volumetric flask, add 50 cm^3 0,5 mol dm^{-3} $CaCl_2$, 25 cm^3 0,5 mol dm^{-3} $MgCl_2$ and 40 cm^3 1 mol dm^{-3} KCl solution respectively and make up to volume with LiCl solution
Working calcium and magnesium standards are prepared from the above solution. Use LiCl solution for dilution

Ca (low system): 0,5 to 7 cmol(+) dm^{-3}
Ca (high system): 5 to 15 cmol(+) dm^{-3}

Mg (low system): 0,25 to 3,5 cmol(+) dm^{-3}
Mg (high system): 2,5 to 7,5 cmol(+) dm^{-3}

Potassium and sodium

Potassium and sodium are determined by flame emission spectroscopy as illustrated in Fig. 11.5

Standard working solution

Use LiCl solution as matrix and make up in a 1 dm^3 volumetric flask, 50 cm^3 0,5 mol dm^{-3} $CaCl_2$, 10 cm^3 0,5 mol dm^{-3} $MgCl_2$, 10 cm^3 1mol dm^{-3} NaCl and 10 cm^3 1 mol dm^{-3} KCl respectively

Working K and Na standards are prepared from the above solution. Use LiCl solution for dilution

K and Na: 0,25 to 5 cmol(+) dm^{-3}

Cation exchange capacity

Cation exchange capacity in terms of released Li^+ is determined by flame emission spectroscopy
Working standards in calcium nitrate solution are used in the range 2,5 to 30 cmol (+) dm^{-3} Li

11.5 Calculation

25 g soil is extracted with 500 cm^3 LiCl solution
Let concentration of element (Ca, Mg, K or Na) be **s** cmol(+) dm^{-3} as read from the calibration curve

$$\text{cmol(+) kg}^{-1}\text{ Ca, Mg, K or Na in soil} = \frac{\mathbf{s} \times 500}{25(\text{g})}$$

CEC

Let the concentration of Li be **a** cmol(+) dm^{-3}

$$\text{CEC cmol(+) kg}^{-1} = \frac{\mathbf{a} \times 500}{25\ (\text{g})}$$

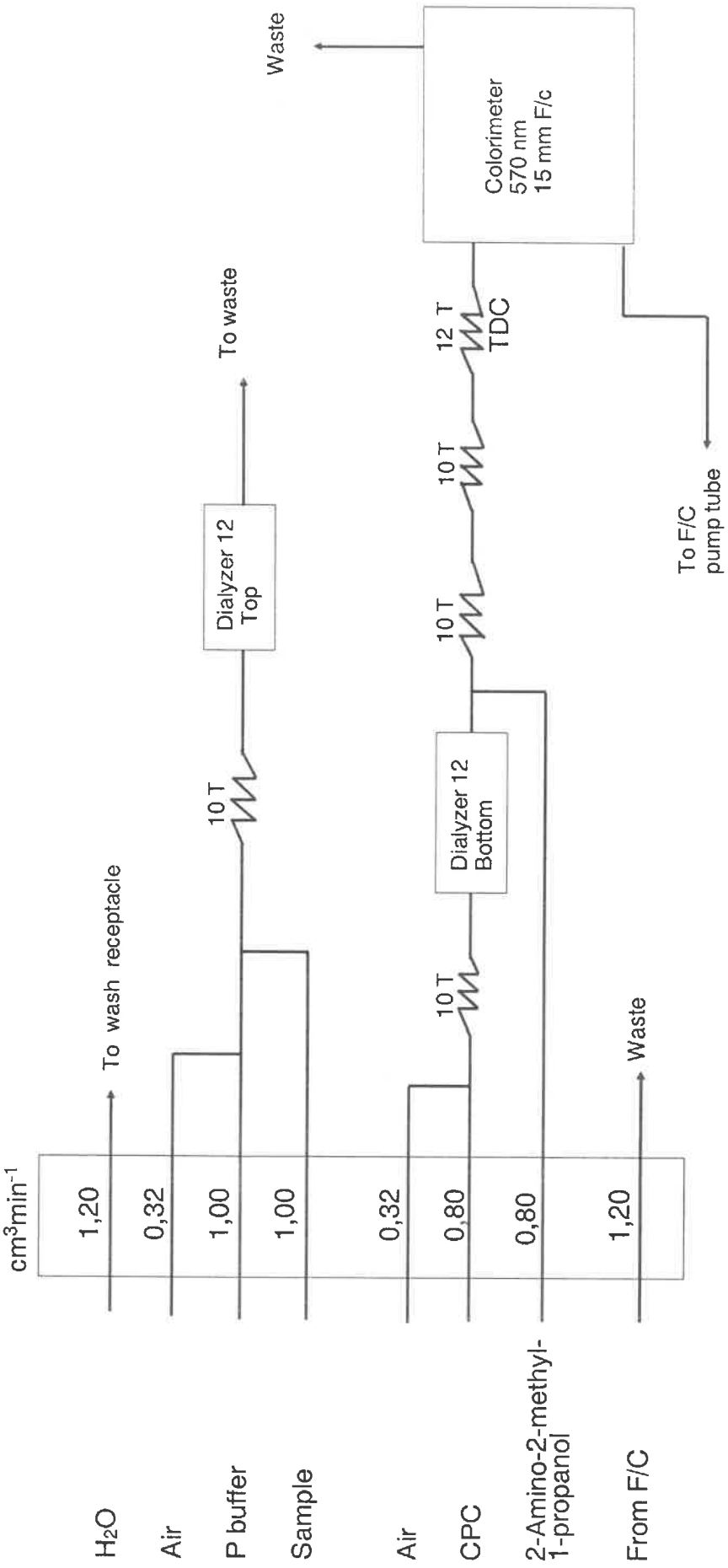

Figure 11.1: Flow system for Ca (Low)

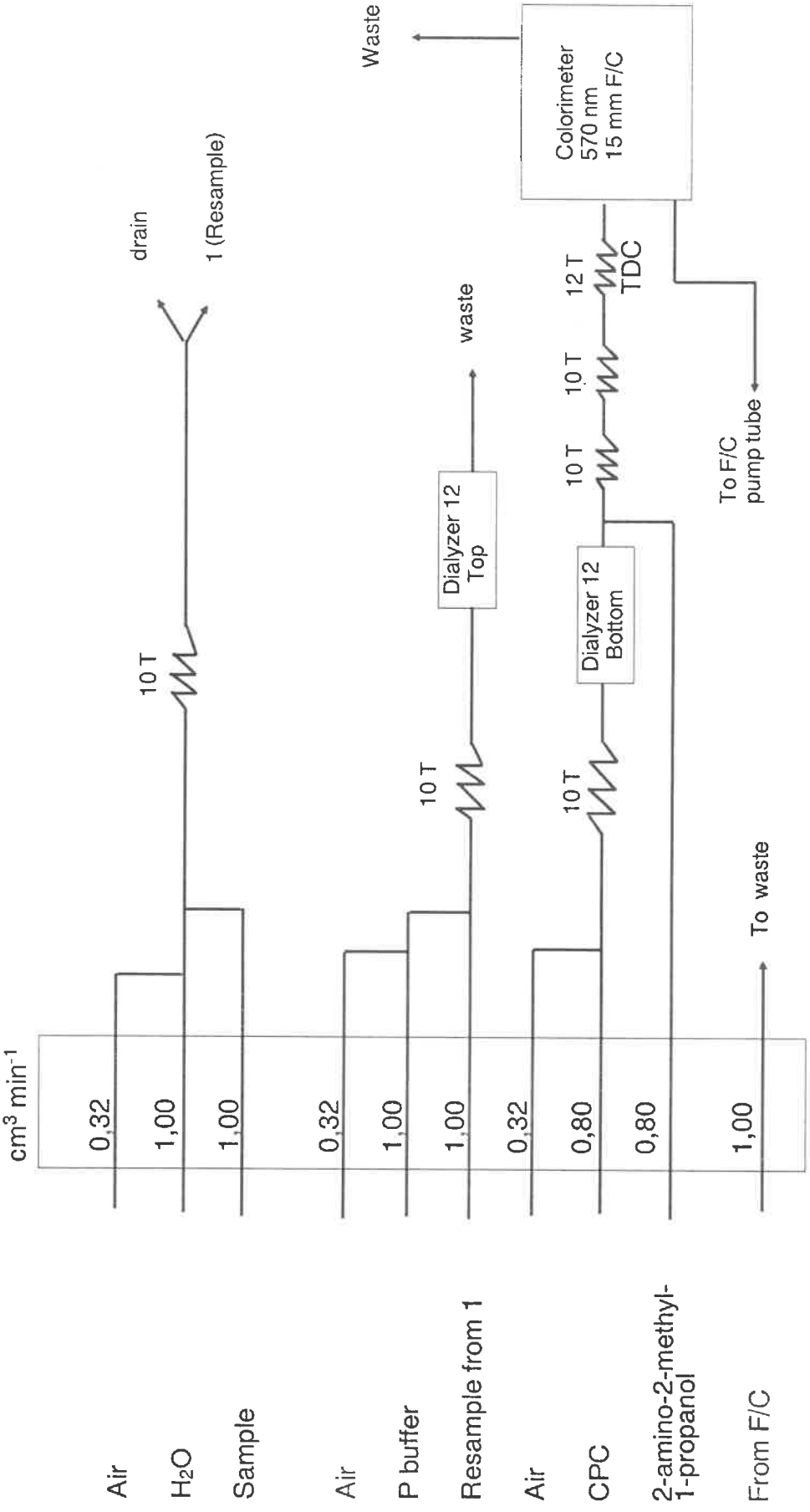

Figure11.2: Flow system for Ca (High)

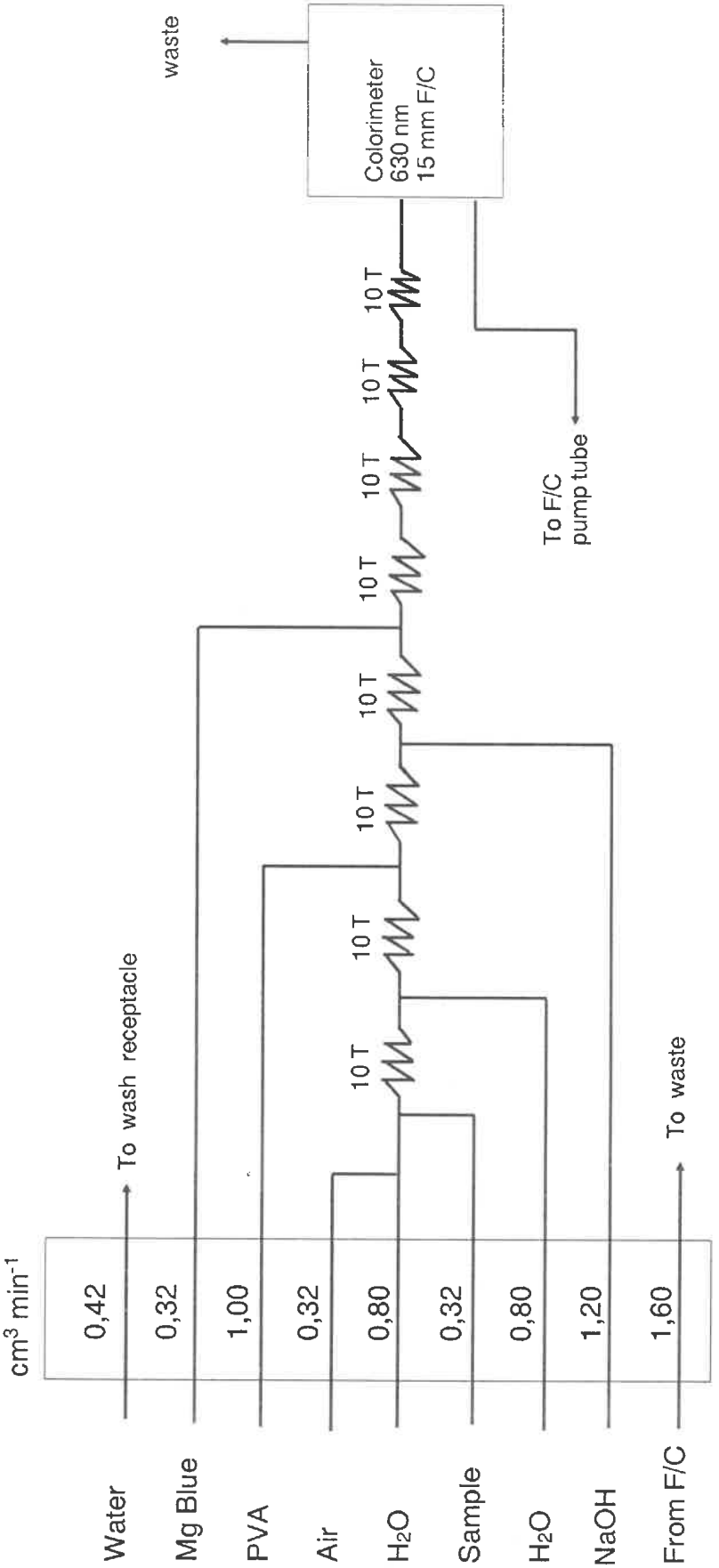

Figure 11.3: Flow system for Mg (Low)

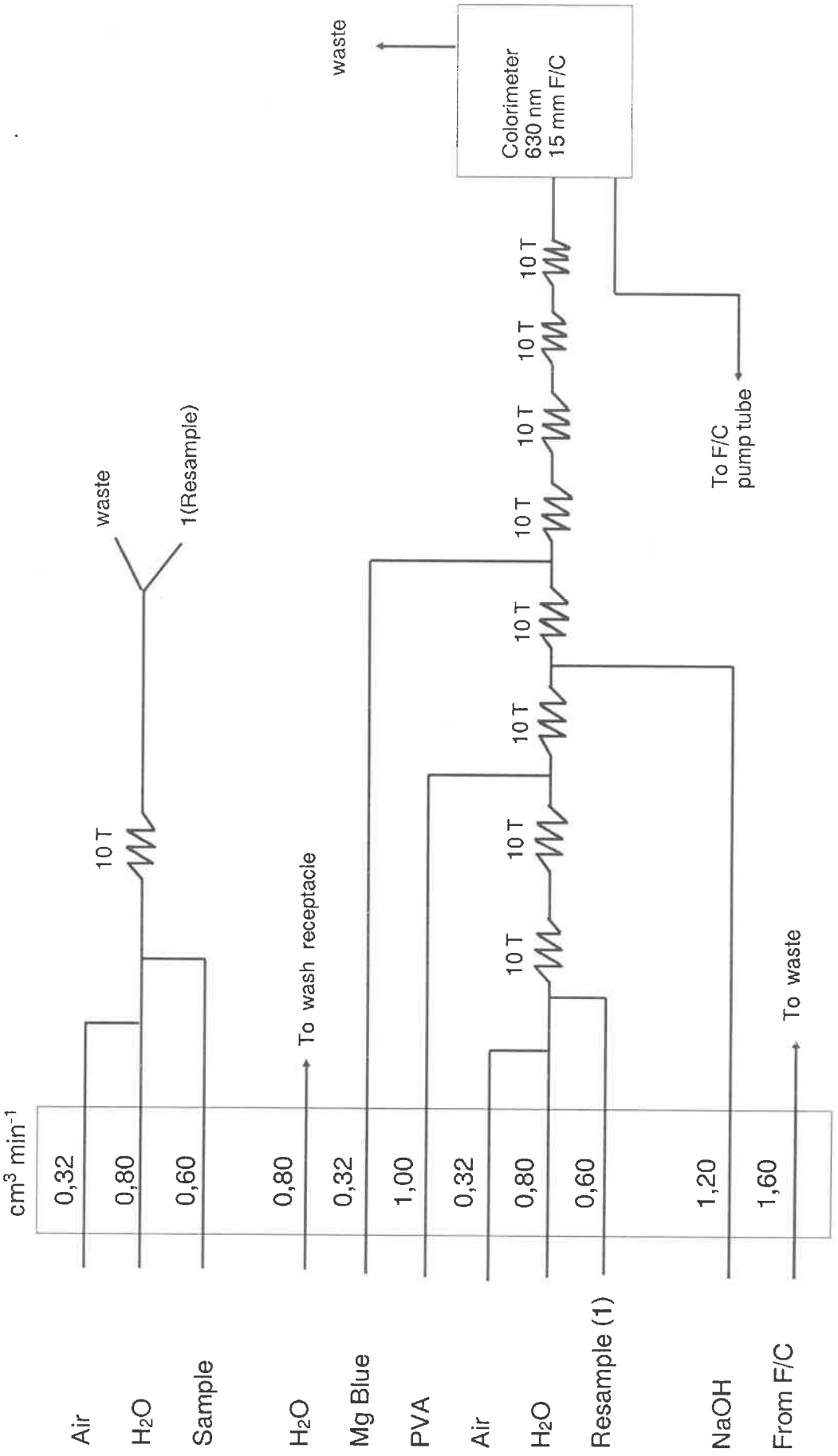

Figure 11.4: Flow system for Mg (High)

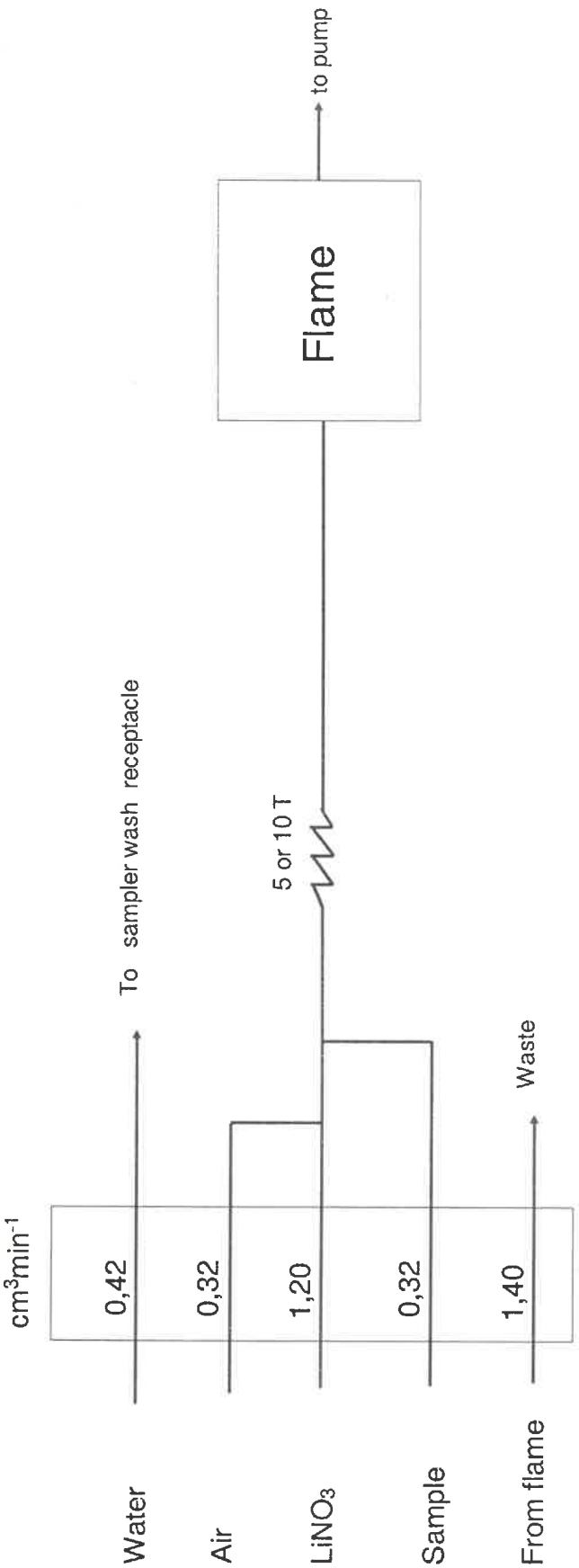

Figure 11.5: Flow system for K

12 CATION EXCHANGE CAPACITY AND EXCHANGEABLE PLUS WATER SOLUBLE CATIONS: AMMONIUM ACETATE (1 mol dm^{-3}, pH 7)

12.1 Introduction

An ammonium acetate solution (1 mol dm^{-3}) serves as extractant for exchangeable plus water soluble cations (Schollenberger & Simon, 1945). The maximum exchange occurs in a few minutes.

In the presence of free lime and gypsum the most questionable cations extracted with this method are Ca^{2+} and Mg^{2+}. In the case of soils containing free lime or gypsum, this method should not be used if accurate results for exchangeable Ca^{2+} and Mg^{2+} or CEC are required. The level of extractable potassium may increase on drying of some soils. However, soil samples can be extracted in a moist state.

The water soluble cations are determined separately in soils containing significant quantities (resistance < 460 ohms) of soluble salts. These are subtracted from extractable cations to obtain the exchangeable cations.

After the exchange complex has been saturated with the index cation, the adsorbed cation and the small amount of solution entrained by the soil after centrifuging can be directly displaced by another salt solution, such as potassium chloride. Ammonia is separated by steam distillation (Bremner & Keeney, 1965) and is taken as equal to the CEC of the soil.

12.2 Apparatus

Centrifuge
Reciprocating shaker - 180 oscillations per minute
Balance accurate to 0,05 g
pH meter
Plastic containers, various volumetric flasks, beakers, pipettes, centrifuge tubes and Erlenmeyer flasks
Flame photometer
Atomic absorption spectrophotometer
Steam distillation unit (Fig. 12.1)
Vortex mixer

12.3 Reagents

Ammonium acetate, 1 mol dm^{-3}, pH 7: Dilute 114 cm^3 glacial acetic acid (AR) with de-ionised water to about 1 dm^3. Add 138 cm^3 concentrated ammonia solution and de-ionised water to a volume of 1 980 cm^3. Adjust pH to 7 by adding more ammonia solution if necessary. Make final solution up to 2 dm^3 with de-ionised water

Ammonium acetate, 0,1 mol dm^{-3}: Dilute the 1 mol dm^{-3} solution ten times with de-ionised water

Potassium chloride, 1 mol dm^{-3}: Dissolve 74,4 g KCl (AR) in 1 dm^3 de-ionised water

Potassium standard and working standards: From commercially available sources make up a standard in de-ionised water containing 1 000 mg dm^{-3} K. Prepare working standards in 1 mol dm^{-3} ammonium acetate (pH 7) to cover a range of 0 to 10 mg dm^{-3} K

Sodium standard and working standards: From commercially available sources make up a standard in de-ionised water containing 1 000 mg dm^{-3} Na. Prepare working standards ranging from 0 to 10 mg dm^{-3} Na in 1 mol dm^3 ammonium acetate

Lanthanum chloride solution: Add 500 cm^3 de-ionised water to 9,4 g La_2O_3 in a 1 dm^3 flask. While swirling, slowly add 40 cm^3 concentrated hydrochloric acid. Mix well to dissolve oxide before making up to volume with de-ionised water. Filter if necessary

Calcium and magnesium standards: Prepare working standards from commercially available stock, ranging from 1 to 5 mg dm^{-3} Ca and Mg. Use 1 mol dm^{-3} ammonium acetate solution (pH 7) in the same proportion as the samples to prepare working standards

Boric acid indicator solution: Dissolve 20 g boric acid (AR) in about 700 cm^3 hot water and transfer the cooled solution to a 1 dm^3 volumetric flask containing 200 cm^3 ethanol (95%) and 20 cm^3 mixed indicator solution, prepared by dissolving 0,330 g bromocresol green and 0,165 g methyl red in 500 cm^3 ethanol (95%). After mixing contents of the flask, add about 0,05 cm^3 1 mol dm^{-3} NaOH carefully until the indicator colour changes from pink to pale green when 1 cm^3 solution is treated with 1 cm^3 water. Make up to 1 dm^3 with de-ionised water

Sulphuric acid: 0,05 mol dm^{-3}, standardised

Magnesium oxide: Heavy (AR)

12.4 Procedure

12.4.1 Extraction

* Place 10 g air-dry, ≤ 2 mm soil in a 100 cm^3 centrifuge tube, stopper and determine mass of tube and soil (X_1 g)
* Add 50 cm^3 1 mol dm^{-3} ammonium acetate solution and shake horizontally for 60 minutes
* Remove samples from shaker and leave overnight
* Centrifuge at 2 000 to 5 000 rpm to obtain a clear supernatant solution (about 10 minutes)
* Decant supernatant liquid as completely as possible into a 100 cm^3 volumetric flask, without losing any soil
* Again add 50 cm^3 1 mol dm^{-3} ammonium acetate solution to the soil and shake tubes well by hand to ensure that the soil has dispersed properly (use a vortex mixer if necessary)
* Place tubes on shaker for 30 minutes, centrifuge and decant clear solution into the same 100 cm^3 volumetric flask. Make up to volume with ammonium acetate solution, filter and keep this solution for the determination of Ca, Mg, Na and K (solution **A**)
* Add 50 cm^3 0,1 mol dm^{-3} ammonium acetate solution to the soil in the centrifuge tube. Shake for 30 minutes ensuring that the soil has dispersed properly. Centrifuge as before. Decant clear supernatant solution into a plastic storing bottle for the determination of NH_4^+ in the occluded solution (solution **B**). Stopper centrifuge tube and determine mass of centrifuge tube plus soil and occluded solution (X_2 g)
* Finally add 50 cm^3 KCl solution (1 mol dm^{-3}) to the soil in the centrifuge tube, shake for 30 minutes as described, centrifuge and decant supernatant solution into a 200 cm^3 volumetric flask. Repeat operation with a second aliquot of 50 cm^3 of KCl solution, again ensuring that the soil has dispersed properly. Fill volumetric flask to volume with 1 mol dm^{-3} KCl solution (solution **C**).

12.4.2 Determination

CEC

* Add 10 cm^3 boric acid indicator solution to a 100 cm^3 Erlenmeyer flask marked to indicate a volume of 50 cm^3
* Place the flask under the exit of the condenser of the steam distillation apparatus
* In separate distillations, pipette 5 cm^3 of the ammonium acetate (solution **B**) or 10 cm^3 of the KCl extract (solution **C**) into the distillation flasks. Increase

the volume to about 20 cm^3 with de-ionised water. Add 1 teaspoon (2,5 cm^3) heavy MgO through a dry funnel into the bulb of the flask

* Connect the distillation flask without delay to the steam generator and distill to a volume of ± 50 cm^3 in the flask containing the boric acid indicator
* Stop distillation by opening the stopcock on the steam by-pass tube and then remove the distillation flask
* Rinse the exit tube of the condenser
* Determine NH_4^+ by titrating with 0,05 mol dm^{-3} sulphuric acid
* The colour change at the end point is from green to a permanent faint pink

Calcium and magnesium

* Pipette 5 cm^3 ammonium acetate extract of the soil into a 200 cm^3 volumetric flask. Add 10 cm^3 La-solution and 10 cm^3 6 mol dm^{-3} HCl to dissolve any precipitate. Make up to volume with de-ionised water. Mix well and filter if necessary
* Determine Ca and Mg on an atomic absorption spectrophotometer

Potassium and sodium

* The wavelength of the spectral line used for determining potassium is 766,5 nm on the atomic absorption spectrophotometer
* The most usable emission spectra for sodium analysis are the 589,0 and 589,6 nm lines. All alkali metals are easily excited by a flame. To reduce interference, a low (cold) flame is recommended
* Alternatively a flame photometer can be used if the matrix of the sample and standards are matched

12.5 Calculations

Cation exchange capacity (CEC)

$$CEC = (T_1 \times 20) - (X_2 - X_1) \times 0,2 \times T_2 \text{ cmol(+) } kg^{-1}$$

where: T_1 = titration value for KCl solution

T_2 = titration value for ammonium acetate solution

X_1 = mass of tube plus soil (g)

X_2 = mass of tube plus occluded solution (g)

Calcium and Magnesium

10 g soil is extracted with 100 cm^3 ammonium acetate solution and 5 cm^3 of this solution is subsequently diluted to 200 cm^3

Let Ca/Mg concentration in this solution be **s** mg dm^{-3}

$$mg\ kg^{-1}\ Ca/Mg\ in\ soil = \frac{s \times 100 \times 40}{10(g)}$$

Potassium and sodium

10 g soil is extracted with 100 cm^3 extractant
Let Na/K concentration of the extract be **n** mg dm^{-3}

$$mg\ kg^{-1}\ Na/K\ in\ soil = \frac{n \times 100}{10\ (g)}$$

Cations

Let concentration in original solution (solution **A**) be **a** mg dm^{-3}, then

$$cmol\ (+)\ kg^{-1}\ Ca = \frac{a}{20,04}$$

$$cmol\ (+)\ kg^{-1}\ Mg = \frac{a}{12,16}$$

$$cmol\ (+)\ kg^{-1}\ K = \frac{a}{39,10}$$

$$cmol\ (+)\ kg^{-1}\ Na = \frac{a}{22,99}$$

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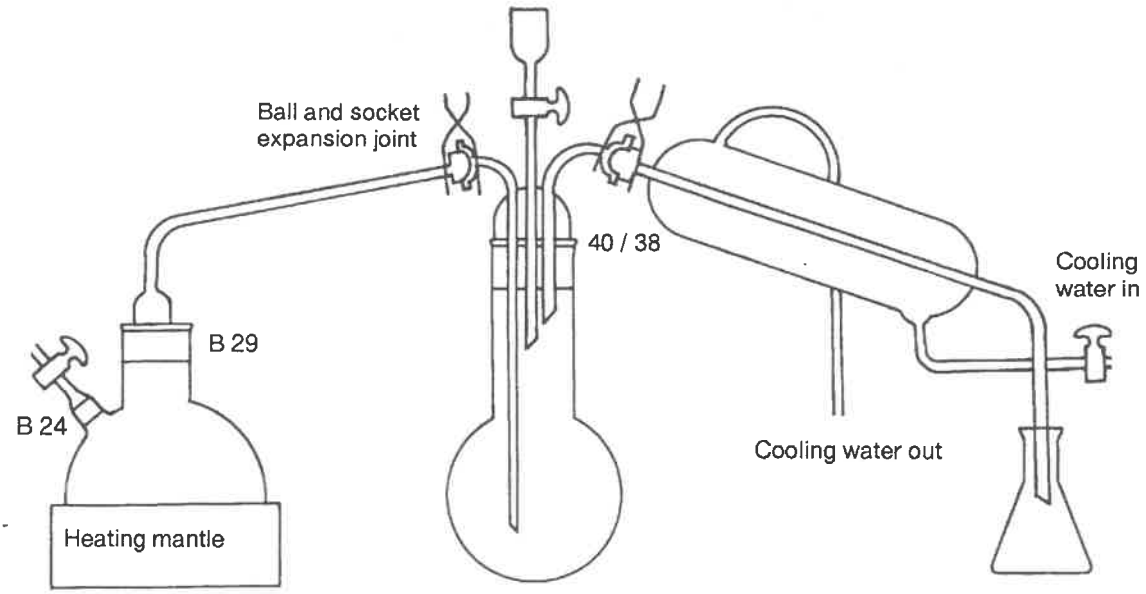

Figure 12.1: Distillation Apparatus

13 CATION EXCHANGE CAPACITY AND EXCHANGEABLE PLUS WATER SOLUBLE CATIONS: AMMONIUM ACETATE (0,2 mol dm^{-3}, pH 7)

13.1 Introduction

An ammonium acetate solution (0,2 mol dm^{-3}) serves as extractant for exchangeable plus water soluble cations.

In the presence of free lime and gypsum the most questionable cations extracted with this method are Ca^{2+} and Mg^{2+}. In the case of soils containing free lime or gypsum, this method should not be used if accurate results for exchangeable Ca^{2+} and Mg^{2+} or CEC are required. The level of extractable potassium may increase on drying of some soils. However, soil samples can be extracted in a moist state.

The soluble water cations are determined separately in soils containing significant quantities (resistance < 460 ohms) of soluble salts. These are subtracted from extractable cations to obtain the exchangeable cations.

After the exchange complex has been saturated with the index cation, the adsorbed cation and the small amount of solution entrained by the soil after leaching can be directly displaced by another salt solution, such as potassium sulphate. Ammonia is separated by Kjeldahl distillation (Wagner-Parnas) and is taken as equal to the CEC of the soil.

13.2 Apparatus

Balance accurate to 0,01 g
Buchner funnels
Witt filter flasks; height 160 mm, inner diameter 100 mm
Stohmann volumetric flasks to be fitted inside suction flasks, 500 cm^3 capacity
Whatman no 50 filter paper
Vacuum system
Kjeldahl nitrogen determination apparatus
Atomic absorption spectrophotometer

13.3 Reagents

Ammonium acetate, 0,2 mol dm^{-3}: Dissolve 15,41 g NH_4OAc in 1 dm^3 de-ionised water. Adjust pH to 7 by adding either ammonia solution or acetic acid (diluted)

Potassium sulphate, 0,2 mol dm^{-3}: Dissolve 34,85 g K_2SO_4 in 1 dm^3 de-ionised water
Nessler's reagent: Dissolve 11,38 g mercury (II) iodide and 8,75 g potassium iodide in 150 cm^3 de-ionised water. Add 28 g potassium hydroxide and make up solution to 250 cm^3. Allow to stand for two days in a dark place. Decant clear liquid into a brown glass bottle
Boric acid: Dissolve 40 g boric acid in 1 dm^3 de-ionised water
Sodium hydroxide: Dissolve 400 g NaOH in 1 dm^3 de-ionised water
Mixed indicator: Dissolve 1,25 g methyl red and 0,825 g methylene blue in 1 dm^3 ethanol (95%)
Standardised hydrochloric acid: 0,1 mol dm^{-3}
Standard potassium solution: 1 000 mg dm^{-3}
Standard sodium solution: 1 000 mg dm^{-3}
Standard calcium solution: 1 000 mg dm^{-3}
Standard magnesium solution: 1 000 mg dm^{-3}
Cesium solution: Dissolve 1,266 g CsCl in de-ionised water. Add 40 cm^3 perchloric acid (70%) and dilute to 1 dm^3
Lanthanum solution: Dissolve 16,709 g $LaCl_3.7H_2O$ in 1 dm^3 de-ionised water. Concentration = 6 250 mg dm^{-3} La
Lanthanum working solution: Dilute 200 cm^3 lanthanum solution to 1 dm^3. Concentration = 1 250 mg dm^{-3} La

13.4 Procedure

13.4.1 Extraction

* Place 20 g air-dry soil (≤ 2 mm) in 125 cm^3 capacity beakers
* Add 50 cm^3 0,2 mol dm^{-3} NH_4OAc solution. Stir and allow to stand for 1 hour
* Determine the mass of a dry Buchner funnel fitted with filter paper
* Carry over contents of each beaker to a Buchner funnel under vacuum. Filtrate is collected in 500 cm^3 capacity Stohmann volumetric flasks contained in the Witt filter flasks. Soil in the Buchner funnels is leached, using 50 cm^3 aliquots of NH_4OAc solution (0,2 mol dm^{-3})
* Leaching time must stretch over a period of at least 1 hour
* Use a suction pump for slow leaching soils
* Use filter pulp for clayey soils to accelerate leaching; the mass of the pulp must be determined
* Care must be taken to prevent leachate exceeding 500 cm^3
* Vacuum is turned off after the last free NH_4OAc solution disappears into the soil in the funnel
* Remove Buchner funnel with soil, wipe stem of funnel and determine the mass of the funnel, soil, filter and occluded solution

* Make volumetric flask up to the 500 cm^3 mark with 0,2 mol dm^{-3} NH_4OAc and mix well
* Retain enough 0,2 mol dm^{-3} NH_4OAc solution to prepare standards
* Replace Buchner funnels with soil on the filter flasks, containing a clean set of 500 cm^3 volumetric flasks
* Leach soil with 50 cm^3 aliquots 0,2 dm^{-3} K_2SO_4 solution for about 1 hour
* Test the final drops of leachate with Nessler's solution for the presence of NH_4^+
* In the absence of ammonium ions in the final leachate, terminate vacuum, remove the volumetric flasks and make up to the mark with 0,2 mol dm^{-3} K_2SO_4 and mix well
* Retain enough K_2SO_4 solution for a blank determination

13.4.2 Determination

CEC

* Place 100 cm^3 K_2SO_4 leachate in a 800 cm^3 Kjeldahl flask
* Add 200 cm^3 de-ionised water and a few glass beads to prevent bumping
* Carefully add 80 cm^3 40% NaOH to the leachate, swirl the flask and connect to the condenser of the distillation unit
* Distill over approximately 200 cm^3 liquid into 60 cm^3 boric acid solution (4%) in a 500 cm^3 wide-mouth Erlenmeyer flask
* Confirm the absence of ammonia in the final drops of distillate with litmus paper
* Add 10 drops of mixed indicator and titrate the boric acid-ammonia solution to first signs of purple with 0,1 mol dm^{-3} HCl
* Prepare a blank sample by diluting a 10 cm^3 aliquot of 0,2 mol dm^{-3} NH_4OAc solution to 500 cm^3 with 0,2 mol dm^{-3} K_2SO_4. Mix well and distillate by Kjeldahl as described above.

Sodium and potassium

Place 10 cm^3 aliquots of sodium and potassium standards (1 000 mg dm^{-3}) in a 100 cm^3 volumetric flask and make up to the mark with de-ionised water. Concentration=100 mg dm^{-3} Na and K. To obtain working standards dilute 0; 2; 4 and 8 cm^3 of the latter solution to 100 cm^3 with Cs solution. Concentrations of Na and K in these solutions are: 0; 2; 4 and 8 mg dm^{-3} respectively.

The ammonium acetate leachates are diluted with Cs solution to ensure a final concentration of 800 mg dm^{-3} Cs (one part leachate and 4 parts Cs-solution).

Sodium and potassium concentrations are determined with an atomic absorption spectrophotometer set up as follows:

Parameters	Sodium	Potassium
Wavelength (nm)	589	766,5
Lamp current (mA)	5,0	5,0
Flame	air-acetylene	air-acetylene
Slit opening (mm)	0,20	0,50

Calcium

Place a 10 cm^3 aliquot of the calcium standard (1 000 mg dm^{-3}) in a 100 cm^3 volumetric flask and make up to the mark with de-ionised water. To make working standards of Ca, pipette 0; 5; 10 and 15 cm^3 of the above solution (100 mg dm^{-3} Ca) in 100 cm^3 volumetric flasks. To each flask add 20 cm^3 6 250 mg dm^{-3} La solution and make up to volume with 0,1 mol dm^{-3} HCl. Working standards contain 0; 5; 10 and 15 mg dm^{-3} Ca.
One part of the ammonium acetate leachate is diluted with four parts of 1 250 mg dm^{-3} La solution to obtain a final dilution containing at least 1 000 mg dm^{-3} La. Ca is determined with an atomic absorption spectrophotometer adjusted as follows:

Parameters for	Calcium
Wavelength (nm)	422,7
Lamp current (mA)	5,0
Flame	Nitrous oxide- acetylene or Air - acetylene
Slit opening (mm)	0,20

Magnesium

Place a 10 cm^3 aliquot of the magnesium standard solution (1 000 mg dm^{-3} Mg) in a 100 cm^3 volumetric flask. Make up to the mark with de-ionised water. This solution contains 100 mg dm^{-3} Mg. Pipette 0; 2; 4 and 8 cm^3 respectively of the 100 mg dm^{-3} Mg solution into 100 cm^3 volumetric flasks. To each flask add 20 cm^3 6 250 mg dm^{-3} La solution and make up to volume with 0,1 mol dm^{-3} HCl. Working standards containing 0; 2; 4 and 8 mg dm^{-3} Mg have been

prepared. The ammonium acetate leachate is diluted with 1 250 mg dm^{-3} La solution (one part leachate and four parts La solution) to obtain a final solution containing at least 1 000 mg dm^{-3} La. Magnesium is determined with an atomic absorption spectrophotometer set to the following parameters:

Parameters for	Magnesium
Wavelength (nm)	285,2
Lamp current (mA)	3,5
Flame	Air-acetylene
Slit opening (mm)	0,20

13.5 Calculations

Cation exchange capacity

Calculate the volume of 0,1 mol dm^{-3} HCl required to neutralise the ammonia generated by the occluded NH_4OAc solution:

$$y = \frac{cm^3 \text{ occluded } NH_4OAc}{10\ cm^3\ NH_4OAc \text{ in blank}} \times cm^3\ 0{,}1 \text{ mol } dm^{-3} \text{ HCl for blank titration}$$

Cation exchange capacity (CEC) in cmol (+) kg^{-1} soil is calculated as follows:

$$CEC = \frac{(cm^3\ 0{,}1 \text{ mol } dm^{-3} \text{ HCl} - y) \times 100 \times \mathbf{M}}{\text{equivalent mass of soil distilled (g)}}$$

Where **M** = concentration (mol dm^{-3}) of the HCl

Equivalent mass of soil distilled

$$= \frac{\text{soil mass (20 g)} \times cm^3 \text{ filtrate distilled (100)}}{\text{Total } cm^3\ K_2SO_4 \text{ filtrate (500 } cm^3)} = 4\ g$$

Potassium, Sodium, Calcium and Magnesium

$$\text{cmol (+) kg}^{-1}\ \text{K in soil} = \frac{(\text{mg dm}^{-3}\ \text{K in sample} - \text{mg dm}^{-3}\ \text{K in blank}) \times \text{dilution}}{390}$$

$$\text{cmol (+) kg}^{-1}\ \text{Na in soil} = \frac{(\text{mg dm}^{-3}\ \text{Na in sample} - \text{mg dm}^{-3}\ \text{Na in blank}) \times \text{dilution}}{230}$$

$$\text{cmol (+) kg}^{-1}\ \text{Ca in soil} = \frac{(\text{mg dm}^{-3}\ \text{Ca in sample} - \text{mg dm}^{-3}\ \text{Ca in blank}) \times \text{dilution}}{200}$$

$$\text{cmol (+) kg}^{-1}\ \text{Mg in soil} = \frac{(\text{mg dm}^{-3}\ \text{Mg in sample} - \text{mg dm}^{-3}\ \text{Mg in blank}) \times \text{dilution}}{122}$$

$$\text{Dilution} = \frac{\text{Volume leachate (500 cm}^3\text{)} \times 5}{\text{soil mass (20 g)}}$$

Uncorrected cations (extractable)

If a given soil contains no soluble salts, it is assumed that extracted cations will be equal to exchangeable cations. It is however, reported as extractable cations.

Corrected cations (exchangeable)

If a given soil contains soluble salts, the concentration of these salts is calculated as follows:

Multiply cation concentration (mmol(+) dm^{-3} extract) in the saturated extract (see method: water soluble cations) by the saturation percentage and divide by 1 000 to convert result to cmol (+) kg^{-1} soil. Subtract this value from the concentration (cmol (+) kg^{-1}) value, calculated for extracted cations.

This procedure is not valid for calcium and magnesium in the presence of carbonates, or calcium in the presence of gypsum, as these salts are soluble in ammonium acetate.

13.6 References

USDA, 1972. Soil survey laboratory methods and procedures for collecting soil samples. Soil Survey Report No.1. U.S. Govern. Printing Office, Washington D.C.

PEECH, M., 1965. Lime requirement. In C.A. Black (ed.). Methods of soil analysis. Agron. Monog. 9. Part 2, 927-932. Am. Soc. Agron. Madison, Wis.

14 EXTRACTABLE ZINC: HCl (0,1 mol dm^{-3})

14.1 Introduction

The method was developed by Nelson, Boawn & Viets (1959) where zinc availability was related to acid extractable Zn and titratable alkalinity. The method is not suitable for predicting micro-element availability in soils with pH above 7, unless additional measurements are made.

14.2 Apparatus

Slopy necked plastic extraction bottles, 100 cm^3 capacity with silicone stoppers
Reciprocating shaker set at 180 oscillations per minute
Whatman no 41 filter paper
Balance
Atomic absorption spectrophotometer

14.3 Reagents

Hydrochloric acid, 0,1 mol dm^{-3}: Dilute 8,9 cm^3 concentrated HCl (32%) (AR) to 1 dm^3 with de-ionised water. Maintain at a temperature of 20 °C
Zinc standard solution: 1 000 mg dm^{-3}

14.4 Procedure

14.4.1 Extraction

* Place 5 g air-dry soil (≤ 2 mm) in an extraction bottle
* Add 20 cm^3 0,1 mol dm^{-3} HCl and stopper with a silicone (zinc-free) stopper
* Shake in a horizontal position on a reciprocating shaker at 180 oscillations for 15 minutes at a temperature of 20 ± 2 °C
* Filter immediately through Whatman no 41 filter paper into a suitable container
* Stopper with zinc-free silicone stoppers

14.4.2 Determination

* Analysis for zinc is conducted on an atomic absorption spectrophotometer. The instrument manufacturers' parameters must be adhered to
* If a dilution of the extract is necessary, 0,1 mol dm^{-3} HCl must be used as diluent
* Prepare zinc standards in 0,1 mol dm^{-3} HCl ranging from 0,5 to 2,0 mg dm^{-3}

14.5 Calculation

Let the zinc content in the extract be **a** mg dm^{-3}

$$mg\ kg^{-1}\ Zn\ in\ soil = \frac{a \times 20}{5}$$

14.6 References

BAKER, D.E. & AMACHER, M.C., 1982. Nickel, copper, zinc and cadmium. In A.L. Page (ed.). Methods of soil analysis. Part 2, 333. Am. Soc. Agron. Madison, Wis.

NELSON, J.L., BOAWN, L.C. & VIETS, F.G., 1959. A method for assessing zinc status of soils using acid-extractable zinc and "titratable alkalinity" values. *Soil Sci.* 88, 275 - 283.

15 EXTRACTABLE MICRO-ELEMENTS (Cu, Mn, Zn & Co) : DI-AMMONIUM EDTA

15.1 Introduction

For the determination of micro-elements in soil samples, the di-ammonium EDTA method (Trierweiler & Lindsay, 1969 as modified by Beyers & Coetzer, 1971) is suitable, bearing in mind that for soils containing free lime, the buffer action of di-ammonium EDTA is inadequate.

15.2 Apparatus

Centrifuge
Balance
Plastic extraction bottles with silicone stoppers, slopy neck, 100 cm^3 capacity or a 100 cm^3 stoppered centrifuge tube
Porcelain mortar and pestle
Whatman no 40 filter paper
Funnels
Reciprocating shaker set at 180 oscillations per minute
Atomic absorption spectrophotometer

15.3 Reagent

Di-ammonium EDTA, 0,02 mol dm^{-3}: Dissolve 6,88 g $(NH_4)_2EDTA.H_2O$ in de-ionised water and make up to 1 dm^3. Maintain temperature at 20 °C

15.4 Procedure

15.4.1 Extraction

* Air-dry soil is initially crushed with a roller mill
* Soil is refined to a fineness of ≤ 1 mm in a porcelain mortar
* Place 5 g air-dry soil in an extraction bottle or centrifuge tube
* Add 15 cm^3 0,02 mol dm^{-3} $(NH_4)_2$ EDTA solution to the soil and seal container with a stopper
* Shake horizontally for 60 minutes at 180 oscillations per minute in a reciprocating shaker at a constant temperature of 20 ± 2 °C
* Centrifuge the samples in the same container for 5 minutes at 2 000 rpm
* Filter immediately through Whatman no 40 paper into suitable containers, using silicone stoppers

* For extraction of manganese, 5 g soil is extracted with 50 cm^3 $(NH_4)_2EDTA$ solution

15.4.2 Determination

Micro-elements are determined with an atomic absorption spectrophotometer fitted with an oxidising air-acetylene flame
Instrument parameters must be adhered to
It may be necessary to dilute the extracts ten times when manganese is determined. Dilutions must be done with $(NH_4)_2EDTA$ as diluent. This dilution factor must be taken into account when the calculations are made

Standards are prepared as follow:

Zinc: Prepare calibration standards ranging from 0,5 to 2 $\mu g\ cm^{-3}$ Zn in 0,02 mol dm^{-3} $(NH_4)_2EDTA$ solution
Copper: Prepare calibration standards ranging from 1 to 10 $\mu g\ cm^{-3}$ Cu in 0,02 mol dm^{-3} $(NH_4)_2EDTA$
Manganese: Prepare calibration standards ranging from 1 to 4 $\mu g\ cm^{-3}$ Mn in 0,02 mol dm^{-3} $(NH_4)_2$ EDTA
Cobalt: Prepare calibration standards ranging from 2 to 10 $\mu g\ cm^{-3}$ in 0,02 mol dm^{-3} $(NH_4)_2EDTA$

15.5 Calculations

Let elemental content of sample be **w** $\mu g\ cm^{-3}$
Total extractant is 15 cm^3 representing 5 g soil

$$mg\ kg^{-1}\ Cu/Co/Zn/Mn\ in\ soil = \frac{15 \times \mathbf{w}}{5}$$

15.6 References

BEYERS, C.P. DE L. & COETZER, F.J., 1971. Effect of concentration, pH and time on the properties of di-ammonium EDTA as a multiple soil extractant. *Agrochemophysica* 3, 49-54.

TRIERWEILER, J.F. & LINDSAY, W.L., 1969. EDTA- Ammonium Carbonate soil test for zinc. *Soil Sci. Soc. Am. Proc.* 33, 49 - 54.

16. EXTRACTABLE BORON: HOT WATER

16.1 Introduction

Water soluble boron is considered to be immediately available to plants. Boron is extracted in a 1:2 soil to water ratio and the boron is determined photometrically by the curcumin method.

16.2 Apparatus

Soda glass Erlenmeyer flasks 50 cm^3
Cork stoppers
Plastic measuring cylinder 50 cm^3
Plastic funnels
Plastic bottles 50 cm^3 capacity
Whatman no 542 and no 41 filter paper
Hotplate
Laboratory oven
Pipettes
Burette 50 cm^3
Vitreosil silica crucibles 30 cm^3
Spectrophotometer
Balance accurate to 0,1 g

NOTE: Do not use Pyrex, Jena or any other borosilicate glass under any circumstances.

16.3 Reagents

Calcium chloride, 0,05 mol dm^{-3}: Dissolve 7,35 g $CaCl_2 .2H_2O$ in de-ionised water and make up to 1 dm^3. Store in a plastic bottle
De-ionised water: Stored in a plastic bottle
Curcumin solution: Dissolve 0,04 g curcumin and 5 g oxalic acid in 100 cm^3 ethanol 95%. This solution is stable for 2 to 3 days (5 days if kept in a refrigerator)
Boron stock standard solution, 100 mg dm^{-3}: Dissolve 0,572 g boric acid (AR) in 1 dm^3 de-ionised water. Store solution in a plastic bottle
Boron standard solution, 0,5 mg dm^{-3}: Dilute 5 cm^3 of the boron stock solution to 1 dm^3 with de-ionised water

16.4 Procedure

16.4.1 Extraction

* Place 20 g air dry (≤ 2 mm) soil into a soda glass Erlenmeyer flask
* Add 40 cm^3 de-ionised water and shake by rotating the flask
* Stopper the flask and heat on a hotplate until the temperature reaches 80 °C (± 5 minutes)
* Place the Erlenmeyer flask for 5 minutes in an oven set at 80 °C
* Add 3 to 5 drops 0,05 mol dm^{-3} calcium chloride solution and shake the flask
* Filter through Whatman no 542 filter paper fitted to a plastic funnel into a plastic bottle
* Run a blank using 40 cm^3 de-ionised water and treat in the same manner as the original sample

NOTE: The cork stoppers reduce evaporation to a minimum

16.4.2 Determination

* Pipette 1; 2; 3 and 5 cm^3 of standard solution into crucibles. Use 1 cm^3 de-ionised water for the blank
* Pipette 1 cm^3 soil extract for each sample into a crucible
* Add 4 cm^3 curcumin solution to each crucible
* Place crucibles in oven at 50 ± 3 °C until dry, leave in oven for an extra 15 minutes to ensure complete dryness
* Wash the salts (using ethanol) into a 25 cm^3 volumetric flask and make up to volume with ethanol
* Shake the flask and filter through Whatman no 41 filter paper, using plastic funnels
* Zero the spectrophotometer with the blank sample and read the absorbance for each sample at 540 nm
* Plot a curve (absorbance against μg cm^3 B) and read the μg cm^3 B for each sample from the curve

16.5 Calculation

Let B content of sample be **b** μg cm^3

$$\text{mg kg}^{-1}\text{ B in soil} = \frac{\mathbf{b} \times 40}{20}$$

16.6 Reference

FERTILIZER SOCIETY OF SOUTH AFRICA, 1974. Manual of soil analysis methods. FSSA Publication no.37.

17 EXTRACTABLE BORON: $CaCl_2$ (0,02 mol dm^{-3})

17.1 Introduction

Hydrolysed boron fertilizer supplies boron to the plant as boric acid. Boric acid is extracted from the soil for analytical purposes by boiling the sample in a solution of 0,02 mol dm^{-3} $CaCl_2$. The amount of boric acid extracted during boiling is time dependent and a function of the residual boron fertilizer available for hydrolysis.

The procedure for the determination of boric acid in the extract is based on the formation of a coloured product soluble in ethanol when solutions of $B(OH)_3$, oxalic acid and curcumin are evaporated to dryness. At 540 nm, absorbance of an ethanolic solution of the rosocyanin is proportional to that of the B concentration. The method is suitable for B concentrations ranging from 0,1 to 2 $\mu g\ cm^{-3}$ B.

17.2 Apparatus

Balance
Plastic bottles, 100 cm^3 capacity
Flask for boiling: low-boron quality glass, 500 cm^3 capacity
Water-cooled condenser: low-boron quality
Hotplate
Whatman no 41 filter paper
Funnels
Spectrophotometer
Porcelain evaporation dishes
Waterbath set at 55 ± 3 °C

17.3 Reagents

Calcium chloride, 0,02 mol dm^{-3}: Dissolve 3 g $CaCl_2.2H_2O$ (72 to 76% $CaCl_2$) in 1 dm^3 de-ionised water. Store in a plastic container
Ethanol-redistilled, 95%
Curcumin-oxalic acid solution: Dissolve 0,04 g finely ground curcumin and 5 g oxalic acid in 100 cm^3 redistilled ethanol
Prepare calibration standards from a stock solution of B ranging from 0,1 to 2 $\mu g\ cm^{-3}$ B in de-ionised water

17.4 Procedure

17.4.1 Extraction

Boil 25 g air-dry soil (≤ 2 mm) with 50 cm^3 0,02 dm^{-3} $CaCl_2$ solution under reflux for 15 minutes
Filter hot through Whatman no 41 filter paper fitted to a plastic funnel into a plastic bottle

17.4.2 Determination

* Pipette 1 cm^3 of the sample or standard into porcelain evaporation dishes
* Add 4 cm^3 of the curcumin-oxalic acid solution and mix
* Place on the waterbath set at 55 °C and evaporate to dryness
* Leave for a further 15 minutes on the waterbath
* Cool dishes and add 25 cm^3 ethanol to the dishes
* Dissolve complex, use a rubber policeman to remove residues
* Filter through Whatman no 41 paper
* Read the B content of solution using a spectrophotometer set at 540 nm

17.5 Calculation

Let B content of sample be **b** μg cm^{-3}
25 g soil was extracted with 50 cm^3 0,02 mol dm^{-3} $CaCl_2$ solution

$$\text{mg kg}^{-1}\text{ B in soil} = \frac{\mathbf{b} \times 50}{25}$$

17.6 References

BINGHAM, F.T, 1982. Boron. In A.L. Page (ed.). Methods of soil analysis. Part 2, 433. Am. Soc. Agron. Madison, Wis.

18 EXTRACTABLE PHOSPHORUS, POTASSIUM, CALCIUM, MAGNESIUM, ZINC, COPPER, MANGANESE AND IRON: AMBIC-1

18.1 Introduction

This method was developed by Van der Merwe, Johnson and Ras (1984) by modifying the Hunter (1974) method. Thompson (1978), Farina and Channon (1979) and Van der Merwe (1980) established that this method is suitable for the determination of P on a wide range of soils (acid to alkaline, sand to clay). The extractant is also suitable for the determination of K, Ca, Mg, Cu, Zn, Fe and Mn, provided certain precautions are taken (Van der Merwe *et al.*, 1984).

18.2 Apparatus

Plastic bottles with silicone rubber stoppers, 100 cm^3 capacity. KARTELL is recommended (Zn and Cu free). Alternatively 100 cm^3 centrifuge tubes with stoppers
Whatman no 42 filter paper
Funnels and racks
Balance accurate to 0,1 g
Continuous flow analyser (e.g. AutoAnalyzer)
Atomic absorption spectrophotometer

18.3 Reagents

Ambic-1 extraction solution; 0,25 mol dm^{-3} NH_4HCO_3 + 0,01 mol dm^{-3} $(NH_4)_2$ EDTA + 0,01 mol dm^{-3} NH_4F + Superfloc (N-100 or 127): Prepare the Superfloc by slowly adding 0,5 g Superfloc (N-100 or 127) to 250 cm^3 luke-warm water while stirring at 400 rpm. The final solution should be viscous and gel-like. Dissolve 197,65 g ammonium bicarbonate, 32,6 g anhydrous di-ammonium EDTA and 3,7 g ammonium fluoride in about 5 dm^3 de-ionised water. Add the Superfloc solution. Mix well and make up to 10 dm^3 with de-ionised water. Leave overnight. Mix thoroughly and adjust pH to 8,1 ± 0,1 with concentrated ammonia solution

Ascorbic acid reagent: Dissolve 17,6 g ascorbic acid in 440 cm^3 de-ionised water and 50 cm^3 acetone (AR). Finally add 0,5 cm^3 phosphate free wetting agent (Wetting agent A supplied by Technicon)

Ammonium molybdate in sulphuric acid: Dissolve 10 g ammonium molybdate $[(NH_4)_6Mo_7O_{24}.4H_2O]$ in 1 dm^3 1,1 mol dm^{-3} H_2SO_4. Filter and store in a dark bottle

Sulphuric acid, 1,1 mol dm^{-3}: Add 60 cm^3 concentrated H_2SO_4 (AR) to de-ionised water while stirring. After cooling, make up to 1 dm^3 with de-ionised water to obtain an approximately 1,1 mol dm^{-3} solution

Phosphorus standards: Dissolve 0,4394 g KH_2PO_4 dried at 105 °C for 1 hour in 1 dm^3 de-ionised water in a 1 dm^3 volumetric flask. Concentration: 0,1 mg cm^{-3} P

$LiNO_3$: Dissolve 2,37 g $LiNO_3$ (AR) in 2 dm^3 de-ionised water in a volumetric flask. Before making up to the mark, add 1 cm^3 Brij solution as wetting agent

Potassium standard stock solution, 1 000 mg dm^{-3} K: Prepare a stock solution, using commercially available standard solution concentrate

Micro-element standard stock solutions: Commercially available standard solutions for Zn, Cu, Fe and Mn are diluted in a 1 dm^3 volumetric flasks to the mark with de-ionised water, to contain 1 000 mg dm^{-3} of each micro-element

Calcium standard stock solution, 1 000 mg dm^{-3}: Prepare a stock solution from commercially available standard solution

Magnesium standard stock solution, 1 000 mg dm^{-3}: Prepare a stock solution from commercially available standard solution

Hydrochloric acid AR: Concentrated

Lanthanum chloride solution: Add 500 cm^3 de-ionised water to 9,38 g La_2O_3 in a 1 dm^3 flask. Mix well and slowly add 40 cm^3 concentrated hydrochloric acid. Mix well before making up to the mark with de-ionised water. Filter if necessary

18.4 Procedure

18.4.1 Extraction

* Measure 5,0 g finely ground (≤1 mm), air-dry soil into a plastic bottle or a centrifuge tube of 100 cm^3 capacity with stopper
* Add 50 cm^3 extraction solution to the soil. The extraction solution must have a temperature of 20 ± 2 °C
* Swirl container gently to expel air bubbles
* Allow to stand for 20 minutes
* Swirl again
* Seal with a Cu and Zn free stopper
* Shake horizontally on a reciprocating shaker for 30 minutes at 180 oscillations per minute at an ambient temperature of 20 ± 2 °C
* Carefully remove extraction container from the shaker and allow to stand for 5 minutes
* Carefully remove stoppers
* Filter solution through Whatman no 41 filter paper or alternatively centrifuge at 5 000 rpm for 5 min and decant clear solution into a suitable container

* Transfer a 25 cm^3 aliquot of this solution into a 50 cm^3 volumetric flask. Add exactly 2,5 cm^3 concentrated HCl and swirl flask gently
* Allow for precipitation of organic material overnight
* Make up to volume with de-ionised water and shake well
* Filter the solution through Whatman no 41 paper into a suitable container
* The extract must be analysed for P, Ca, Mg, Cu, Zn, Fe, Mn and K within a week

18.4.2 Determinations

Phosphorus

Phosphorus is determined on a continuous flow analyser with the manifold set up as shown in Fig. 18.1. Standards are made up from the P stock solution with AMBIC solution and HCl(c) ensuring that the matrix of the samples and standards is exactly the same. The range of the standards should be 0,2 to 4 mg dm^{-3} P.

Prepare a wash solution by adding 50 cm^3 concentrated HCl to 500 cm^3 AMBIC solution while swirling gently until the reaction has subsided. Make up to 1 dm^3 with de-ionised water. This solution must be prepared daily and stored in a plastic container.

If any further dilution is necessary the wash solution should be used as diluent to keep the matrix constant.

After each day's analysis the flow system must be cleaned properly especially the wash receptacle on the sampler. Small white crystals tend to form in the receptacle if it is not cleaned regularly. These crystals affect the baseline. A 1:1 ammonia solution can be used to clear any crystals from the tubing and wash receptacle.

Calcium and Magnesium

Avoid glassware because Ca contamination can occur especially if calcium silicate glassware is used

Pipette 5 cm^3 original AMBIC extract into a 100 cm^3 volumetric flask. Add 5 cm^3 La solution (8 mg cm^{-3}) and 5 cm^3 6 mol dm^{-3} HCl to dissolve any precipitate

Make up to the mark with de-ionised water. Shake and filter if necessary

Determine Ca and Mg against the standards on an atomic absorption spectrophotometer using an air-acetylene flame

Prepare standards from the stock solutions ranging from 1 to 5 mg dm^{-3} Ca and Mg. Use AMBIC solution to prepare the standards.

Copper, Zinc, Iron and Manganese

Working standards: Prepare working standards with AMBIC as matrix. Ranges to be covered are:

Copper : 0,5 to 2 mg dm^{-3}
Zinc : 0,5 to 2,5 mg dm^{-3}
Iron : 10 to 30 mg dm^{-3}
Manganese : 3 to 12 mg dm^{-3}

Use the undiluted extract for these analyses.

Measure absorption with a suitable atomic absorption spectrophotometer against the standards. An air-acetylene flame is used. Iron standards should not be kept for extended periods. Rubber and some plastics may contain zinc and therefore, glass or Kartell plastic and silicone rubber stoppers should be used.

Potassium

Potassium is determined on a continuous flow analyser fitted with a flame emission spectrophotometer as illustrated in Fig. 18.2.

Potassium working standards are prepared from the stock solution ranging from 5 to 40 mg dm^{-3} K in the AMBIC extractant.

18.5 Calculations

Phosphorus

5 g soil is extracted with 50 cm^3 AMBIC solution and then diluted twice.
Let concentration of P be **p** mg dm^{-3} as read from the calibration curve

$$\text{mg kg}^{-1}\text{ P in soil} = \frac{\mathbf{p} \times 2 \times 50}{5}$$

Calcium and Magnesium

5 g soil is extracted with 50 cm^3 AMBIC solution

5 cm^3 of this extract is diluted to 100 cm^3
Let Ca/Mg concentration in the solution be **c** mg dm^{-3}

$$\text{mg kg}^{-1}\text{ mg Ca/Mg in soil} = \frac{\mathbf{c} \times 20 \times 50}{5}$$

Micro-Elements

5 g soil is extracted with 50 cm^3 AMBIC solution
Let concentration of micro-element as read from the calibration curve be **w** mg dm^{-3}.

$$\text{mg kg}^{-1}\text{ micro-element in soil} = \frac{\mathbf{w} \times 50}{5}$$

Potassium

5 g soil is extracted with 50 cm^3 AMBIC solution and diluted twice.
Let concentration of potassium as read from the calibration curve be
k mg dm^{-3}

$$\text{mg kg}^{-1}\text{ K in soil} = \frac{\mathbf{k} \times 2 \times 50}{5}$$

18.6 References

VAN DER MERWE, A.J., JOHNSON, J.C. & RAS, L.S.K., 1984. An NH_4HCO_3-NH_4F - $(NH_4)_2$- EDTA, method for the determination of extractable P, K, Ca, Mg, Cu, Fe, Mn, and Zn in soils. *SIRI Inf. Bull.* B2/2.

TECHNICON AUTOANALYZER II INDUSTRIAL METHOD: No 94-70W/B. 1976. Ortho phosphate in water and wastewater.

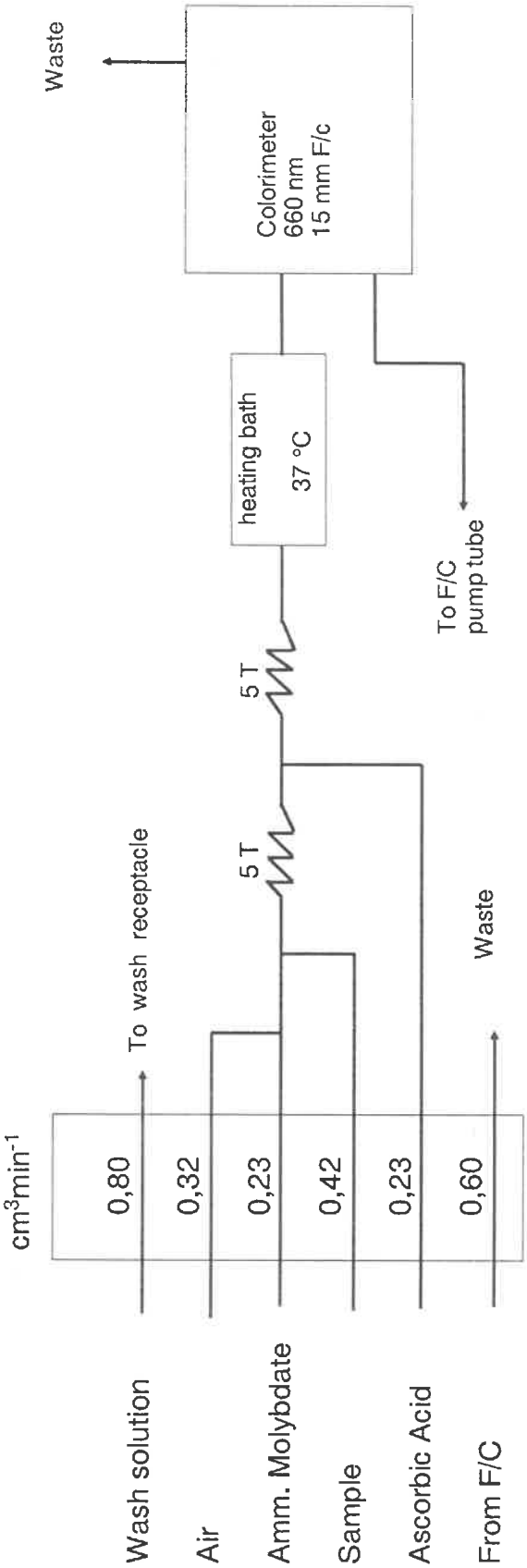

Figure 18.1: Flow system for P (Ambic-1)

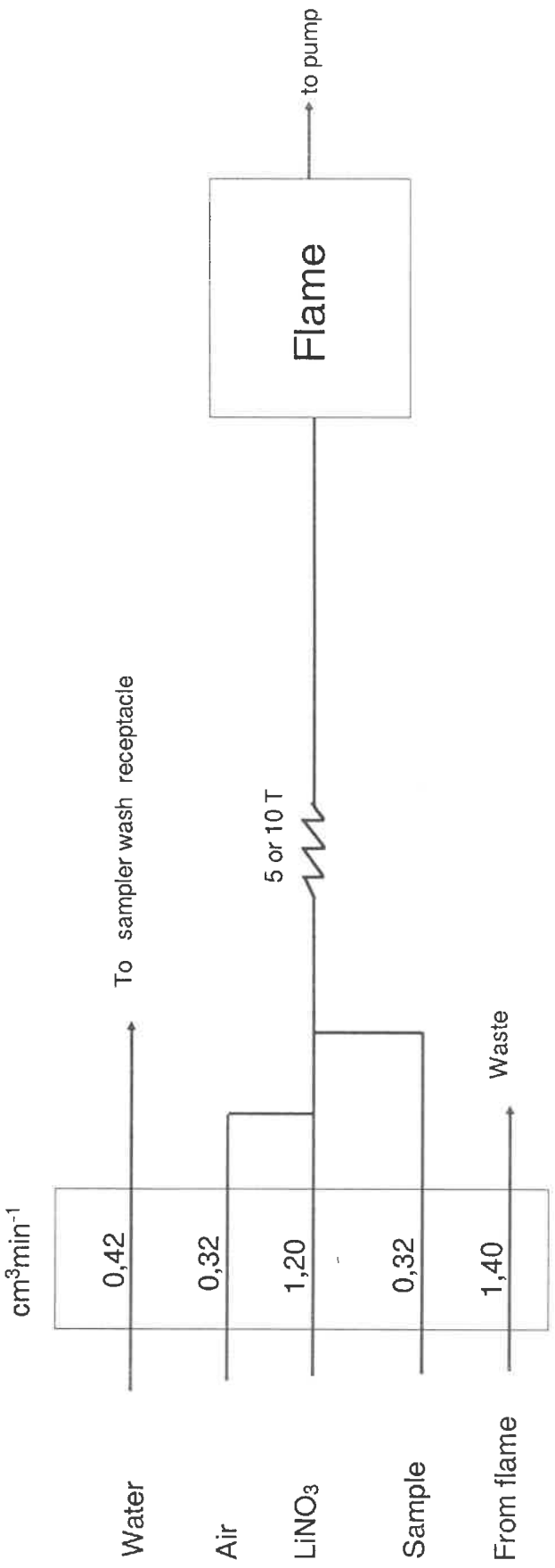

Figure 18.2 : Flow system for K

19. EXTRACTABLE PHOSPHORUS, POTASSIUM, ZINC, COPPER, MANGANESE AND IRON: AMBIC - 2

19.1 Introduction

The Ambic methods are modifications of the Hunter (1974) or ISFEI method introduced by Van der Merwe, Johnson & Ras (1984). The main difference between Ambic-1 and Ambic-2 is that extraction in the case of Ambic-2 is based on a volume of soil; no acid is used to clarify coloured solutions; di-sodium EDTA is used instead of di-ammonium EDTA; and stirring is applied instead of reciprocal shaking. This method is suitable for the determination of P and other micro-elements in a wide range of soils.

19.2 Apparatus

Scoop 2,5 cm^3
Sample cups
Whatman no 1 filter paper
Funnels and racks
Stirrers
Spectrophotometer

19.3 Reagents

Ambic-2 extraction solution, 0,25 mol dm^{-3} NH_4HCO_3 + 0,01 mol dm^{-3} Na_2 EDTA + 0,01 mol dm^{-3} NH_4F + Superfloc: The Superfloc solution is prepared by slowly adding 5 g Superfloc N-100 or N-127 to 1 dm^3 lukewarm de-ionised water while stirring at 400 rpm. The final solution should be viscous and gel-like. Dissolve 197,6 g ammonium bicarbonate, 37,2 g di-sodium EDTA and 3,7 g ammonium fluoride in about 5 dm^3 de-ionised water. Add 100 cm^3 Superfloc. Mix well and make up to 10 dm^3. After allowing to stand overnight adjust pH to 8,0 with concentrated ammonia solution

Concentrated colour reagent: Place 2 g antimony potassium tartrate in a 2 dm^3 pyrex volumetric flask. Add about 800 cm^3 de-ionised water. Add slowly, while mixing, 300 cm^3 concentrated H_2SO_4. Allow to cool overnight
Dissolve 15,0 g ammonium molybdate in about 600 cm^3 de-ionised water
When the acid antimony potassium tartrate solution is cool, add the ammonium molybdate solution and make up to 2 dm^3 with de-ionised water

NOTE: This solution is heat and light sensitive but when stored in a dark bottle in the refrigerator it may be kept for several months without deterioration

Diluted colour reagent: On the day of use, dilute 150 cm^3 of concentrated colour reagent to 1 dm^3 with a solution containing 1 g gelatin per litre. (The gelatin should be dissolved in warm de-ionised water). Then add about 1g ascorbic acid and mix

NOTE: Gelatin is sometimes contaminated with P but Riedel-de Haën gelatin has been found to be virtually free of phosphorus

The diluted colour reagent should be prepared fresh each day as this solution does not keep for longer than about 24 hours

Phosphate stock standard: Dissolve 0,439 g KH_2PO_4 in approximately 400 cm^3 de-ionised water contained in a 1 dm^3 volumetric flask. Add 25 cm^3 3,5 mol dm^{-3} H_2SO_4 (i.e. 9,5 cm^3 98% H_2SO_4 made up to 50 cm^3) and make up to the mark with de-ionised water. This gives a stock solution containing 100 mg dm^{-3} P. Store in a plastic container in the refrigerator

Phosphate working standards: Take 0; 10; 20; 40 and 60 cm^3 stock P solution and make each up to 1 dm^3 with NH_4HCO_3 extracting solution (giving standards of 0; 1; 2; 4; 6 mg dm^{-3} P in solution i.e. final concentrations of 0; 10; 20; 40; 60 mg dm^{-3} P in soil)

Potassium stock standard: Take 600 cm^3 of 1 000 mg dm^{-3} K standard and make up to 1 dm^3 with de-ionised water. The stock now has a concentration of 600 mg dm^{-3}

Potassium working standards: Take 0; 10; 20; 50; 100 cm^3 of stock K solution and make each up to 1 dm^3 in NH_4HCO_3 extracting solution (standards of 0; 6; 12; 30; 60 mg dm^{-3} K in soil)

Zinc stock standard: Take 50 cm^3 of 1 000 mg dm^{-3} Zn standard and make up to 1 dm^3 with de-ionised water. The stock now has a concentration of 50 mg dm^{-3}

Zinc working standards: Take 0; 2; 4; 10; 20 cm^3 of stock Zn solution and make each up to 1 dm^3 in NH_4HCO_3 extracting solution (standards of 0; 0,1; 0,2; 0,5; 1,0 mg dm^{-3} Zn in solution i.e. final concentrations of 0; 1; 2; 5; 10 mg dm^{-3} Zn in soil)

19.4 Procedure

19.4.1 Extraction

* Since the quantity of P extracted from a soil is temperature dependent, the laboratory and extracting solution temperature must be kept at 20 ± 2 °C
* Scoop 2,5 cm^3 soil (≤ 1 mm) into a sample cup
* Add 25 cm^3 extraction solution to the soil

* Stir for 10 minutes at 400 rpm
* Filter extract into a clean sample cup, using Whatman no1 filter paper

19.4.2 Determinations

Phosphorus

To a 2 cm^3 aliquot of the extract, 8 cm^3 of de-ionised water and 10 cm^3 of diluted colour reagent is added
After 40 minutes the absorbance values are read on a spectrophotometer set at 670 nm. The standards must be treated in the same way to obtain a calibration graph.

Potassium

Dilute 5 cm^3 extract to 25 cm^3 with de-ionised water and determine K on an atomic absorption spectrophotometer.
Set the instrument to the manufacturer's specifications.

Zinc, Copper, Manganese and Iron

These elements are determined directly on the undiluted extract with an atomic absorption spectrophotometer.

19.5 Calculations

Phosphorus

$$\text{mg dm}^{-3}\ \text{P in soil} = \frac{\mathbf{a} \times 25}{2{,}5}$$

where **a** = mg dm^{-3} P in the extract

Potassium

$$\text{mg dm}^{-3}\ \text{K in soil} = \frac{\mathbf{b} \times 25 \times 5}{2{,}5}$$

where **b** = mg dm^3 K in the extract

Zinc, Copper, Manganese and Iron

$$\text{mg dm}^{-3}\ \mathbf{A}\ \text{in soil} = \frac{\mathbf{c} \times 25}{2{,}5}$$

where **A** = either Zn, Cu, Mn or Fe and **c** = mg dm^{-3} **A** in the extract.

19.6 References

HUNTER, A.H., 1974. Tentative ISFEI soil extraction procedure. International Soil Fertility Evaluation and Improvement Project. N.C. State University Raleigh, N.C.

VAN DER MERWE, A.J., JOHNSON, J.C. & RAS, L.S.K., 1984. An NH_4HCO_3-NH_4F- $(NH_4)_2$ EDTA method for the determination of extractable P, K, Ca, Mg, Cu, Fe, Mn and Zn in soils. *SIRI Inf. Bull.* B2/2.

20 EXTRACTABLE PHOSPHORUS: BRAY-1

20.1 Introduction

A known mass of soil is shaken manually with Bray-1-solution. Contact time between soil and extractant should not exceed 60 seconds. This procedure extracts the more soluble phosphorus and is of most significance when analysing cultivated soils.

Total inorganic phosphates in the extracts are determined by automated colorimetric analysis by first converting condensed phosphates present to orthophosphate by hydrolysis with sulphuric acid at 90 °C. The total phosphate concentration is then determined by the reduction of phosphomolybdic acid to yield an intense blue colour, suitable for photometric determination at 660 nm. The reducing agent in this case is 1-amino-2-naphthol-4-sulfonic acid.

20.2 Apparatus

Balance to determine mass accurately to 0,01 g
Extracting bottles, wide mouth with stopper, 100 cm^3 slopy neck
Whatman no 2V filter paper
Continuous flow analyser (e.g. AutoAnalyzer)

20.3 Reagents

Ammonium fluoride stock solution: Dissolve 185,5 g NH_4F (AR) in about 4 dm^3 de-ionised water. Mix and make up to 5 dm^3
Bray-1 extracting solution: Decant 600 cm^3 NH_4F solution in a 20 dm^3 aspirator bottle. Add 10 dm^3 de-ionised water and 50 cm^3 concentrated HCl (AR) (32%). Dilute to 20 dm^3 with de-ionised water and mix well
Flocculant: Add 100 mg Superfloc N-100 or N-127 slowly to 100 cm^3 lukewarm de-ionised water. Stir at 400 rpm or shake gently till dissolved
1-amino-2-naphthol-4-sulfonic acid (ANSA) stock solution: Dissolve 137 g $Na_2S_2O_5$ and 5 g Na_2SO_3 in 800 cm^3 warm de-ionised water. Add 2,5 g ANSA and dilute to 1 250 cm^3 with de-ionised water. Filter into an amber glass bottle and store in a cool place
ANSA working reagent: Dilute 100 cm^3 stock solution to 1 dm^3 with de-ionised water. For best results make up fresh daily
Ammonium molybdate/Sulphuric acid: Dissolve 7,5 g ammonium molybdate in 800 cm^3 de-ionised water containing 53 cm^3 concentrated sulphuric acid. After cooling make up to 1 dm^3 in a volumetric flask. The reagent must be clear

and a solution exhibiting a blue colour should not be used. No precipitates should form later

Lubricating solution: Dissolve 150 g dodecyl sulfate sodium salt in 1 dm^3 de-ionised water. Store in a plastic container in a refrigerator. Warm solution to ambient temperature prior to use

Dodecyl sulphate sodium salt working solution (DSS): Make up 10 cm^3 of the stock solution to 1 dm^3 with de-ionised water. Add 10 cm^3 lubricating solution to the ANSA working solution and the ammonium molybdate/sulphuric acid solution, respectively

Phosphorus standard stock solution: Dissolve 0,930 g ammonium dihydrogen phosphate (AR), dried at 105 °C, in 1 dm^3 de-ionised water in a volumetric flask. Concentration = 250 mg dm^{-3} P

Phosphorus working solution: Prepare calibration standards in Bray-1 solution ranging from 0,5 to 15 mg dm^{-3} P

20.4 Procedure

20.4.1 Extraction (at 20 ± 2 °C)

* Place 6,67 g soil (≤ 2 mm) in an extraction bottle
* Add 50 cm^3 Bray-1 solution (20 °C)
* Stopper the bottle and shake contents manually (up and down) for 60 seconds
* Add 2 drops flocculant
* Filter immediately through Whatman no 2V filter paper into a suitable bottle

NOTE: The mass of soil taken for analysis can be varied from as little as 4 g to suit individual requirements, provided the soil/extractant ratio remains 1 : 7,5 and thorough extraction is ensured

20.4.2 Determination

Set continuous flow analyser up as per Fig. 20.1 and determine the P concentration of the extracts against the standard solutions

20.5 Calculation

6,67 g soil is extracted with 50 cm^3 Bray-1 solution
Let concentration of phosphorus as read from the calibration curve be
q mg dm^{-3}

$$\text{mg kg}^{-1}\ \text{P in soil} = \frac{\mathbf{q} \times 50}{6{,}67\ (\text{g})}$$

20.6 References

BRAY, R.H. & KURTZ, L.T., 1945. Determination of total, organic and available forms of phosphorus in soils. *Soil Sci.* 59, 39-45.

TECHNICON AUTOANALYZER METHODOLOGY: INDUSTRIAL METHOD 4 - 68W, 1969. Total inorganic phosphate in water and wastewater.

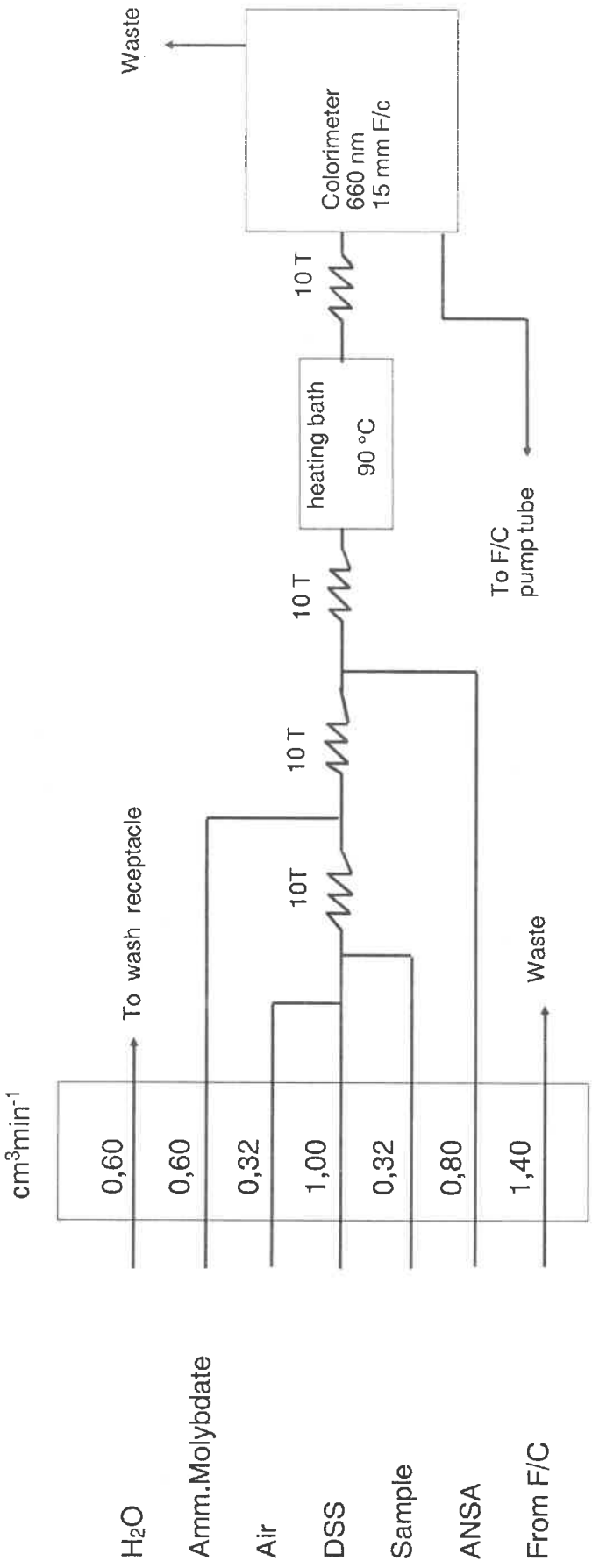

Figure 20.1: Flow system for P (Bray-1)

21 EXTRACTABLE PHOSPHORUS: BRAY - 2

21.1 Introduction

The extraction of P by this procedure is based on the solubilisation effect of H^+ on soil P and the ability of F^- to lower the activity of Al^{3+} and to a lesser extent that of Ca^{2+} and Fe^{3+} in the extraction system. F^- also complexes Al^{3+} and thereby increases the solubility of aluminium phosphate compounds and by precipitation as CaF, releases P from calcium phosphate compounds. This extraction method is therefore suitable for moderate to highly weathered soils of low to medium CEC. However, soils having free $CaCO_3$ or clay soils with high cation exchange capacities and high base saturation percentages will neutralise the extractant and a separate calibration scale should be used for such soils. This method is also suitable for organic soils.

Phosphorus-free charcoal is added to the suspension to remove interfering organic acids and to decolourise the extract. This extract is thus not suitable for the determination of micro-elements.

This Bray procedure developed by Bray & Kurtz (1945), extracts acid soluble and adsorbed or available and reserve phosphates present in soil.

Total inorganic phosphates in the extracts are determined by automated colorimetric analysis by first converting condensed phosphates present to orthophosphate by hydrolysis with sulphuric acid at 90 °C. The total phosphate concentration is then determined by the reduction of phosphomolybdic acid to yield an intense blue colour, suitable for photometric determination at 660 nm. The reducing agent in this case is 1-amino-2-naphthol-4-sulfonic acid.

21.2 Apparatus

Balance, accurate to 0,05 g
Extraction bottles, wide mouth, with screw caps, 100 cm^3 capacity
Buchner funnels
Whatman no 40 filter paper
Whatman no 2V filter paper
Continuous flow analyser (e.g. AutoAnalyzer) set up as in Fig. 21.1

21.3 Reagents

Ammonium fluoride stock solution: Dissolve 186 g NH_4F (AR) in 5 dm^3 de-ionised water. Store in a polythene container

Bray-2 extraction solution: Measure 600 cm^3 NH_4F stock solution into a 20 dm^3 aspirator. Add 10 dm^3 de-ionised water. Add 200 cm^3 concentrated HCl (AR) (32%). Dilute to 20 dm^3 with de-ionised water. Mix well

Flocculant: Dissolve 100 mg Superfloc N-100 or N-127 in 100 cm^3 lukewarm de-ionised water. Shake or stir gently till dissolved

Activated charcoal: Shake 500 g activated charcoal with 1 dm^3 extracting solution in a suitable container on a horizontal shaker for 2 hours. Filter slurry on a Buchner funnel, using Whatman no 2V filter paper

Wash twice with 250 cm^3 aliquots of extracting solution, allowing the charcoal to soak well each time before draining. Place the wet charcoal in the original container and repeat extraction and washing. Check the final washing for the presence of phosphate. If no phosphate is detectable, dry charcoal on a water-bath

1-amino-2-naphthol-4-sulfonic acid (ANSA) stock solution: Dissolve 137 g $Na_2S_2O_5$ and 5 g Na_2SO_3 in 800 cm^3 warm de-ionised water. Add 2,5 g ANSA and dilute to 1 250 cm^3 with de-ionised water. Filter into an amber glass bottle and store in a cool place

ANSA working reagent: Dilute 100 cm^3 stock solution to 1 dm^3 with de-ionised water. For best results make up fresh daily

Ammonium molybdate/sulphuric acid: Dissolve 7, 5 g ammonium molybdate in 800 cm^3 de-ionised water containing 53 cm^3 concentrated sulphuric acid. After cooling make up to 1 dm^3 in a volumetric flask. The reagent must be clear and a solution exhibiting a blue colour should not be used. No precipitates should form later

Lubricating solution: Dissolve 150 g dodecyl sulfate sodium salt in 1 dm^3 de-ionised water. Store in a plastic container in a refrigerator. Warm solution to ambient temperature prior to use

Dodecyl sulfate sodium salt working solution (DSS): Make up 10 cm^3 of the stock solution to 1 dm^3 with de-ionised water. Add 10 cm^3 lubricating solution to the ANSA working solution and the ammonium molybdate/sulphuric acid solution, respectively

Phosphorus standard stock solution: Dissolve 0,930 g ammonium dihydrogen phosphate (AR), dried at 105 °C in 1 dm^3 de-ionised water in a volumetric flask. Concentration = 250 mg dm^{-3} P

Phosphorus working solution: Prepare calibration standards in Bray-2 solution ranging from 0,5 to 15 mg dm^{-3} P

21.4 Procedure

21.4.1 Extraction (at 20 ± 2 °C)

* Place 8 g soil in an extraction bottle
* Add 60 cm^3 Bray-2 solution (20 °C)
* Stopper bottle and shake for 40 seconds by hand

* Filter immediately through Whatman no 2V filter paper into an extraction bottle, discarding the first few drops of filtrate
* Add 1 g phosphorus free charcoal
* Stopper and shake for 40 seconds by hand
* Add 2 drops flocculant
* Filter through Whatman no 40 paper into a suitable container
* Determine P within 24 hours

21.4.2 Determination

Determine the P in the Bray-2 extracts against the standards on a continuous flow analyser system set up as in Fig. 21.1

21.5 Calculation

8 g soil is extracted with 60 cm^3 Bray-2 solution
Let concentration of phosphorus as read from the calibration curve be
q mg dm^{-3}

$$\text{mg kg}^{-1}\ \text{P in soil} = \frac{\mathbf{q} \times 60}{8\ (g)}$$

21.6 References

BRAY, R.H. & KURTZ, L.T., 1945. Determination of total, organic and available forms of phosphorus in soils. *Soil Sci.* 59, 39-45.

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KURTZ, L.T., 1942. Elimination of fluoride interference in molybdenum blue reaction. *Ind. Eng. Chem. Anal.* 14, 855.

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THE COUNCIL ON SOIL TESTING AND PLANT ANALYSIS, 1974. Handbook on reference methods for soil testing. The Council on Soil Testing and Plant Analysis, 2400 College Station Road, Athens, Georgia USA.

THOMAS, G.W. & PEASLEE, D.E., 1973. Testing soil for phosphorus. In L. Walsh & J. Beaton (eds.). Soil testing and plant analysis. 115-122. Soil Sci. Am. Madison, Wis.

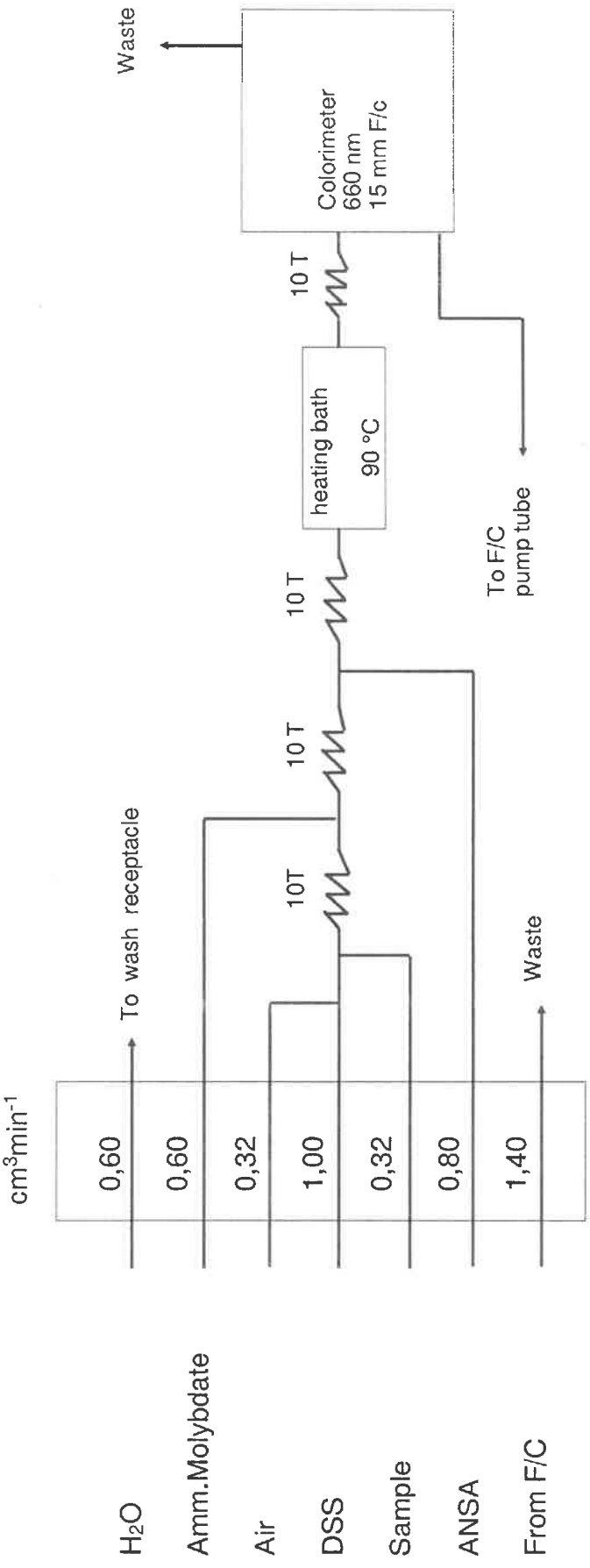

Figure 21.1: Flow system for P (Bray-2)

22 EXTRACTABLE PHOSPHORUS: RESIN BAG

22.1 Introduction

The use of anion exchange resins to extract phosphate from soil was pioneered by Amer, Bouldin, Black & Duke (1955). They showed that the rate of extraction was dependent on the rate of release of phosphate from the soil into the aqueous medium. Resin bags behave very similar to roots and many subsequent trials indicated resin extractable P to correlate better with plant P uptake than chemical extractions. The original method was simplified and standardised by Sibbesen (1978). The simplified method appears to work on any soil type.

22.2 Apparatus

Balance accurate to 0,01 g
Reciprocating shaker
Wide mouthed 200 cm^3 extraction bottles
Resin-filled bags
5 dm^3 beaker
25 cm^3 volumetric flasks
1; 5 and 10 cm^3 pipettes
Spectrophotometer set at 700 nm

22.3 Reagents

0,5 mol dm^{-3} Sodium bicarbonate: Dissolve 42 g $NaHCO_3$ in 1 dm^3 de-ionised water
0,5 mol dm^{-3} Hydrochloric acid: Make 45 cm^3 concentrated HCl up to 1 dm^3 with de-ionised water
2,5 mol dm^{-3} Sulphuric acid: Add 70 cm^3 conc. H_2SO_4 to 430 cm^3 de-ionised water
Ammonium molybdate: Dissolve 20 g $(NH_4)_6Mo_7O_{24}.4H_2O$ in water and make up to 500 cm^3. Store the solution in a Pyrex glass bottle
Ascorbic acid: Dissolve 1,32 g $C_6H_8O_6$ in 75 cm^3 de-ionised water. Prepare only when needed
Potassium antimony tartrate: Dissolve 0,2743 g $K(SbO)C_4H_4O_6$ in 100 cm^3 de-ionised water
Mixed reagent: Mix 125 cm^3 2,5 mol dm^{-3} H_2SO_4 and 37,5 cm^3 ammonium molybdate. Add 75 cm^3 ascorbic acid solution and 12,5 cm^3 potassium antimony tartrate. Prepare only when needed
Phosphate stock: Dissolve 0,1757 g KH_2PO_4 in 1 000 cm^3 de-ionised water

22.4 Procedure

22.4.1 Extraction

Preparation

* Manufacture a number of bags out of 300 μm PES mesh material (supplier: Thomas Robinson & Son, PO Box 269, Bergvlei 2012) using polyester thread (Fig. 22.1). Sieve a quantity of any gel-type strongly-basic type 1 anion exchange resin through a 350 μm sieve and place sufficient of the 350 μm fraction in each bag to provide a total anion exchange capacity of about 10 mmol(-). Using Dowex 1 X 8 this is about 3,5 g. Seal bags by stitching with polyester thread. The resin in the bags is regenerated after each use and can be used many times. The bags are stored under water between use
* Place the bags in a large beaker containing 100 cm^3 0,5 mol dm^{-3} $NaHCO_3$ per bag for 30 minutes, stirring occasionally. Repeat with fresh 0,5 mol dm^{-3} $NaHCO_3$. Wash the bags twice for 30 minutes per wash in de-ionised water and store in the final wash water until use
* Grind the ≤ 2 mm soil to pass through a 300 μm sieve. Place 4,0 g of soil into an 200 cm^3 extraction bottle and add 100 cm^3 de-ionised water and a resin bag. Close the bottle and shake for 17 hours on a reciprocal shaker at 30 rpm, at a temperature of 20 ± 2 °C
* Discard the soil suspension and rinse the bag in the bottle thoroughly with de-ionised water. Add 80 cm^3 0,5 mol dm^{-3} HCl to elute the P from the bags. When the CO_2 generation has subsided, close the bottle and shake for 30 minutes. Determine the P in the acid eluate. The volume of eluate is 80 cm^3 plus the volume of water retained by the bag after the last rinse (about 0,5 cm^3). Determine this retained volume once by weighing a few drained bags and then drying them overnight at 60 °C. Repeat the 0,5 mol dm^{-3} $NaHCO_3$ procedure in preparation for the next extraction

22.4.2 Determination

* Pipette between 0,2 and 20 cm^3 acid eluate into a 25 cm^3 volumetric flask (use 20 cm^3 for soils with a P content of 1-5 mg kg^{-1} and smaller volumes for higher P soils)
* Add 4 cm^3 mixed reagent and bring to volume with de-ionised water. Read the absorbance at 700 nm on a spectrophotometer after 10 minutes
* **Standards:** pipette 2,5 cm^3 of P stock into a 250 cm^3 volumetric flask and make up to volume with de-ionised water. Pipette 0; 2,5; 5,0; 10,0 and 20 cm^3 of this diluted stock into 25 cm^3 volumetric flasks and add 4 cm^3 of mixed reagent. Bring up to volume with de-ionised water. The flasks now contain 0; 1; 2; 4 and 8 μg P respectively

22.5 Calculation

$$\text{Resin extractable P (mg kg}^{-1}) = \frac{(V_1 \times C)}{(V_2 \times M)}$$

where V_1 = volume of acid eluant (cm^3)
V_2 = volume of aliquot used in P determination (cm^3)
C = amount of P in determination sample (μg)
M = dry mass of soil used (g)

22.6 References

AMER, F., BOULDIN, D.R., BLACK, C.A. & DUKE, F.R., 1955. Characterisation of soil phosphorus by anion exchange. *Plant and Soil* 6, 391-408.

MURPHY, J. & RILEY, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* 27, 31-36.

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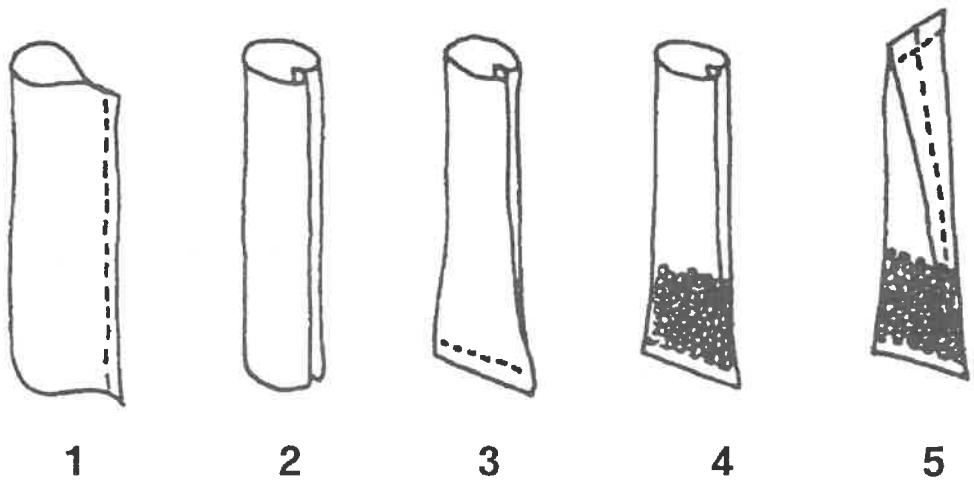

Figure 22.1: Sewing the bags out of polyester mesh. Use polyester thread, since nylon degrades with constant use in acid

23 EXTRACTABLE PHOSPHORUS: RESIN

23.1 Introduction

The extraction of phosphate from soil by means of anion exchange resins was developed by Amer, Bouldin, Black & Duke (1955). They demonstrated that the rate of phosphate uptake by the resin depended solely on the rate of release of phosphate by the soil. In this respect the mechanism is the same as that whereby plants take up phosphate from the soil.

23.2 Apparatus

Balance
Reciprocating shaker set at 50/60 oscillations per minute
Extraction bottles, slopy necked, 100 cm^3 capacity and stoppers
Sieves, 0,15 mm and 0,2 mm
Agate mortar and pestle
Volumetric flasks 100 cm^3
Continuous flow analyser set up as in Fig. 23.1
Waterbath

23.3 Reagents

Amberlite IRA 400 resin: 0,2 mm
Sodium chloride: Dissolve 100 g NaCl (AR) in 1 dm^3 de-ionised water
Ammonium molybdate: Add 70 cm^3 H_2SO_4(c) to approximately 1 600 cm^3 de-ionised water in a 2 dm^3 volumetric flask and allow to cool. To this solution add 20,0 g of ammonium molybdate. Make up to volume with de-ionised water after the ammonium molybdate has dissolved completely. This solution must be stored in a refrigerator
Hydrazine sulphate-Stannous chloride solution: Dissolve 0,4 g stannous chloride ($SnCl_2.2H_2O$) in 4 cm^3 HCl (c) by heating gently in a fume cupboard. Add 70 cm^3 H_2SO_4 (c) to approximately 1 600 cm^3 de-ionised water in a 2 dm^3 volumetric flask and to this solution add 4,0 g hydrazine sulphate and dissolve completely before adding the dissolved stannous chloride solution. Cool the solution and make up to 2 dm^3 with de-ionised water. This solution is stable for 2 weeks if stored in a refrigerator
P standard solution, 1 000 mg dm^{-3}: From commercially available solution make up 1 dm^3 standard

23.4 Procedure

23.4.1 Extraction (at 20 ± 2 °C)

* Grind the ≤ 2 mm air-dry soil in an agate mortar to pass a 0,15 mm sieve
* Shake 5,0 g soil with 1 g resin and 60 cm^3 de-ionised water for 16 hours on a horizontal shaker, set at 50/60 oscillations per minute
* Maintain constant temperature during this period (20 °C)
* Separate resin from soil and water with a 0,15 mm sieve
* Extract phosphate from the resin with 25 cm^3 10% NaCl solution for 45 minutes on a waterbath, followed by leaching with additional aliquots of 10% NaCl, so that about 90 cm^3 filtrate is collected in a 100 cm^3 volumetric flask
* Cool and make up to the mark with 10 % NaCl solution

23.4.2 Determination

Prepare a set of P standards from the stock solution in 10% NaCl
Determine the P in the extracts against the standards on a continuous flow analyser set up as in Fig. 23.1

23.5 Calculations

$$\text{mg kg}^{-1}\ \text{P in soil} = \frac{\mathbf{a} \times 100}{5}$$

where: **a** = mg dm^{-3} P in extract

23.6 References

AMER, F., BOULDIN, D.R., BLACK, C.A. & DUKE, F.R., 1955. Characterization of soil phosphorus by anion exchange resin adsorption and P^{32}-equilibration. *Plant and Soil* 6, 391-408.

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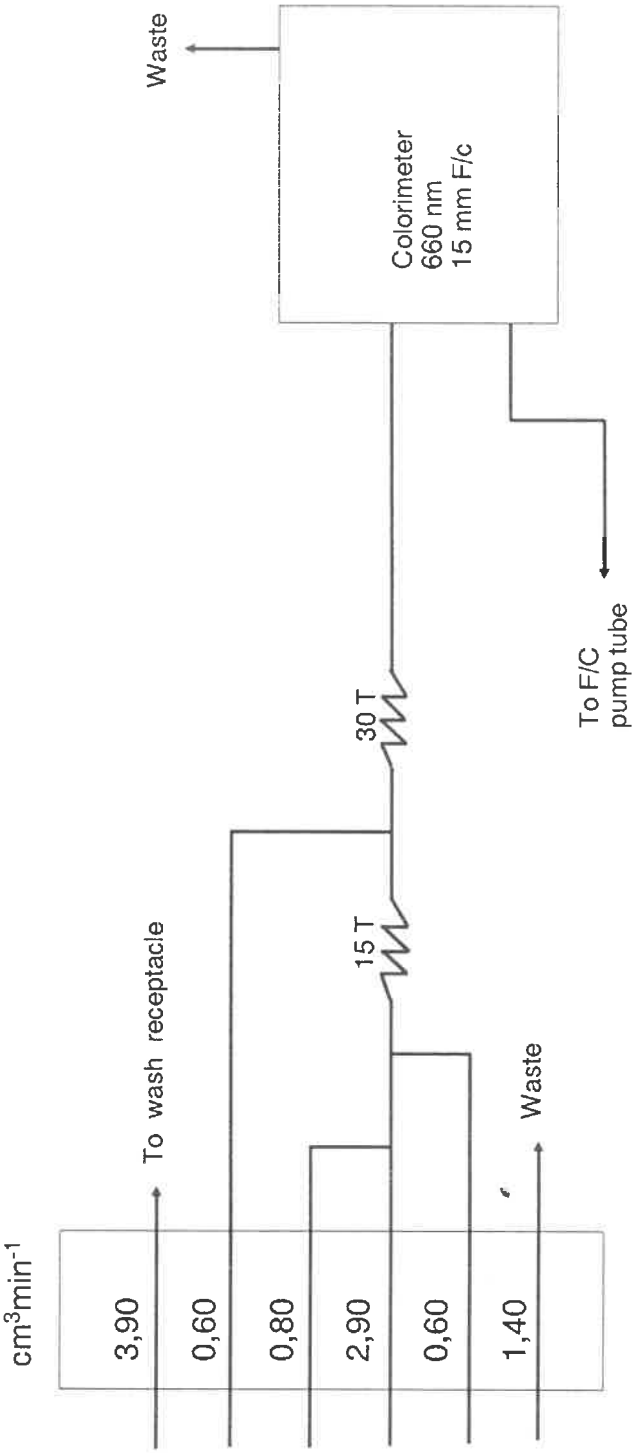

Figure 23.1: Flow system for P (resin extraction)

24 EXTRACTABLE PHOSPHORUS: $NaHCO_3$ (OLSEN)

24.1 Introduction

The extractant is 0,5 mol dm^{-3} $NaHCO_3$ (pH = 8,5). The solubility of phosphate in calcareous, alkaline or neutral soil is increased because of precipitation of Ca^{2+} as $CaCO_3$. In acid soils the phosphate concentration in solution increases when variscite ($AlPO_4.2H_2O$) and strengite ($FePO_4.2H_2O$) are present in equilibrium with gibbsite. Secondary precipitation reactions are reduced in acid and calcareous soils because Fe, Al and Ca concentrations remain low in the extract.

24.2 Apparatus

Extraction bottles, 250 cm^3 capacity with stoppers
Reciprocating shaker, 180 oscillations per minute
Whatman no 40 filter paper
Funnels
Balance
Volumetric flasks
Buchner funnel
Spectrophotometer, wavelength set at 882 nm

24.3 Reagents

Sodium bicarbonate, 0,5 mol dm^{-3}: Dissolve 42 g $NaHCO_3$ (AR) in de-ionised water and dilute to 1 dm^3. Adjust pH of the solution to 8,5 with 50% NaOH. Add mineral oil to avoid absorption of CO_2. Store in a polythene bottle. Check pH monthly

Activated charcoal, carbon-free: Merck's extra pure active charcoal is recommended. Shake 50 g activated charcoal with 100 cm^3 extracting solution on a horizontal shaker for 2 hours. Filter on a Buchner funnel, using Whatman no 40 filter paper. Wash twice with 50 cm^3 aliquots of extracting solution, allowing the charcoal to soak well each time before draining. Repeat extraction until filtrate is phosphate-free

Ammonium molybdate solution: Dissolve 12 g ammonium molybdate in 250 cm^3 de-ionised H_2O. In 100 cm^3 of de-ionised H_2O dissolve 0,2908 g antimony potassium tartrate. Add both of the dissolved reagents to 1 dm^3 of 2,5 mol dm^{-3} H_2SO_4 (148 cm^3 concentrated H_2SO_4 dm^{-3}) mix thoroughly and make up to 2 dm^3. Store in a pyrex glass bottle in a dark and cool place

Colour reagent: Dissolve 1,056 g ascorbic acid in 200 cm^3 ammonium molybdate solution and mix. This reagent should be prepared as required as it does not keep for longer than 24 hours

24.4 Procedure

24.4.1 Extraction (at 20 ± 2 °C)

* Place 2,5 g air-dry soil (≤ 2 mm) in a 250 cm^3 extraction bottle
* Add 1 g phosphate-free charcoal
* Add 50 cm^3 $NaHCO_3$-solution and stopper
* Shake for 30 minutes on a reciprocating shaker set at 180 oscillations per minute. Extraction flask must be mounted horizontally
* Filter extract through Whatman no 40 filter paper into a suitable container
* Determine P in the extract within 24 hours of extraction

24.4.2 Determination

* Determine the volume of 2,5 mol dm^{-3} H_2SO_4 required to bring the pH of 5 cm^3 $NaHCO_3$ extracting solution to 5
* Pipette 5 cm^3 aliquots of the extracts into 25 cm^3 volumetric flasks
* Add 2,5 mol dm^{-3} H_2SO_4 solution to bring the pH to 5 and add 10 cm^3 de-ionised water followed by 4 cm^3 colour reagent
* Make up to volume with de-ionised water and mix well
* The colour is stable for 24 hours and maximum intensity is obtained in 10 minutes
* The absorbance of the solution is determined on a spectrophotometer at a wavelength of 882 nm
* Calibrate the method using standard P solutions prepared in the same manner as above

24.5 Calculations

$$\text{mg kg}^{-1}\text{ P in soil} = \frac{\mathbf{c} \times 50}{2{,}5}$$

where: **c** = mg dm^{-3} P in the extract

24.6 References

LINDSAY, W.K. & MORENO, E.C., 1960. Phosphate phase equilibria in soils. *Soil Sci. Soc. Amer. Proc.* 24, 177-182.

MURPHY, J. & RILEY, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta.* 27, 31-36.

OLSEN, S.R., COLE, D.V., WATANABE, F.S. & DEAN, L.A., 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circ. No 939.

OLSEN, S.R. & DEAN, L.A., 1965. Phosphorus. In C.A. Black (ed.). Methods of soil analysis. Part 2, 1044-1046. Am. Soc. Agron. Madison, Wis.

THE COUNCIL ON SOIL TESTING AND PLANT ANALYSIS, 1974. Handbook on Reference Methods for Soil Testing and Plant Analysis. 2400 College Station Road, Athens, Georgia USA.

WATANABE, F.S. & OLSEN, S.R., 1965. Test of an ascorbic acid method for the determining of phosphorus in water and $NaHCO_3$ extracts. *Soil Sci. Soc. Am. Proc.* 29, 677 - 678.

25 EXTRACTABLE PHOSPHORUS, POTASSIUM AND ZINC: MODIFIED ISFEI METHOD (HUNTER)

25.1 Introduction

Phosphorus is extracted using a slightly modified version of the ISFEI method described by Hunter (1974). Instead of a 1:10 soil to solution ratio on a volume basis a 1:10 ratio on a mass basis is used. Stirring is replaced by shaking.

Ammonium molybdate and potassium antimony tartrate react with orthophosphate in an acid medium to form an antimony-phosphomolybdate complex, which on reduction with ascorbic acid, yields an intense blue colour suitable for photometric measurement at 660 nm.

Soil extracts must be hydrolysed with hot sulphuric acid prior to the determination of orthophosphate as a molybdenum blue complex.

25.2 Apparatus

Reciprocating shaker set at 180 oscillations per minute
Balance
Whatman no 2V filter paper
Extraction bottles, slopy necked, 100 cm^3 capacity, stoppers
Continuous flow analyser (e.g. AutoAnalyzer)
Flame emission spectrophotometer
Atomic absorption spectrophotometer

25.3 Reagents

Sodium bicarbonate, 0,25 mol dm^{-3}: Dissolve 210 g $NaHCO_3$ (AR) in 1 dm^3 de-ionised water
Di-sodium EDTA, 0,01 mol dm^{-3}: Dissolve 37,2 g Na_2EDTA in 1 dm^3 de-ionised water
Ammonium fluoride, 0,01 mol dm^{-3}: Dissolve 3,7 g NH_4F (AR) in 1 dm^3 de-ionised water
Superfloc: Carefully dissolve 0,5 g Superfloc 127 or N-100 in 1 dm^3 lukewarm de-ionised water stirred at 400 rpm for 2 hours. Allow to cool
Extracting solution: Mix the above four solutions and make up to 10 dm^3 after adjusting pH to 8,5 with concentrated NaOH
Phosphate-free charcoal: Merck's extra pure active charcoal is recommended. Shake 50 g activated charcoal with 100 cm^3 extracting solution for

2 hours on a horizontal shaker. Filter and wash repeatedly with extracting solution until phosphate-free

Sulphuric acid: Add 362 cm^3 concentrated sulphuric acid (AR) to 400 cm^3 de-ionised water in a 1 dm^3 beaker (197 g). Mix well and allow to cool before making up to 1 dm^3 in a volumetric flask

Ammonium molybdate: Dissolve 27 g ammonium molybdate-4-hydrate $[(NH_4)_6Mo_7O_{24}.4H_2O]$ in 500 cm^3 de-ionised water at 50 °C. Allow to cool before making up to 1 dm^3 with de-ionised water

Ascorbic acid: Dissolve 2,5 g ascorbic acid in 85 cm^3 de-ionised water. Prepare daily

Potassium antimony tartrate: Dissolve 2 g potassium antimony tartrate in 1 dm^3 de-ionised water

Combined colour reagent: Mix above reagents in the following order:

Sulphuric acid	80 cm^3
Ammonium molybdate	25 cm^3
Ascorbic acid	85 cm^3
Potassium antimony tartrate	10 cm^3

Make up in a 200 cm^3 plastic container. Shake after each addition. Keep in a dark container. Prepare daily

Sulphuric acid for hydrolysis: Add 354 g (192 cm^3) concentrated sulphuric acid to 500 cm^3 de-ionised water, mix and cool. Make up to 1 dm^3

Phosphorus standard stock solution: Dissolve 0,372 g ammonium dihydrogen phosphate (AR), dried at 105 °C in 1 dm^3 de-ionised water in a volumetric flask. Concentration = 0,1 mg cm^{-3} P

$LiNO_3$ Reference Solution: Dissolve 2,37 g $LiNO_3$ (AR) in 2 dm^3 de-ionised water in a volumetric flask. Before making up to the mark, add 1 cm^3 Brij solution as wetting agent

Potassium standard stock solution: Prepare a stock solution containing 1 mg cm^{-3} K, using commercially available standard solution concentrate

Zinc standard stock solution: A commercially available standard solution is diluted to contain 1 mg cm^{-3} Zn

25.4 Procedure

25.4.1 Extraction

* Extraction to be performed at 20 ± 2 °C
* Place 5 g soil in a 100 cm^3 extraction bottle
* Add 50 cm^3 extracting solution and stopper the bottle
* Shake in a horizontal position on a reciprocating shaker set at 180 oscillations per minute for 30 minutes
* Filter immediately through Whatman no 2V filter paper

* If the solution is dark brown after filtration, add 1 g phosphate-free activated charcoal, shake and filter again to obtain a clear solution

25.4.2 Determination

Phosphorus

Phosphorus is determined on a continuous flow analyser with the manifold set up as in Fig. 25.1
Calibration standards are made up from the stock solution to give a range of 0,5 to 5 mg dm^{-3} P
The standards must be made up in ISFEI solution to keep the matrix of the standards the same as the extracts.

Potassium

Potassium is determined on a continuous flow analyser fitted with a flame spectrophotometer and the manifold set up as in Fig. 25.2
$LiNO_3$ is used as a constant reference
Calibration standards ranging from 1 to 20 mg dm^{-3} K are prepared in ISFEI extractant.

Zinc

Zinc in the ISFEI extracts is determined with an atomic absorption spectrophotometer using an air-acetylene flame and parameters set as recommended by the instrument manufacturer
Calibration standards are made up in the ISFEI solution, ranging from 0,1 to 1,0 mg dm^{-3} Zn.

25.5 Calculations

Phosphorus

5 g soil is extracted with 50 cm^3 ISFEI extractant. Let concentration of phosphorus as read from the calibration curve be **p** mg dm^{-3}

$$\text{mg kg}^{-1}\text{ P in soil} = \frac{\mathbf{p} \times 50}{5}$$

Potassium

5 g soil is extracted with 50 cm^3 ISFEI extractant. Let concentration of potassium as read from the calibration curve be **k** mg dm^{-3}

$$mg\ kg^{-1}\ K \text{ in soil} = \frac{\mathbf{k} \times 50}{5}$$

Zinc

5 g soil is extracted with 50 cm^3 ISFEI solution. Let concentration of zinc as read from the calibration curve be **z** mg dm^{-3}

$$mg\ kg^{-1}\ Zn \text{ in soil} = \frac{\mathbf{z} \times 50}{5}$$

25.6 Reference

HUNTER, A.H., 1974. Tentative ISFEI soil extraction procedure. International Soil Fertility Evaluation and Improvement Project. N.C. State University Raleigh, N.C. USA.

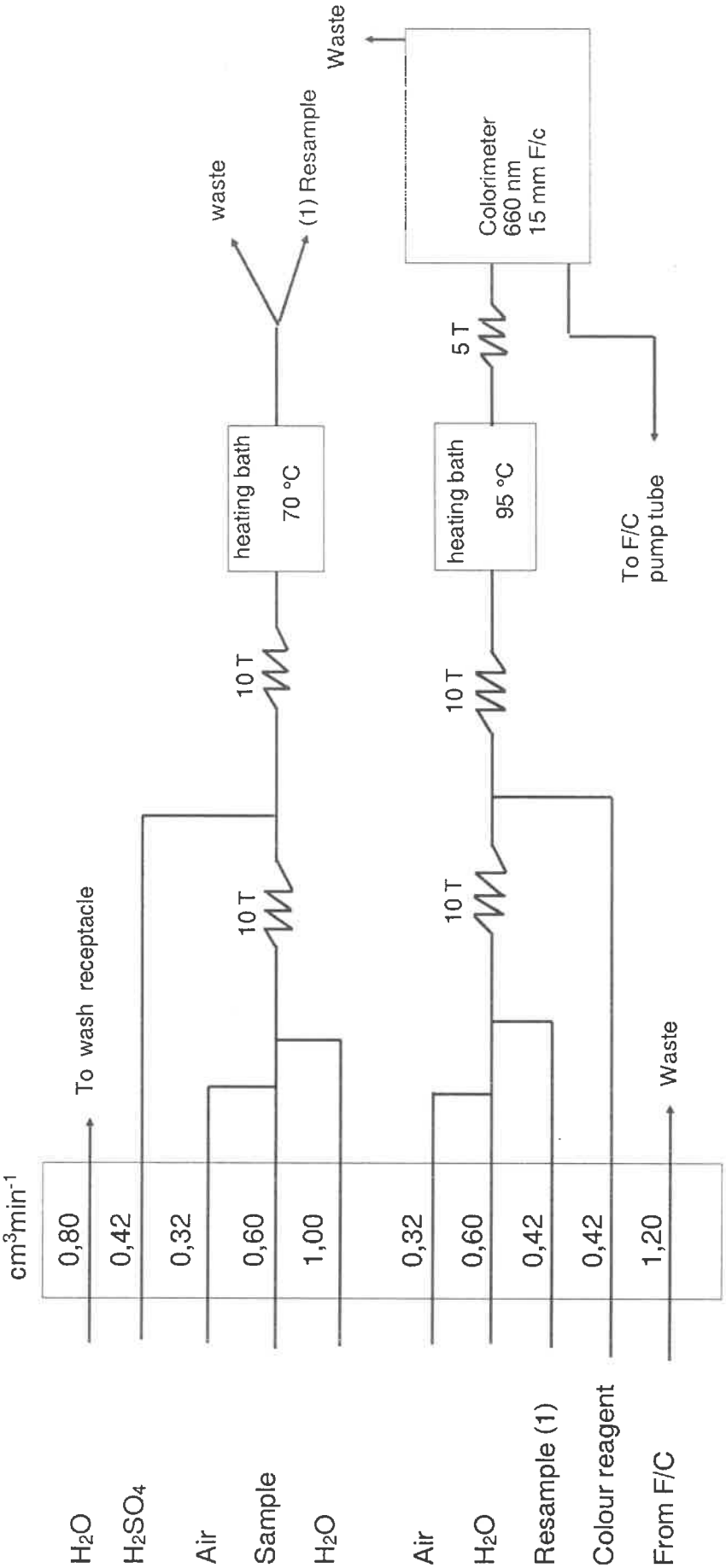

Figure 25.1: Flow system for P (ISFEI)

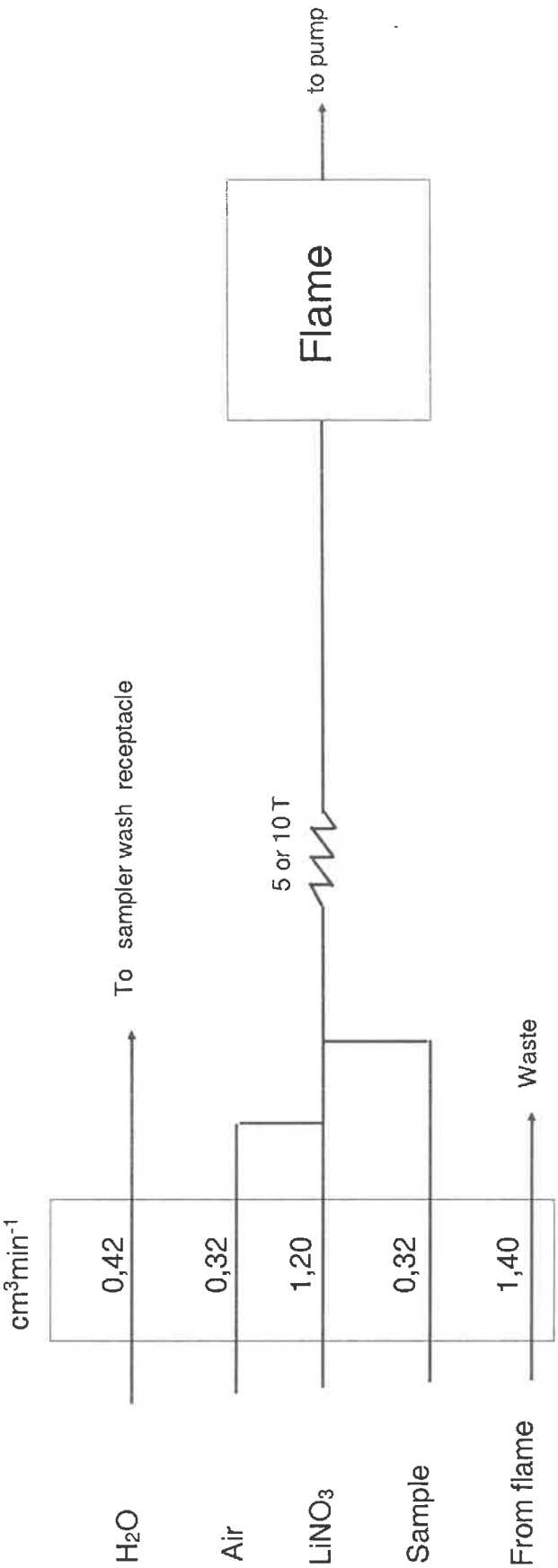

Figure 25.2: Flow system for K

26 EXTRACTABLE PHOSPHORUS, POTASSIUM, SODIUM, CALCIUM AND MAGNESIUM: CITRIC ACID (1%)

26.1 Introduction

The extraction of P from soils by means of 1% citric acid was originally developed by Dyer (1894). Citric acid increases the solubility of calcium phosphates, aluminium phosphates and to a slight extent iron phosphates while exchangeable cations are displaced from the exchange complex of soils. Re-adsorption of phosphate is prevented by the formation of citric acid complexes.

26.2 Apparatus

Erlenmeyer flasks, 500 cm^3 capacity with rubber stoppers
Balance
Whatman no 40 filter paper
Drying oven set at 80 °C
Waterbath
Beakers
Volumetric flasks, 100 cm^3

26.3 Reagents

Citric acid, 1%: Heated to 80 °C
Hydrochloric acid (AR): Concentrated
Nitric acid (AR): Concentrated

26.4 Procedure

* Place 20 g air-dry soil (≤ 2 mm) in an Erlenmeyer flask (500 cm^3)
* Add 200 cm^3 1% citric acid heated to 80 °C to the soil in the flask
* Stopper the flask and after shaking, place in the oven set at 80 °C
* Shake every 10 minutes
* Remove after one hour
* Filter through Whatman no 40 paper into a beaker
* Re-filter through the same filter paper if solution is turbid
* A 50 cm^3 aliquot (after cooling) is heated to dryness on the waterbath
* The residue is then heated for 2 hours to remove organic material
* After cooling, add 5 cm^3 concentrated HCl and 5 cm^3 concentrated HNO_3
* Evaporate to dryness on the waterbath. Repeat this step

* Add 5 cm^3 concentrated HNO_3 and 20 cm^3 de-ionised water to the dry residue and heat until dissolved
* Filter directly into a 100 cm^3 volumetric flask, using Whatman no 40 filter paper
* Wash filter paper repeatedly with de-ionised water
* Make up to the mark after the solution has cooled
* Determine P, Ca, Mg, Na and K with a suitable method

26.5 References

DIVISION OF CHEMICAL SERVICES, 1956. Analytical methods. Division of Chemical Services, Department of Agriculture, RSA.

DU PLESSIS, S.F. & BURGER, R. DU T., 1964. A comparison of chemical extraction methods for the evaluation of phosphate availability of top soils. *S. Afr. J. Agric. Sci.* 8, 1113.

DYER, B., 1894. On the analytical determinations of probably available "mineral plant-food in soil". *J.Chem. Soc.* 65, 115.

EKSTEEN, L.L, 1974. Fosforbemesting van gewasse na aanleiding van navorsingsresultate. *Misstofver. S. Afr. J.* 1, 67-70.

ELOFF, J.F., 1971. Studies oor die toeganklike fosforstatus van sekere Vaalhartsgronde. M.Sc. Tesis, U.O.V.S., Bloemfontein.

KOMITEE VAN ONDERSOEK, 1972. Verslag van die Komitee van Ondersoek: Koördinering van Grondontledingsdienste. Departement Landbou-Tegniese Dienste, RSA.

27 EXTRACTABLE PHOSPHORUS: MODIFIED TRUOG METHOD

27.1 Introduction

The solubility of calcium and aluminium is increased by the presence of H^+. Phosphate is extracted by this acidic solution and sulphate prevents the re-adsorption of phosphate brought into solution by H^+.

27.2 Apparatus

Balance accurate to 0,01 g
Whatman no 1 filter paper
Plastic cups, 125 cm^3 capacity with stoppers
Reciprocal shaker (180 oscillations per minute)

27.3 Reagent

Sulphuric acid, 0,01 mol dm^{-3}: Dilute 1 g concentrated H_2SO_4 (AR) to 1 dm^3 with de-ionised water. Standardise against 0,01 mol dm^{-3} Na_2CO_3 with bromophenol blue as indicator

27.4 Procedure (at 20 ± 2 °C)

27.4.1 Extraction

* Place 2 g soil in the plastic cup
* Add 100 cm^3 0,01 mol dm^{-3} H_2SO_4
* Seal the cup
* Shake for 20 minutes using a reciprocal shaker set at 180 oscillations per minute
* Filter immediately through Whatman no 1 paper into a suitable container

27.4.2 Determination

Determine P with a suitable method.

27.5 Reference

KOMITEE VAN ONDERSOEK, 1972. Verslag van die Komitee van Ondersoek: Koördinering van Grondontledingsdienste. Departement Landbou-Tegniese Dienste, RSA.

TRUOG, E., 1930. The determination of the readily available phosphorus of soil. *J. Am. Soc. Agron.* 22, 874.

28 EXTRACTABLE ALUMINIUM: KCl (1 mol dm^{-3})

28.1 Introduction

Exchangeable or extractable Al is most commonly displaced with an unbuffered salt solution such as KCl, $CaCl_2$ or $BaCl_2$. Extractable Al is a component of total extractable acidity and its proportion can vary from 30 to 90% depending on organic matter content, clay mineralogy and other properties. In assessing the effects of Al on plant growth it is important to measure directly the concentration of displaced Al in the KCl extract. It is proposed that extractable Al be measured by spectrophotometry using the Chrome Azurol-S (CAS) method.

28.2 Apparatus

Balance
Horizontal shaker
Centrifuge fitted with polythene centrifuge tubes
Filter funnels and racks
Whatman no 42 filter paper
Conical flasks
Spectrophotometer

28.3 Reagents

Potassium chloride, 1 mol dm^{-3}: Dissolve 74,5 g KCl (AR) in de-ionised water and make up to 1 dm^3

Chrome Azurol-S: Dissolve 0,4066 g CAS in de-ionised water and make up to 1 dm^3 with de-ionised water to provide a final concentration of 1,64 x 10^{-4} mol dm^{-3}

Hexamine buffer, 0,8 mol dm^{-3}: Dissolve 112,2 g hexamine in 800 cm^3 de-ionised water. Adjust pH to 4,9 with concentrated HCl before making up to 1 dm^3 with de-ionised water

Ascorbic acid: Dissolve 0,5 g ascorbic acid in 1 dm^3 de-ionised water

Standards: Prepare calibration standards containing 0; 5; 10; 15 and 20 mg dm^{-3} Al. Add 1 cm^3 1 mol dm^{-3} HCl to each standard before making up to 1 dm^3 with de-ionised water

28.4 Procedure

28.4.1 Extraction

* Place 5 g soil ≤ 2 mm in a 100 cm^3 capacity polythene centrifuge tube. Add 50 cm^3 1 mol dm^{-3} KCl
* Shake for 30 minutes at 180 oscillations per minute
* Centrifuge for 10 minutes at 2 500 rpm
* Filter supernatant through Whatman no 42 filter paper into a suitable container
* A constant temperature of 20 ± 2 °C during the extraction is necessary

28.4.2 Determination

* Transfer 1 cm^3 soil extract to a small conical flask
* Add 10 cm^3 1 mol dm^{-3} KCl, 10 cm^3 hexamine buffer, 10 cm^3 ascorbic acid and 10 cm^3 CAS reagent
* Treat standards in the same manner
* Allow to stand for 20 minutes before reading absorbance at 567 nm against the standards. Method is suitable for up to 200 mg kg^{-1} Al in soil

28.5 Calculation

Let Al content of KCl extract be **k** mg dm^{-3}

$$\text{mg kg}^{-1}\ \text{Al in soil} = \frac{\mathbf{k} \times 50}{5}$$

28.6 References

BARNHISEL, R. & BERTSCH, P.M., 1982. Aluminium. In A.L. Page (ed.). Methods of soil analysis. Part 2, 282-283. Am. Soc. Agron. Madison, Wis.

KENNEDY, J.A. & POWELL, H.K., 1986. Colorimetric determination of Al (III) with Chrome Azurol S and the reactivity of hydrolysed Al species. *Anal. Chim. Acta* 18, 329-333.

29 EXTRACTABLE MOLYBDENUM: AMMONIUM OXALATE

29.1 Introduction

In this procedure, the soil is extracted with acid ammonium oxalate solution buffered at pH 3,3 and molybdenum is determined in the extract.

Mo is determined by the formation of an iron-molybdenum-thiocyanate complex after extraction with amyl alcohol. This chemical method is suitable for the determination of Mo at levels below 1 mg kg^{-1} . The method was modified to prevent emulsification during the second extraction but is based on the original work by Johnson & Arkley (1954).

29.2 Apparatus

Balance
Erlenmeyer flasks, 500 cm^3 capacity
Filter funnels and rack
Whatman no 42 filter paper
Waterbath
Muffle furnace
Spectrophotometer
Separating funnels fitted with greaseless Teflon stopcocks
Reciprocating shaker
Centrifuge
Plastic syringes
Disposable syringe filters

29.3 Reagents

Acid ammonium oxalate: Dissolve 24,9 g ammonium oxalate and 12,605 g oxalic acid in 1 dm^3 de-ionised water. Adjust pH to 3,3
Hydrochloric acid (AR): Concentrated
Hydrochloric acid solution: Prepare a 6,5 mol dm^{-3} solution in de-ionised water
Hydrochloric acid/Iron (III) chloride solution: Dissolve 0,5 g $FeCl_3.6H_2O$ in 1 dm^3 6,5 mol dm^{-3} HCl
Potassium thiocyanate: Dissolve 25 g KSCN in 50 cm^3 de-ionised water
Tin chloride solution: Suspend 40 g $SnCl_2.2H_2O$ in 20 cm^3 6,5 mol dm^{-3} HCl and 80 cm^3 de-ionised water
Amyl alcohol (AR)

Molybdenum standards: Standards are prepared from a commercially available Mo standard (1 mg cm^{-3} Mo), diluted with de-ionised water to a final concentration of 0,1 $\mu g\ cm^{-3}$ Mo
Calibration standards are prepared by adding respectively 0; 10; 20; 40 and 50 cm^3 of the final standard solution to 5 separating funnels
These calibration standards will represent 0; 0,1; 0,2; 0,4; and 0,5 $\mu g\ cm^{-3}$ Mo in amyl alcohol respectively

29.4 Procedure

29.4.1 Extraction

* Place 25 g air-dry soil ≤ 2 mm in a 500 cm^3 Erlenmeyer flask
* Add 250 cm^3 acid ammonium oxalate solution, stopper and shake overnight at a constant temperature (20 ± 2 °C)
* Filter through Whatman no 42 filter paper
* Evaporate 200 cm^3 filtrate in a beaker to dryness on a waterbath
* Heat beaker in a muffle furnace for 4 hours at 450 °C to destroy organic matter
* After cooling dissolve residue in 10 cm^3 de-ionised water and 10 cm^3 concentrated HCl
* Filter into a 100 cm^3 volumetric flask, using Whatman no 42 filter paper
* Wash paper with small portions of de-ionised water and make up to the mark
* This solution contains extractable molybdenum from 20 g soil

29.4.2 Determination of Molybdenum as Fe [$MoO(SCN)_5$]

* Pipette an aliquot of the extract containing from 1 to 3 μg Mo into a separating funnel. Add 10 cm^3 $HCl/FeCl_3$ solution. Make solution volume up to about 50 cm^3 with de-ionised water. Add 1 cm^3 KSCN solution, stopper and shake manually for 30 seconds. Add 2 cm^3 $SnCl_2$ solution, using a plastic syringe fitted with a disposable syringe filter if the solution is turbid
* Swirl to mix and remove brown colour
* Add 10 cm^3 amyl alcohol, stopper separating funnels
* Mount on a shaker (upside down for efficient mixing) and shake for three minutes
* Remove funnels, remount vertically and drain aqueous phase after 5 minutes. Discard aqueous phase
* Add 5 cm^3 de-ionised water and 2 cm^3 $SnCl_2$ solution
* Stopper and shake manually for 15 seconds
* Drain aqueous phase after 5 minutes and discard

* Drain alcohol phase into centrifuge bottles and centrifuge at 1 200 rpm for 30 minutes
* Read absorbance against standards at 470 nm on a spectrophotometer

29.5 Calculation

Let Mo content of soil sample be **m** $\mu g\ cm^{-3}$ in amyl alcohol
Let aliquot used be **c** cm^3 (out of a total of 100 cm^3 = 20 g soil)

$$\mu g\ kg^{-1}\ \text{Mo in soil} = \frac{100 \times \mathbf{m} \times 1\,000 \times 10}{\mathbf{c} \times 20} \quad (10\ cm^3\ \text{amyl alcohol used})$$

29.6 References

BESSINGER, F., 1989. Recommended modifications to the spectrophotometric determination of molybdenum as $Fe[MoO(SCN)_5]$. *S.Afr. J. Plant Soil* 6(3), 214-215.

JOHNSON, C.M. & ARKLEY, T.H., 1954. Determination of molybdenum in plant tissue. *Anal. Chem.* 26, 572-574.

PURVIS, E.R. & PETERSON, N.K., 1956. Methods of soil and plant analysis for molybdenum. *Soil Sci.* 81, 223-228.

30 EXTRACTABLE ALUMINIUM, IRON AND CARBON: SODIUM PYROPHOSPHATE

30.1 Introduction

The sodium pyrophosphate method is used to determine Fe, Al and organic C produced in recent weathering and during the evolution of soils.
Pyrophosphate solutions only remove the amorphous or organic bonded iron and aluminium compounds from soils. At an alkaline pH the organic matter in which the iron is incorporated is more soluble, while crystalline iron compounds are less soluble.
The advantage of the method is that extraction of colloidal organic matter, organic complexes of Fe and Al and amorphous forms of Fe is obtained (Bascomb, 1968).

30.2 Apparatus

Balance accurate to 0,01 g
Centrifuge
Horizontal shaking machine
Steambath
Centrifuge tubes 125 cm^3 with stoppers
Erlenmeyer flasks 250 cm^3
Burette
Funnels
Filter paper Whatman no 40
Atomic absorption spectrophotometer

30.3 Reagents

Sodium pyrophosphate ($Na_4P_2O_7.10H_2O$), 0,1 mol dm^{-3}: Dissolve 44,6 g sodium pyrophosphate (AR) in 1 dm^3 de-ionised water. Adjust pH to 10 with sodium hydroxide solution
Superfloc (N-100) solution, 0,1 %: In de-ionised water
Potassium dichromate ($K_2Cr_2O_7$), 0,083 mol dm^{-3}: 24,52 g $K_2Cr_2O_7$ in 1 dm^3 de-ionised water
Ferrous sulphate, 0,25 mol dm^{-3}: Dissolve 70 g $FeSO_4.7H_2O$ in de-ionised water. Add 40 cm^3 concentrated H_2SO_4, cool, and dilute to 1 dm^3. Standardise this solution daily by titrating against 10 cm^3 0,083 mol dm^{-3} $K_2Cr_2O_7$ as described
Barium diphenylaminesulfonate indicator: 0,16% solution in water
Sulphuric acid (H_2SO_4): Concentrated (at least 96%)

Phosphoric acid (H_3PO_4): Concentrated (at least 86%)
Potassium chloride (KCl) diluent: Dissolve 4,75 g KCl in 1 dm^3 de-ionised water to obtain 2 500 mg dm^{-3} K
Standard Al and Fe solutions: 1 000 mg dm^{-3}

30.4 Procedure

30.4.1 Extraction

* Place 1 g (use 3 g for soil samples low in extractable Fe and Al) air-dry , ≤ 2 mm soil in a 125 cm^3 capacity centrifuge tube. Add 100 cm^3 0,1 mol dm^{-3} sodium pyrophosphate solution to the soil, cap and shake overnight on a horizontal shaker at 180 oscillations per minute. Quantities may be changed to suit experimental conditions as long as soil to extractant ratio remains 1:100
* Add 0,4 cm^3 Superfloc solution, shake and centrifuge at 1 500 to 2 000 rpm (Sheldrick & McKeague, 1975) or centrifuge suspension without Superfloc at approximately 13 000 rpm for about 10 minutes
* Transfer the clear supernatant directly (or through filter paper if it contains floating particulate organic fragments) into a glass or plastic container and reserve for aluminium, iron and organic carbon determinations

30.4.2 Determinations

Organic Carbon (Walkley-Black)

Transfer 5 cm^3 clear pyrophosphate extract to a 250 cm^3 Erlenmeyer flask. Evaporate to dryness on a steambath. Add 10 cm^3 0,083 mol dm^{-3} $K_2Cr_2O_7$ to the warm Erlenmeyer flask. Rapidly add 20 cm^3 concentrated H_2SO_4 , directing the stream into the solution. Immediately swirl vigorously for 1 minute and leave on the steambath for approximately 30 minutes with intermittent swirling. Add 100 cm^3 de-ionised water and 10 cm^3 H_3PO_4. Just before titrating add 0,5 cm^3 barium diphenylaminesulfonate indicator. Titrate by adding $FeSO_4$ dropwise till a light green endpoint is reached.

NOTE: If more than 6 cm^3 of the available 10 cm^3 $K_2Cr_2O_7$ is reduced, repeat the determination using less extract

Iron and Aluminium

Prepare a set of standard solutions with final concentrations of 0 to 50 mg dm^{-3} Al and Fe by pipetting 1 000 mg dm^{-3} standard Al and Fe solutions into 50 cm^3

volumetric flasks. Add 10 cm^3 of blank sodium pyrophosphate solution. Make up to volume with the 2 500 mg dm^{-3} potassium solution. Dilute an aliquot of the prepared sodium pyrophosphate extracts with the 2 500 mg dm^{-3} potassium solution in a ratio of 1 : 4. Establish standard curves for Al (use nitrous oxide-acetylene flame) and Fe (use air-acetylene flame) on an atomic absorption spectrophotometer. Match readings of the potassium solution diluted extracts with curve readings. If necessary, the diluted extracts can be further diluted with the potassium chloride solution.

30.5 Calculations

Carbon

$$\text{Concentration of } FeSO_4 = \frac{10\ cm^3\ K_2Cr_2O_7 \times 0{,}083 \times 6}{cm^3\ FeSO_4}\ \text{mol dm}^{-3}$$

$$\%\ \text{carbon} = \frac{(T-S) \times M \times 0{,}3}{\text{g soil in 5 cm}^3\ \text{pyrophosphate aliquot}}$$

S = Standardisation blank titration; cm^3 of approximately 0,25 mol dm^{-3} $FeSO_4$ solution

T = Sample titration; cm^3 of approximately 0,25 mol dm^{-3} $FeSO_4$ solution

M =Concentration of $FeSO_4$ solution (mol dm^{-3})

Iron and Aluminium

$$\%\ Fe/Al = \frac{\mathbf{a} \times \text{volume of extractant (cm}^3) \times 5}{\text{mass soil (g)}} \times 10^{-4}$$

where: **a** = mg dm^{-3} Al/Fe in extract.

30.6 References

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31 EXTRACTABLE IRON, ALUMINIUM AND MANGANESE : DITHIONITE-CITRATE-BICARBONATE

31.1 Introduction

This method is used to determine free Fe and Al oxides in soils.
Free iron and aluminium oxides, particularly hematite and goethite are easily removed by sodium dithionite with sodium citrate at pH 7,3. Sodium bicarbonate acts as a buffer to keep the pH at 7,3 and to prevent the formation and precipitation of FeS and S. The removal of the sesquioxides is rapid and complete without a significant influence on the CEC even in soils containing amorphous allophane.
The method has no destructive effect on iron silicate clay minerals.

31.2 Apparatus

Balance accurate to 0,1 g
Sieve 0,18 mm
Centrifuge
Waterbath
Centrifuge tubes 125 cm^3

31.3 Reagents

Sodium bicarbonate, 1 mol dm^{-3}: Dissolve 84 g $NaHCO_3$ (AR) in 1 dm^3 de-ionised water
Sodium citrate, 0,3 mol dm^{-3}: Dissolve 88,25 g $Na_3C_6H_6O_7.2H_20$ in 1 dm^3 de-ionised water
Sodium dithionite ($Na_2S_2O_4$)
Potassium chloride (KCl) diluent: Dissolve 4,75 g KCl in 1 dm^3 de-ionised water to give 2 500 mg dm^{-3} K
Standard Al , Mn and Fe solutions, 1 000 mg dm^{-3}: Prepare standard solutions from commercially available stock in de-ionised water

31.4 Procedure

31.4.1 Extraction

* Place a 4 g soil or clay sample (grind nodular material to pass a 0,180 mm sieve) in a centrifuge tube, capacity 125 cm^3. Add 40 cm^3 0,3 mol dm^{-3} sodium citrate and 5 cm^3 1 mol dm^{-3} $NaHCO_3$. Place tube in a waterbath set at 77 ± 2 °C. Do not exceed 80 °C. Allow temperature to stabilise before

adding 1 g $Na_2S_2O_4$ powder. Stir rapidly for 1 minute and place back in waterbath. Keep sample in waterbath and stir intermittently for a further 15 minutes

* Centrifuge tubes at 1 500 to 3 000 rpm for 10 minutes
* Decant clear supernatant in a 200 cm^3 volumetric flask
* Repeat the described extraction
* Add 60 cm^3 de-ionised water to the residue in the centrifuge tube, warm to 77 °C before centrifuging at 1 500 to 3 000 rpm for 10 minutes. Decant clear supernatant into the 200 cm^3 volumetric flask. Make up to volume with de-ionised water
* If the liquid in the volumetric flask is not clear, centrifuge a large enough aliquot at approximately 3 000-13 000 rpm for about 10 minutes. Transfer an aliquot of the clear solution to a container and reserve for aluminium and iron determinations
* Depending on experimental conditions, the quantities of soil and extractant can be changed as long as the recommended soil to extractant ratio remains the same

31.4.2 Determinations

Prepare a set of standard solutions with final concentrations of 0 - 50 mg dm^{-3} Al/Fe and 0 -10 mg dm^{-3} Mn by pipetting 1 000 mg dm^{-3} standard Al, Mn and Fe solutions into 50 cm^3 volumetric flasks. Add 10 cm^3 of blank dithionite-bicarbonate-citrate solution. Make up to volume with the 2 500 mg dm^{-3} potassium solution. Dilute an aliquot of the prepared dithionite-bicarbonate-citrate extract with the 2 500 mg cm^{-3} potassium solution in a ratio of 1 : 4. Establish standard curves for Al (nitrous oxide-acetylene flame), Fe and Mn (air-acetylene flame) on an atomic absorption spectrophotometer. Match readings of the potassium solution diluted extracts with curve readings. If necessary, diluted extracts can be further diluted with potassium choride solution.

31.5 Calculations

Iron and aluminium

$$\% \text{ Fe/Al} = \frac{\mathbf{a} \times 200 \times 5}{\text{mass soil (g)}} \times 10^{-4}$$

where **a** = mg dm^{-3} Fe/Al in soil extract.

Manganese

$$\text{mg kg}^{-1}\text{ Mn in soil} = \frac{\mathbf{b} \times 200 \times 5}{\text{mass soil(g)}}$$

Where **b** = mg dm^{-3} Mn in soil extract.

31.6 References

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32 EXTRACTABLE FULVIC ACID: AMMONIUM OXALATE

32.1 Introduction

The acid ammonium oxalate method is used to identify podzols and podzolised soils.
Acid ammonium oxalate is a strong complexing agent for Fe and Al and extracts these metals from fulvic metal complexes thereby making it water soluble. Humic acid is poorly extracted by acid ammonium oxalate, therefore it is relatively selective towards organic matter involved in the translocation of Fe and Al in the podzolisation process.

32.2 Apparatus

Mechanical shaker
Centrifuge
Balance accurate to 0,01 g
Spectrophotometer
Centrifuge tubes 125 cm^3 with stoppers

32.3 Reagents

Oxalic acid, 0,2 mol dm^{-3}: Dissolve 25,2 g $H_2C_2O_4$ in 1 dm^3 de-ionised water
Ammonium oxalate, 0,2 mol dm^{-3}: Dissolve 28,3 g ammonium oxalate $[(NH_4)_2C_2O_4.H_2O]$ in 1 dm^3 de-ionised water . Adjust pH of ammonium oxalate solution to 3 by addition of 0,2 mol dm^{-3} oxalic acid

32.4 Procedure

* Transfer 1 g (≤ 2mm) soil to a centrifuge tube
* Add 50 cm^3 acid ammonium oxalate solution (0,2 mol dm^{-3}) to the soil, cap tube and shake for 2 hours on a horizontal shaker at 180 oscillations per minute
* Centrifuge for 10 minutes at 1 500 to 2 000 rpm and decant supernatant in a suitable container
* Measure the optical density of the clear oxalate extract with a spectrophotometer at 430 nm
* Because fulvic acid in a specific soil profile should have similar spectrometric properties, no direct calibration of the spectrophotometer is necessary. The optical density of the oxalate extracts down the profile are directly compared. The ratios of the optical density of the oxalate extracts of the B and A or E

horizons reflect the expression of podzolic character. A ratio > 1,0 indicates podzolised soils and podzols.

32.5 Reference

DALY, B.K., 1982. Identification of podzols and podzolised soils in New Zealand by relative absorbance of oxalate extracts of A and B horizons. *Geoderma* 28, 29-38.

33 EXTRACTABLE INORGANIC NITROGEN: KCl (1 mol dm^{-3})

33.1 Introduction

Extractable inorganic N in soils is defined as NH_4^+, NO_3^- and NO_2^- extractable at room temperature with a 1,0 mol dm^{-3} KCl solution (SSSA, 1977). Nitrite is seldom present in detectable amounts and usually its analysis is unwarranted. Methods for analysis of extractable inorganic N involve simultaneous extraction of these forms of N by either an equilibrium or a leaching procedure and their determination in the extract by steam distillation or colorimetric techniques. Bremner & Keeney (1966) listed the following requirements for satisfactory preparation of soil extracts for determination of inorganic nitrogen:

i) Essentially quantitative extraction of the forms of N under analysis
ii) No biological or chemical reactions leading to changes in amount of extractable NH_4^+, NO_3^- or NO_2^-
iii) Compatibility and freedom from interferences with the methods of analysis to be used
iv) Provision of an extract that can be safely stored for several days before analysis
v) A relatively simple and rapid method. Equilibrium or leaching extraction of a soil sample with 1 mol dm^{-3} KCl (Bremner, 1965; Keeney & Nelson, 1982) meets these requirements when the ratio of extractant to soil is 10:1.

Steam distillation methods are based on separation of NH_3 volatilised from NH_4^+ in a weak alkaline solution. Nitrate and nitrite are reduced to NH_4^+ by Devarda alloy (Keeney & Nelson, 1982).

The colorimetric determination of NH_4^+-N depends on the formation of a green colour when ammonium, sodium salicylate, sodium nitroprusside and sodium hypochlorite react in a buffered alkaline medium at a pH of 12,8 to 13,0.

Determination of NO_3^--N and NO_2^--N by the colorimetric method depends on reduction of NO_3^- to NO_2^- by a copper-cadmium reduction column. The nitrite reacts with sulfanilamide under acidic conditions to form a diazo compound which is then coupled with N-1-naphthylethylenediamine dihydrochloride to form a reddish-purple azo dye.

33.2 Apparatus

Balance to measure accurately to 0,05 g
250 cm^3 wide mouth extraction bottles with stoppers

100 cm^3 volumetric flasks
Mechanical reciprocating or end-over-end shaker
Centrifuge with centrifuge tubes
110 mm diameter filter funnels
110 mm Whatman no 2V filter papers or equivalent
Erlenmeyer flasks, glass beakers, pipettes, etc. as required
Steam distillation unit or alternatively modified continuous flow analyser for NH_4^+ -N, based on the industrial method no. 329-74 W/B of Technicon (1977)
Modified continuous flow analyser for (NO_3^- + NO_2^-)-N, based on the industrial method no. 100-70 W/B of Technicon (1978)

33.3 Reagents

Potassium chloride solution, 1 mol dm^{-3}: Dissolve 75 g commercial grade potassium chloride (KCl) in de-ionised water and dilute to 1 dm^3 to obtain a 1 mol dm^{-3} KCl extraction solution

Reagents for the steam distillation

Magnesium oxide: Heavy
Devarda alloy: Powder
Sulfamic acid: Dissolve 2 g sulfamic acid (NH_2SO_3H) in 100 cm^3 de-ionised water. Store in a refrigerator
Mixed indicator: Dissolve 0,300 g bromocresol green and 0,165 g methyl red in 500 cm^3 ethanol
Boric acid-indicator: Dissolve 20 g pure boric acid in about 700 cm^3 of hot de-ionised water and transfer the cooled solution to a 1 dm^3 volumetric flask containing 200 cm^3 ethanol and 20 cm^3 of the mixed indicator. Mix the contents of the flask and add 0,05 mol dm^{-3} NaOH cautiously until the colour changes from pink to pale green when 1 cm^3 solution is treated with 1 cm^3 de-ionised water. Dilute solution to volume with de-ionised water and mix thoroughly
Sulphuric acid: 0,0025 mol dm^{-3} standardised
Standard (NH_4^+ + NO_3^- + NO_2^-)-N solution: Dissolve 0,2358 g $(NH_4)_2SO_4$, 0,3609 g KNO_3 and 0,2463 g $NaNO_2$ in de-ionised water, dilute to 1 dm^3 in a volumetric flask and mix thoroughly. If pure, dry reagents are used, this solution contains 50 µg NH_4^+-N, 50 µg NO_3^--N and 50 µg NO_2^--N cm^{-3}. Store in a refrigerator

Reagents for the colorimetric NH_4^+ -N determination

Concentrated sodium hydroxide: Dissolve 500 g NaOH in de-ionised water and dilute to 1 dm^3

Diluted sodium hydroxide: Dilute 400 g of the concentrated NaOH solution to 1 dm^3 with de-ionised water

Potassium sodium tartrate stock solution: Dissolve 200 g $C_4H_4KNaO_6.4H_2O$ in de-ionised water and dilute to 1 dm^3

Buffer stock solution: Dissolve 71 g Na_2HPO_4 or 134 g $Na_2HPO_4.7H_2O$ in 750 cm^3 de-ionised water, add 40 cm^3 of the concentrated NaOH solution and dilute to 1 dm^3 with de-ionised water

Working buffer solution: Dissolve 0,8 g sodium thiosulphate ($Na_2S_2O_3.5H_2O$) in de-ionised water, then add 800 cm^3 buffer stock solution, 1 000 cm^3 potassium sodium tartrate stock solution and 1 000 cm^3 diluted NaOH solution and dilute to 4 dm^3 with de-ionised water. Add 4 cm^3 Brij-35. Prepare fresh every second day

Sodium salicylate-nitroprusside: Dissolve 600 g sodium salicylate and 1,2 g sodium nitroprusside in de-ionised water and dilute to 4 dm^3. Add 4 cm^3 Brij-35. Store in amber bottle

Sodium hypochlorite: Dilute 60 cm^3 of a 5,25% NaOCl solution to 1 dm^3 with de-ionised water and add 1 cm^3 Brij-35

Standard NH_4^+-N solution: Dissolve 0,0472 g $(NH_4)_2SO_4$ in de-ionised water and dilute to 1 dm^3. If pure, dry $(NH_4)_2SO_4$ is used, this solution contains 10 mg dm^{-3} NH_4^+-N. Store in refrigerator. Immediately before use, dilute 1; 5; 10 and 20 cm^3 of this stock NH_4^+ solution to 100 cm^3 in volumetric flasks with the 1 mol dm^{-3} KCl solution used for the extraction. These three working standards contain respectively 0,5; 1,0 and 2,0 $\mu g\ cm^{-3}$ NH_4^+-N

Reagents for the colorimetric determination of (NO_3^- + NO_2^-)-N

Ammonium chloride: Dissolve 10 g NH_4Cl in alkaline water and dilute to 1 dm^3. Add 0,5 cm^3 of Brij-35 per dm^3. Alkaline water is prepared by adding just enough NH_4OH to the de-ionised water to attain a pH of 8,5

Colour reagent: To approximately 1 500 cm^3 de-ionised water add 200 cm^3 concentrated phosphoric acid and 20 g sulfanilamide and dissolve completely. Add 1,0 g of N-1-naphthylethylenediamine dihydrochloride and dissolve. Dilute to 2 dm^3 with de-ionised water and add 1 cm^3 Brij-35. Store in cool, dark place

Cadmium powder: Rinse coarse cadmium powder twice with 1 mol dm^{-3} HCl followed by de-ionised water to remove grease and dirt. Allow the metal to air-dry and store in a stoppered bottle

Copper sulphate, 2%: Dissolve 20 g $CuSO_4.5H_2O$ in de-ionised water and dilute to 1 dm^3

Standard NO_3^--N solution: Dissolve 0,0722 g KNO_3 in de-ionised water and dilute to 1 dm^3. If pure, dry KNO_3 is used, this solution contains 10 mg dm^{-3} NO_3^--N. Store in refrigerator. Immediately before use, pipette 5; 10 and 20 cm^3 of this stock NO_3^- solution into separate 100 cm^3 volumetric flasks

and dilute to volume with the 1 mol dm^{-3} KCl solution. These three working standards contain respectively 0,5; 1,0 and 2,0 µg cm^{-3} NO_3^--N

Standard NO_2^--N solution: Dissolve 0,0493 g $NaNO_2$ in de-ionised water and dilute to 1 dm^3. If pure, dry $NaNO_2$ is used, this solution contains 10 mg dm^{-3} NO_2^--N. Store in refrigerator. Immediately before use, pipette 5; 10 and 20 cm^3 of this stock NO_2^- solution into separate 100 cm^3 volumetric flasks and dilute to volume with the 1 mol dm^{-3} KCl solution. These three working standards contain respectively 0,5; 1,0 and 2,0 µg cm^{-3} NO_2^--N

33.4 Procedure

33.4.1 Extraction

Equilibrium extraction

Place 10,0 ± 0,05 g ≤ 2,0 mm air-dry soil into a 250 cm^3 wide mouth extraction bottle. Add 100 cm^3 1,0 mol dm^{-3} KCl, stopper and shake for at least 30 minutes on a shaker. Filter or centrifuge to obtain a clear extract. If the extract cannot be analysed within 24 hours, it must be stored in a refrigerator until analysis can be performed. Determine NH_4^+, $N0_3^-$ and $N0_2^-$ contents.

Leaching extraction

Transfer 10,0 ± 0,05 g ≤ 2,0 mm air-dry soil to a filter paper in a funnel mounted above a 100 cm^3 volumetric flask. Leach with 100 cm^3 of 1,0 mol dm^{-3} KCl in 25 cm^3 increments and make up filtrate in flask to volume with KCl solution.

Comments

* Some batches of commercial grade KCl contain NH_4^+ and/or $N0_3^-$. The presence of these N forms may influence the results if appropriate precautions are not taken
* Filter papers are sometimes contaminated with NH_4^+ and $N0_3^-$ which may cause erroneous results
* K_2SO_4 or NaCl can also be used as extractant instead of KCl.

33.4.2 Determination

Steam distillation

NH_4^+-N

Put 10 cm^3 boric acid indicator solution in an Erlenmeyer flask marked at volumes of 25 and 50 cm^3. Place the flask under the exit of the steam distillation unit so that the end of the condenser dips into the boric acid. Pipette an aliquot (usually 20 to 50 cm^3) of soil extract into the distillation flask, add 0,2 g MgO and connect without delay to the steam generator. Commence steam distillation. When the distillate reaches the 25 cm^3 mark, lower the Erlenmeyer flask and continue distillation to the 50 cm^3 mark. Determine NH_4^+-N in the distillate by titration with the 0,0025 mol dm^{-3} H_2SO_4. The colour changes at the endpoint from green to a permanent faint pink. A volume of 1 cm^3 acid is equivalent to 35 µg NH_4^+-N.

(NO_3^- + NO_2^-)-N

After removal of NH_4^+-N from the sample as described in the previous section, remove the distillation flask from the steam generator, quickly add 0,2 g Devarda alloy, reconnect without delay to the steam generator and commence steam distillation into another Erlenmeyer flask containing 10 cm^3 boric acid indicator solution. Determine the NH_4^+-N liberated from NO_3^- and NO_2^- by steam distillation as described in the section above.

(NH_4^+ + NO_3^- + NO_2^-)-N

Proceed as described for NH_4^+-N, but add 0,2 g Devarda alloy to distillation flask immediately after addition of MgO and before connection of flask to the steam distillation unit.

(NH_4^+ + NO_3^-)-N

Proceed as described for (NO_3^-+ NO_2^-)-N, but treat the sample in the distillation flask with 1 cm^3 sulfamic acid and swirl flask for a few seconds to convert NO_2^--N to N_2 before addition of MgO and Devarda alloy.

NO_3^--N

* Follow the procedure described for the determination of (NO_3^- + NO_2^-)-N, but perform the analysis on a sample treated with sulfamic acid to remove NO_2^- as described in section for (NH_4^+ + NO_3^-)-N
* Controls should be run in each series of analyses to allow for NH_4^+-N derived from the reagents, including reagents used for extraction. The steam distillation procedures should be checked in each series of analyses by analysing aliquots of the standard (NH_4^+ + NO_3^- + NO_2^-)-N solution.

Colorimetric method

NH_4^+-N

Use continuous flow system shown in Fig. 33.1

(NO_3^- + NO_2^-)-N

Use the automated system illustrated in Fig. 33.2 but keep in mind that the eluant passing through the reduction column contains the NO_2^--N initially present in the soil extract plus that formed from the reduction of the NO_3^--N present. Therefore, to determine the actual NO_3^--N and NO_2^--N content a separate NO_2^- measurement must be performed on the automated system. This can be done simply by omitting the reduction column from the system.

Preparation of reduction column:

A 35 cm length of Tygon tubing of 2,06 mm inner diameter is used for the reduction column. Sleeve both ends with 2,29 mm inner diameter Tygon tubing and insert a N-5 nipple on one end of the tube. Before filling the column, prepare the Cd in the following manner:

- The Cd metal is ground and sized so that particles used in the column will pass a 0,50 mm sieve, but are held back by a 0,212 mm sieve
- New or used Cd particles (10 grams) are cleaned with 50 cm^3 of 6 mol dm^{-3} HCl for 1 minute. Decant the HCl and wash the Cd with another 50 cm^3 6 mol dm^{-3} HCl for 1 minute
- Decant the HCl and wash the Cd several times with de-ionised water
- Decant the water and add 50 cm^3 of 2% $CuSO_4$. Wash the Cd until no blue colour remains in solution
- Rinse the Cd several times with de-ionised water and decant
- Add another 50 cm^3 2% $CuSO_4$, decant and wash with de-ionised water until no blue colour remains in solution

- Fill the reduction column with the NH_4Cl solution and transfer the prepared Cd particles to the column using a Pasteur pipette. Do not allow any air bubbles to be trapped in the column
- When the entire column is filled with granules, insert glass wool in both ends of the tube. Connect the end of the tube without a nipple directly to the A-2 debubbler. Preparing the column in this fashion keeps it effective for several hundred samples
- Prior to analysis, condition the column with 10 mg dm^{-3} NO_3^--N for 5 minutes followed by 10 mg dm^{-3} NO_2^--N for 10 minutes

33.5 Calculations

Steam distillation

A titre of 1 cm^3 0,0025 mol dm^{-3} H_2SO_4 equals 35 µg N and 10 g soil was extracted with 100 cm^3 KCl, therefore:

$$\mu g\ g^{-1}\ N \text{ in soil} = \frac{\text{Volume } H_2SO_4\ (cm^3) \times 35 \times 100}{\text{Volume of extract distilled } (cm^3) \times 10}$$

Colorimetric

a) Concentration of NH_4^+-N obtained from calibration curve is µg cm^{-3} N and 10 g of soil was extracted with 100 cm^3 KCl, therefore:

$$\mu g\ g^{-1}\ NH_4^+\text{-N in soil} = \frac{\mu g\ N \times 100}{10}$$

b) Concentration of NO_3^--N plus NO_2^--N obtained from calibration curve is µg cm^{-3} N and 10 g of soil was extracted with 100 cm^3 KCl, therefore:

$$\mu g\ g^{-1}\ NO_3^- + NO_2^-\text{-N in soil} = \frac{\mu g\ N \times 100}{10}$$

c) Concentration of NO_2^--N obtained from calibration curve is µg cm^{-3} N and 10 g of soil was extracted with 100 cm^3 KCl, therefore:

$$\mu g\ g^{-1}\ NO_2^-\text{-N in soil} = \frac{\mu g\ N \times 100}{10}$$

$$\mu g\ g^{-1}\ NO_3^-\text{-N in soil} = b - c$$

33.6 References

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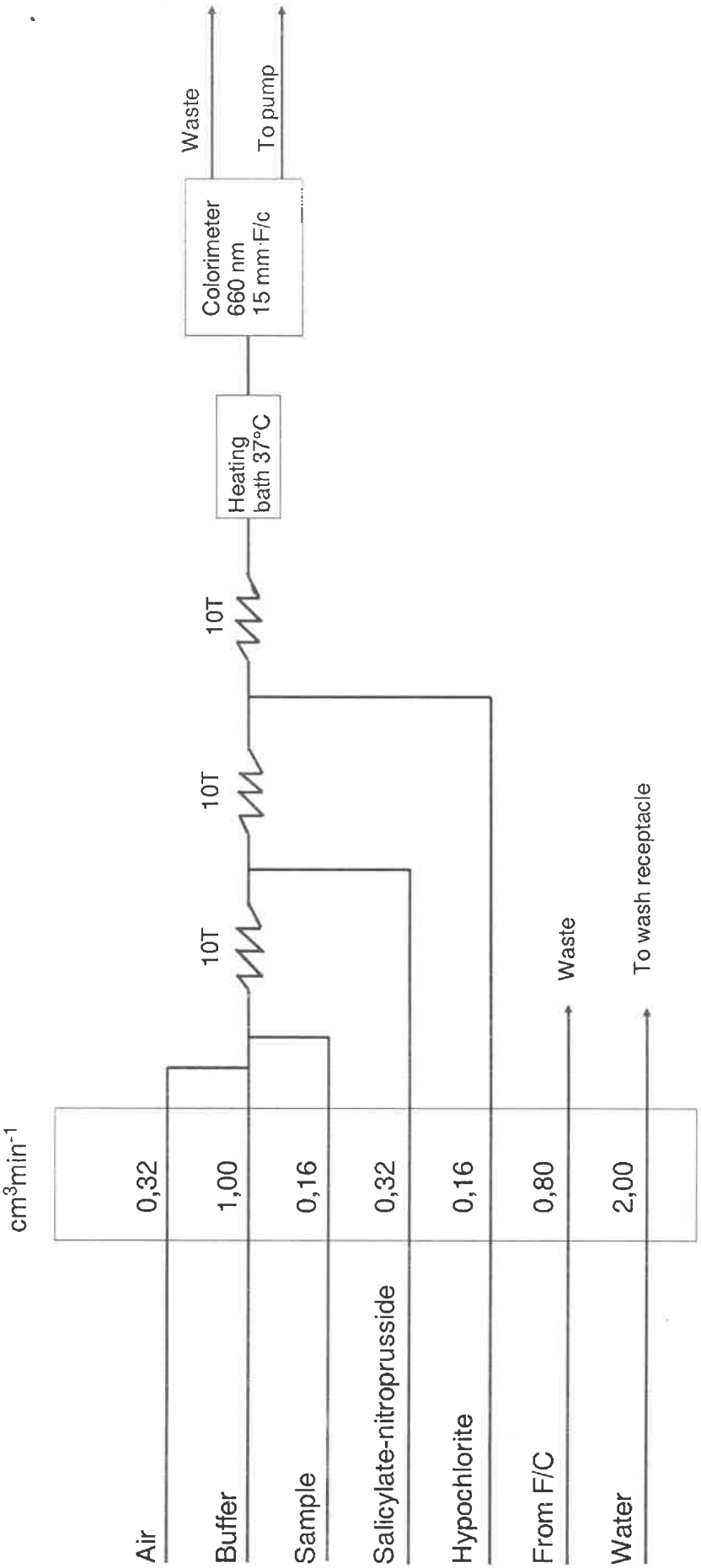

Figure 33.1: Flow System for NH_4^+ -N

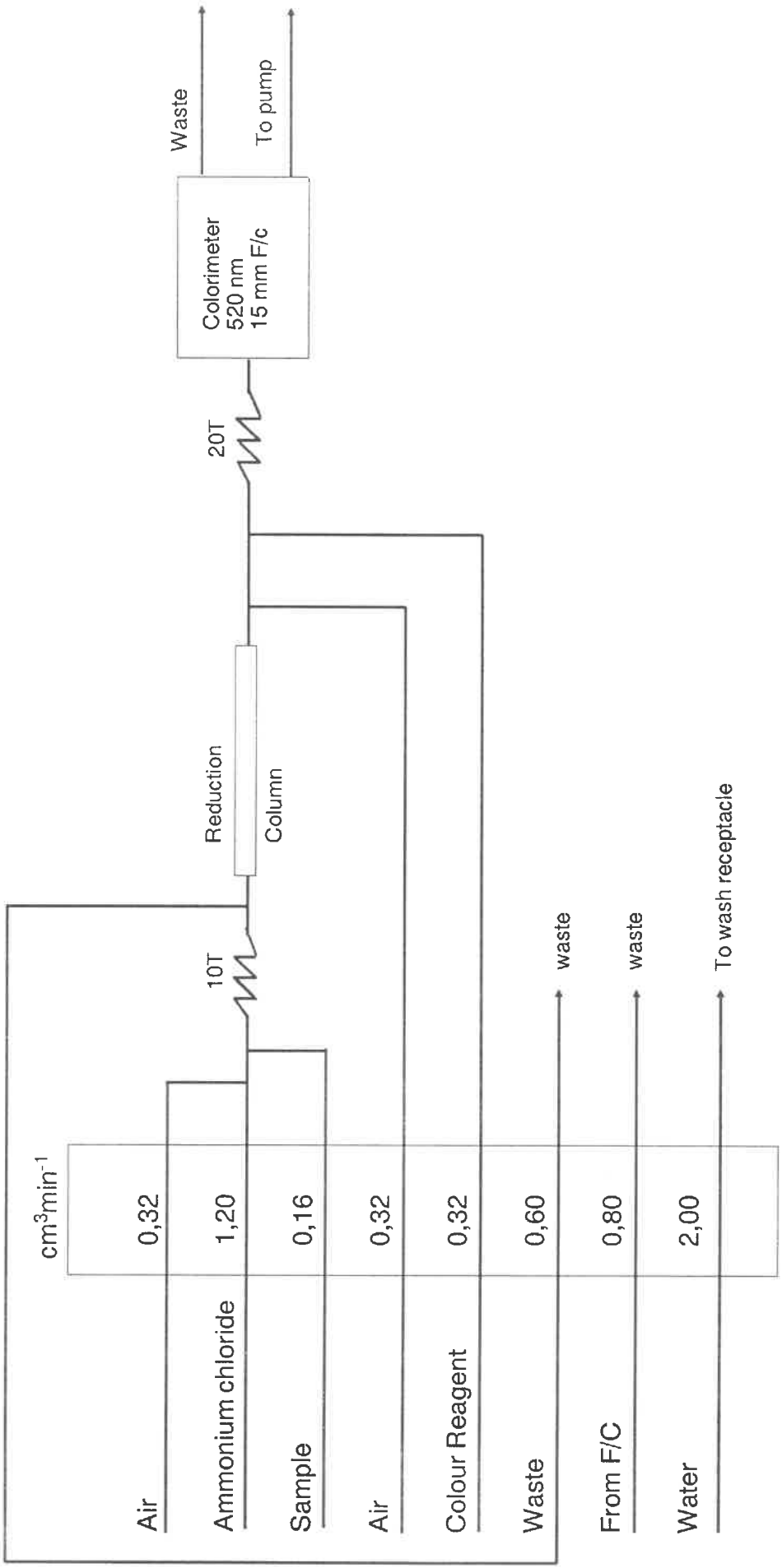

Figure 33.2: Flow System for (NO_3^- + NO_2^-)-N

34 ORGANIC CARBON : WALKLEY-BLACK

34.1 Introduction

Schollenberger (1927) proposed that organic material in soil may be oxidised by treatment with a hot mixture of $K_2Cr_2O_7$ and sulphuric acid, according to the equation:

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

After completion of the reaction, the excess dichromate is titrated with iron (II) ammonium sulphate hexahydrate. The reduced dichromate is assumed to be equivalent to the organic C present in the sample, assuming that soil organic matter has an average valence of zero.

34.2 Apparatus

Balance
Erlenmeyer flasks 500 cm^3
Burette
Various pipettes

34.3 Reagents

Potassium dichromate, 0,167 mol dm^{-3}: Dissolve 49,04 g potassium dichromate (AR), dried at 105 °C, in de-ionised water and make up to 1 dm^3 in a volumetric flask
Sulphuric acid: Concentrated, AR grade
Ortho-phosphoric acid: Concentrated
Iron (II) ammonium sulphate, 0,5 mol dm^{-3}: Dissolve 196 g iron (II) ammonium sulphate hexahydrate in 500 cm^3 de-ionised water, add 5 cm^3 concentrated H_2SO_4, cool and make up to 1 dm^3 with de-ionised water
Indicator: Barium diphenylamine sulphonate: Dissolve 0,4 g indicator in 100 cm^3 de-ionised water

34.4 Procedure

* Standardise the iron (II) ammonium sulphate solution daily against 10 cm^3 0,167 mol dm^{-3} $K_2Cr_2O_7$ as described below
* Grind the soil to pass a 0,35 mm sieve, using a porcelain mortar and pestle
* Transfer 1 g (0,5 g or less if high in organic carbon) air dry soil to a 500 cm^3 Erlenmeyer flask. Add 10 cm^3 $K_2Cr_2O_7$ solution by pipette to the soil sample

* Swirl the flask to disperse the soil in the solution. Rapidly add 20 cm^3 concentrated sulphuric acid, directing the stream into the solution. Again swirl flask gently until soil and reagents are mixed, then more vigorously for a total time of 1 minute. Allow the flask to cool on a sheet of asbestos for 30 minutes
* Add 150 cm^3 de-ionised water and 10 cm^3 concentrated ortho-phosphoric acid
* Add 1 cm^3 indicator and titrate excess dichromate with iron (II) ammonium sulphate solution. As the endpoint is approached, the solution colour changes to a dark violet brown. Add iron (II) ammonium sulphate drop by drop until the colour changes sharply to green. Repeat the determination with less soil if more than 75% of the dichromate is reduced.

34.5 Calculation

Calculate the carbon content according to the following formula, using a recovery factor of **f** = 1,3 or a more suitable value established experimentally

$$\text{Concentration of Fe } (NH_4)_2\,(SO_4)_2 \text{ mol } dm^{-3} = \frac{10\ cm^3\ K_2Cr_2O_7 \times 0{,}167 \times 6}{cm^3\ Fe\ (NH_4)_2(SO_4)_2}$$

$$\text{Organic C \%} = \frac{[cm^3\ Fe(NH_4)_2(SO_4)_2 \text{ blank} - cm^3\ Fe(NH_4)_2(SO_4)_2 \text{ sample}] \times \mathbf{M} \times 0{,}3 \times \mathbf{f}}{\text{soil mass (g)}}$$

Where **M** = Concentration of the Fe $(NH_4)_2(SO_4)_2$ in mol dm^{-3}

34.6 References

NELSON, D.W. & SOMMERS, L.E., 1982. Total carbon, organic carbon and organic matter. In Methods of soil analysis. Part 2, 570-571. Am. Soc. Agron. Madison, Wis.

WALKLEY, A., 1935. An examination of methods for determining organic carbon and nitrogen in soils. *J. Agr. Sci.* 25, 598-609.

35 PARTICLE SIZE DISTRIBUTION: PIPETTE

35.1 Introduction

Soil particles are discrete units comprising the solid phase of the soil. They generally cluster together as aggregates, but can be separated from one another by chemical and mechanical means. Particles have diverse composition and structure and generally differ from one another in both size and shape. The method described will apply only to the inorganic particles, typically single crystalline fragments. The particle size distribution of a soil expresses the proportions of the various sizes of particles it contains. The methods of fractionation and particle size analysis described are limited to sieving and sedimentation procedures.

Particle size classes used for describing soil are given in Table 1.

Table 1. Soil particle size classes

Class	Diameter (mm)	Method of separation
Gravel	> 2	sieve
Coarse sand	2,0 - 0,5	sieve
Medium sand	0,5 - 0,25	sieve
Fine sand	0,25 - 0,106	sieve
Very fine sand	0,106 - 0,05	sieve
Coarse silt	0,05 - 0,02	sedimentation
Fine silt	0,02 - 0,002	sedimentation
Clay	< 0,002	sedimentation

Soils generally contain organic matter, sometimes gypsum and often iron oxides/hydroxides, aluminium oxides/hydroxides and carbonate coatings that bind particles and may prevent dispersion. Pretreatments are used to overcome such problems. However, these treatments can result in destruction and dissolution of certain soil minerals. After pretreatment, chemical dispersion is accomplished by using sodium hexametaphosphate.
The sedimentation analysis is based on the fact that spherical particles in suspension settle at a velocity that can be calculated from Stokes' equation.

35.2 Apparatus

Glass sedimentation cylinders, 1 dm^3 (height of 1 dm^3 mark approximately 36 cm above base)
Hand stirrer, 50 cm long brass rod joined to the centre of a circular brass plate 1,5 mm thick (Fig. 35.1)

Lowy pipette, 25 cm^3 capacity and pipette stand
Constant temperature room or sedimentation cabinet
Set of sieves 100 mm diameter with lid and receiving pan: Sieve opening (mm): 2,0; 0,5; 0,25; 0,106 and 0,053

Hotplate, waterbath, beakers, thermometer, drying oven, high speed stirrer or reciprocating shaker, crucibles, Pasteur - Chamberlain filter candles (fineness "F")

35.3 Reagents

Hydrogen peroxide (H_2O_2): 30-35 volume percent
Sodium acetate (NaOAc), 1 mol dm^{-3}, pH 5: Dissolve 82 g NaOAc in 1 dm^3 de-ionised water. Adjust to pH 5 with acetic acid
Sodium hydroxide (NaOH), 0,1 mol dm^{-3}: Dissolve 4 g NaOH in 1 dm^3 de-ionised water
Hydrochloric acid (HCl), 0,2 mol dm^{-3}: Dilute 18 cm^3 concentrated HCl to 1 dm^3 with de-ionised water
Calgon dispersing solution: Dissolve 35,7 g sodium hexametaphosphate [$(NaPO_4)_6$] and 7,94 g sodium carbonate (Na_2CO_3) in 1 dm^3 de-ionised water
Sodium citrate/bicarbonate solution: Dissolve 88,4 g sodium citrate ($Na_3C_6H_5O_7.2H_2O$) in 1 dm^3 de-ionised water and adjust pH to 5. Add 125 cm^3 1 mol dm^{-3} sodium bicarbonate (84 g $NaHCO_3$ dissolved in 1 dm^3 de-ionised water) to each 1 dm^3 of citrate solution
Sodium dithionite ($Na_2S_2O_4$)

35.4 Procedure

Coarse fraction (>2 mm)

* Spread the entire field sample on a large sheet of paper or plastic and leave till air dry. Determine the mass of the sample. After gentle crushing in a porcelain mortar, pass through a 2 mm sieve. If fine earth adheres to the larger particles, wash the coarse material with water. Determine the mass of dry, washed >2 mm particles and express as a percentage of entire sample.

Fine soil (≤2 mm)

Determine the mass of a representative ≤ 2 mm air-dry soil sample (10 g for clays, 20 g for loams, 40 g for sandy loams and 80 g for sands)

Depending on the properties of the sample, one or more of the following pretreatments should be followed to remove cementing and/or flocculation compounds:

Removal of carbonates

* Carbonate removal is only necessary when soil pH (H_2O) is greater than 6,8
* Place soil sample into a 250 cm^3 centrifuge tube. Add approximately 100 cm^3 1 mol dm^{-3}, NaOAc (pH 5). When CO_2 bubbles are no longer generated, centrifuge until supernatant is clear. Decant supernatant. Wash the soil twice by shaking with 50 cm^3 de-ionised water, centrifuging and discarding the supernatant when it is clear
* Highly calcareous samples may require two or more treatments with 1 mol dm^{-3} NaOAc (pH 5)
* In certain calcareous materials 1 mol dm^{-3} NaOAc (pH 5) does not effectively remove carbonates. Use 0,2 mol dm^{-3} HCl in these cases
* A filter candle can be used as a substitute for centrifugation

Removal of siliceous cementing agents

* Remove siliceous cementing agent by soaking overnight in 0,1 mol dm^{-3} NaOH
* Wash free of salts by centrifugation or by a filter candle

Removal of organic matter

* Transfer sample to a 250 cm^3 glass beaker with de-ionised water
* Add 5 cm^3 H_2O_2 to the suspension. Stir and cover with a watch glass
* When frothing has ceased, remove cover and heat on a waterbath
* Evaporate excess water but not to dryness. Continue adding H_2O_2 and heat until most of the organic material has been destroyed (judged by the frothing and bleached colour of the sample). After the final addition of H_2O_2, heat for approximately 1 hour to destroy excess H_2O_2. Wash free of soluble compounds by centrifugating or by a filter candle. Dry the sample overnight in an oven at 105 °C and determine the mass. The mass of the oven dry H_2O_2 treated sample is the base mass **(F)** for calculating the percentages of the various size fractions

Removal of iron oxides

Certain highly weathered, iron oxide rich soils do not completely disperse with Calgon as dispersing agent. Prior to Calgon treatment, add 150 cm^3 citrate-bi-

carbonate buffer to the H_2O_2 treated sample. Shake to disperse the sample. Add 3 g $Na_2S_2O_4$ gradually as the sample may froth. Heat for 30 minutes in a waterbath at 80 °C. Stir the suspension intermittently. Remove from waterbath and centrifuge. Keep the clear supernatant and subsequent washings for determination of iron. If the sample is not completely grey, repeat the citrate-bi-carbonate-dithionite treatment. Wash the sample twice with 50 cm^3 de-ionised water. If the supernatant is not clear use a high speed centrifuge. Dry the sample overnight at 105 °C and determine the mass.

Comments

It is necessary to remove iron, manganese and aluminium oxides and/or hydroxides for complete dispersion only in the cases of highly sesquioxidic soils.

The total mass loss as a result of sesquioxide removal is added to that of the clay fraction and reported as clay.

The amount of carbonates, silica and organic matter removed by the foregoing pretreatments, must be expressed as a percentage of the original oven-dry mass of ≤ 2 mm soil.

Gypsum occurs in significant amounts in some arid region soils. All existing methods of removing gypsum are time-consuming and usually ineffective. Strong cation and anion resins (particle size 0,1- 0,2 mm) can, however, be used effectively to dissolve gypsum quickly. The resultant sample can only be used to determine silt and clay. The presence of the resin prevents the determination of sand fractions.

Dispersion of the sample

Add 10 cm^3 Calgon dispersing solution to the pretreated oven dried soil. Transfer suspension quantitatively to a 250 cm^3 centrifuge bottle. Make volume up to approximately 150 cm^3 with de-ionised water, stopper and shake overnight on a horizontal reciprocating shaker. Alternately the suspension can be transferred to a dispersion cup and mixed for 5 minutes with an electric mixer.

Separation of sand fractions

Wash the dispersed sample on a 0,053 mm sieve, passing the silt and clay through the sieve *via* a funnel into a 1 000 cm^3 cylinder. Continue washing until the percolate is clear. Remove the sieve from the cylinder and quantitatively

transfer the sand to a tared evaporating dish or beaker. Dry at 105 °C to constant mass. Transfer the dried sand to a nest of sieves arranged from top to bottom with decreasing size in the following order: 0,5; 0,25; 0,106; 0,053 mm and pan. Shake the sieves on a sieve shaker for approximately 10 minutes. Determine the mass of each sand fraction **(A)** and the residual silt plus clay **(G)** that passed through the 0,053 mm sieve. A precision of 0,01 g is sufficient.

Determination of silt and clay with pipette

Fill the cylinder with the silt and clay suspension to the 1 dm^3 mark. Cover the cylinder with a watch glass. Place the cylinder in a constant temperature waterbath or room at a temperature of 20 °C. After equilibration, stir the suspension thoroughly with a hand stirrer for 30 sec. in a vertical direction. Note the time when stirring is terminated. After the appropiate time interval (Table 2) for determining the 0,05 mm fraction (coarse silt + fine silt + clay), lower the closed Lowy pipette to a depth of 30 cm into the suspension. Withdraw a 25 cm^3 sample with gentle suction (about 12 sec). Discharge the sample into a tared evaporating dish. Rinse the pipette with de-ionised water and add to suspension in dish. Evaporate the water and dry at 105 °C to constant mass, cool in desicator and determine the mass. Repeat this procedure at the specified times to determine the 0,02 mm fraction (fine silt + clay) and the 0,002 mm fraction (clay). In these two determinations the sample is withdrawn at a depth of 10 cm. For the clay fraction a sampling depth of 7 cm can be used to reduce settling time in order to complete the determination during an 8 hour working day.

Table 2: Sedimentation times of fine silt and clay as a function of temperature (calculated for the Calgon concentration used in this method and a particle density of 2,65 g cm^{-3})

Temperature	0,05 mm (coarse silt)		0,02 mm (fine silt)		0,002 mm (clay)		0,002 mm (clay)	
°C	30 cm Depth		10 cm Depth		10 cm Depth		7 cm Depth	
	Minutes	Seconds	Minutes	Seconds	Hours	Minutes	Hours	Minutes
15	1	31	5	17	8	48	6	10
16	1	29	5	09	8	34	6	01
17	1	27	5	01	8	21	5	51
18	1	25	4	53	8	09	5	42
19	1	22	4	46	7	57	5	34
20	1	20	4	39	7	45	5	26
21	1	18	4	32	7	34	5	30
22	1	16	4	26	7	23	5	17
23	1	15	4	20	7	13	5	03
24	1	13	4	14	7	03	4	56
25	1	11	4	08	6	53	4	49

35.5 Calculations

A = mass (g) of sand fraction on sieve
B = mass (g) of pipetted coarse silt plus fine silt plus clay
C = mass (g) of pipetted fine silt plus clay
D = mass (g) of pipetted clay
E = mass correction of dispersing agent (0,01 g)
F = mass (g) of pretreated oven dry total sample
G = mass (g) of residual silt and clay that passed through the 0,053 mm sieve

Sand fractions:

$$\text{Percentage of sieved sand fractions} = \frac{\mathbf{A} \times 100}{\mathbf{F}}$$

Silt and clay fractions:

$$\text{Percent coarse silt} = \frac{(\mathbf{B} - \mathbf{C}) \times 1\,000 \times 100}{\mathbf{F} \times 25} + \frac{\mathbf{G} \times 100}{\mathbf{F}}$$

$$\text{Percent fine silt} = \frac{(\mathbf{C} - \mathbf{D}) \times 1\,000 \times 100}{\mathbf{F} \times 25}$$

$$\text{Percent clay} = \frac{(\mathbf{D} - \mathbf{E}) \times 1\,000 \times 100}{\mathbf{F} \times 25}$$

Determination of textural class by means of a textural triangle

If the particle size distribution of a soil is known, the textural class may be determined from a diagram defining particle size limits of the various textural classes.

The textural triangles used in the Republic of South Africa are shown in Fig. 35.2 and 35.3 and are based on the international classification for soil separates.

The method used to determine a textural class must be reported, as classes obtained from a textural triangle will not necessarily correspond with those of a finger test.

35.6 References

USDA, 1972. Soil survey laboratory methods and procedures for collecting soil samples. Soil Survey Report No.1, U.S. Govern. Printing Office. Washington D.C.

GEE, G.W. & BAUDER, J.W.,1986. Particle size analysis. In A. Klute (ed.). Method of soil analysis no. 9. Part 1, 383-411. Am. Soc. Agron. Madison, Wis.

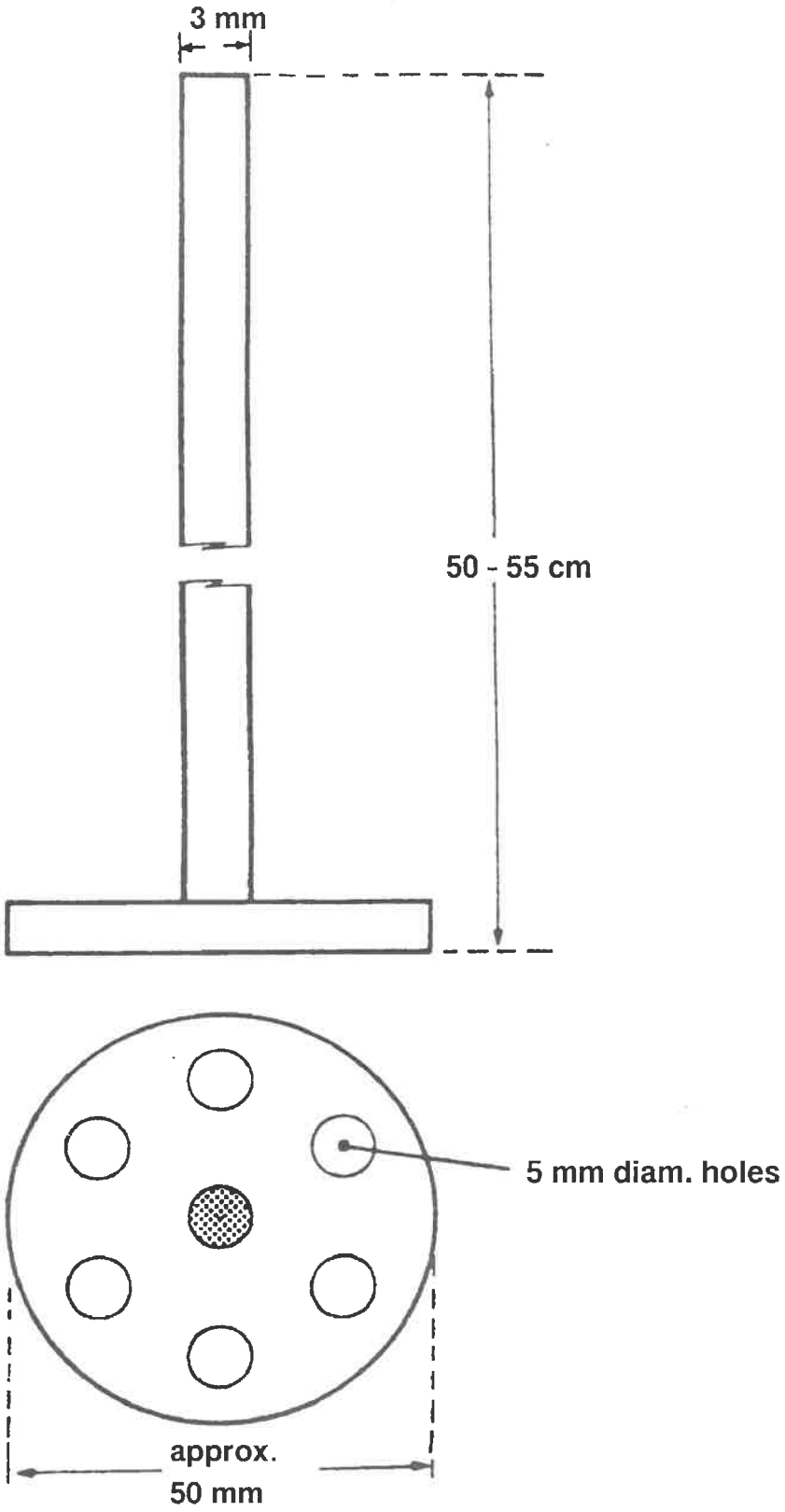

Figure 35.1: Dimensions of hand stirrer

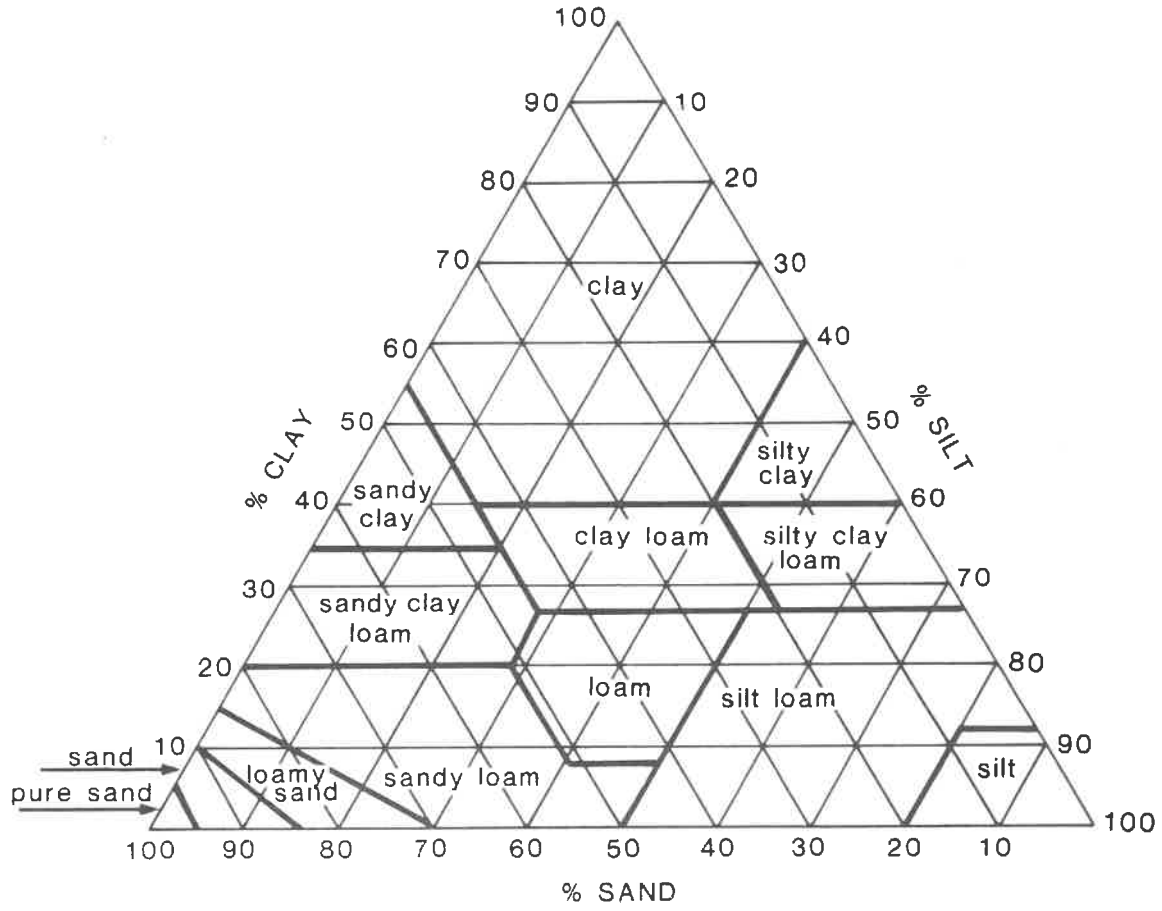

Figure 35.2: Chart showing the percentages of clay (below 0,002 mm), silt (0,002 - 0,05 mm) and sand (0,05 - 2 mm) in the basic soil textural classes.

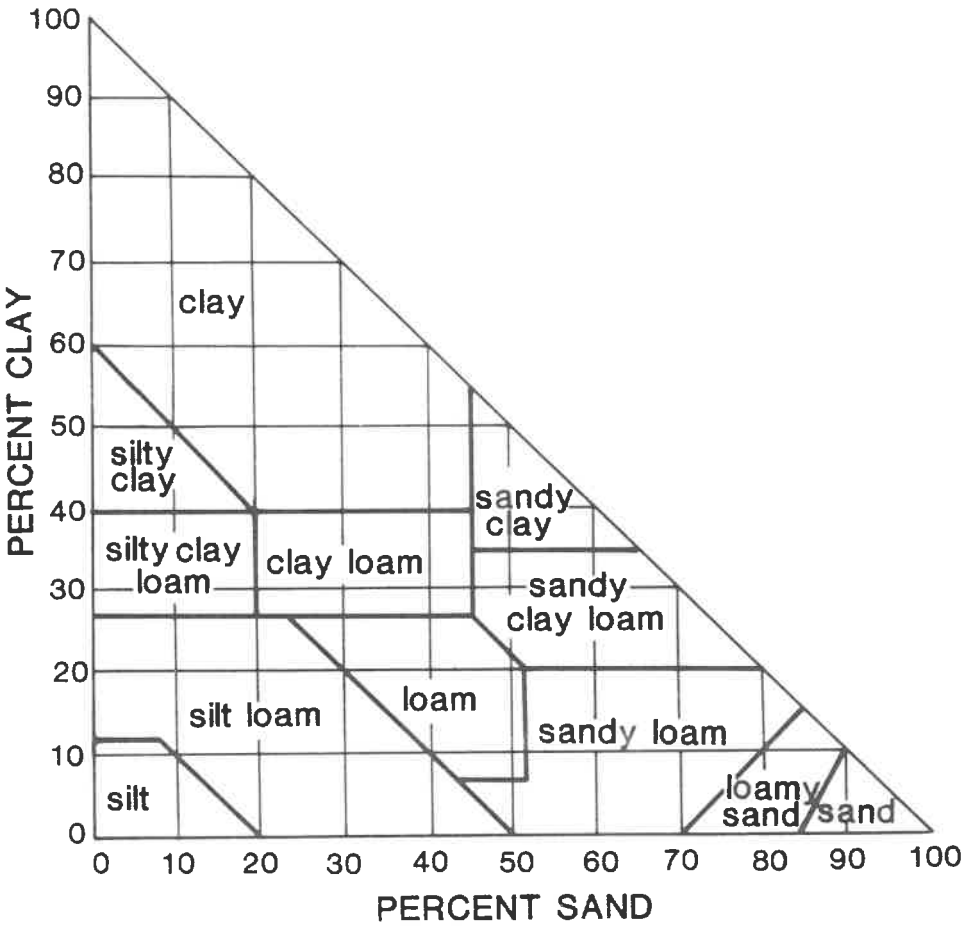

Figure 35.3: Textural triangle for soil textural analysis using the USDA classification scheme

PROCEDURES FOR SOIL ANALYSIS

Compiled and edited
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SIXTH EDITION

2002

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Procedures

Procedures for soil analysis / L.P. van Reeuwijk (ed.).-
Wageningen : International Soil Reference and Information Centre.-
(Technical Paper / International Soil Reference and Information
Centre. ISSN 0923-3792 : no. 9)
1e dr.: 1986.- Met lit. opg.
ISBN 90-6672-044-1
Trefw.: bodemkunde.

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).

---

* 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 $\times 10^{-4}$	Temp. °C	B $\times 10^{-4}$	Temp. °C	B $\times 10^{-4}$
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%

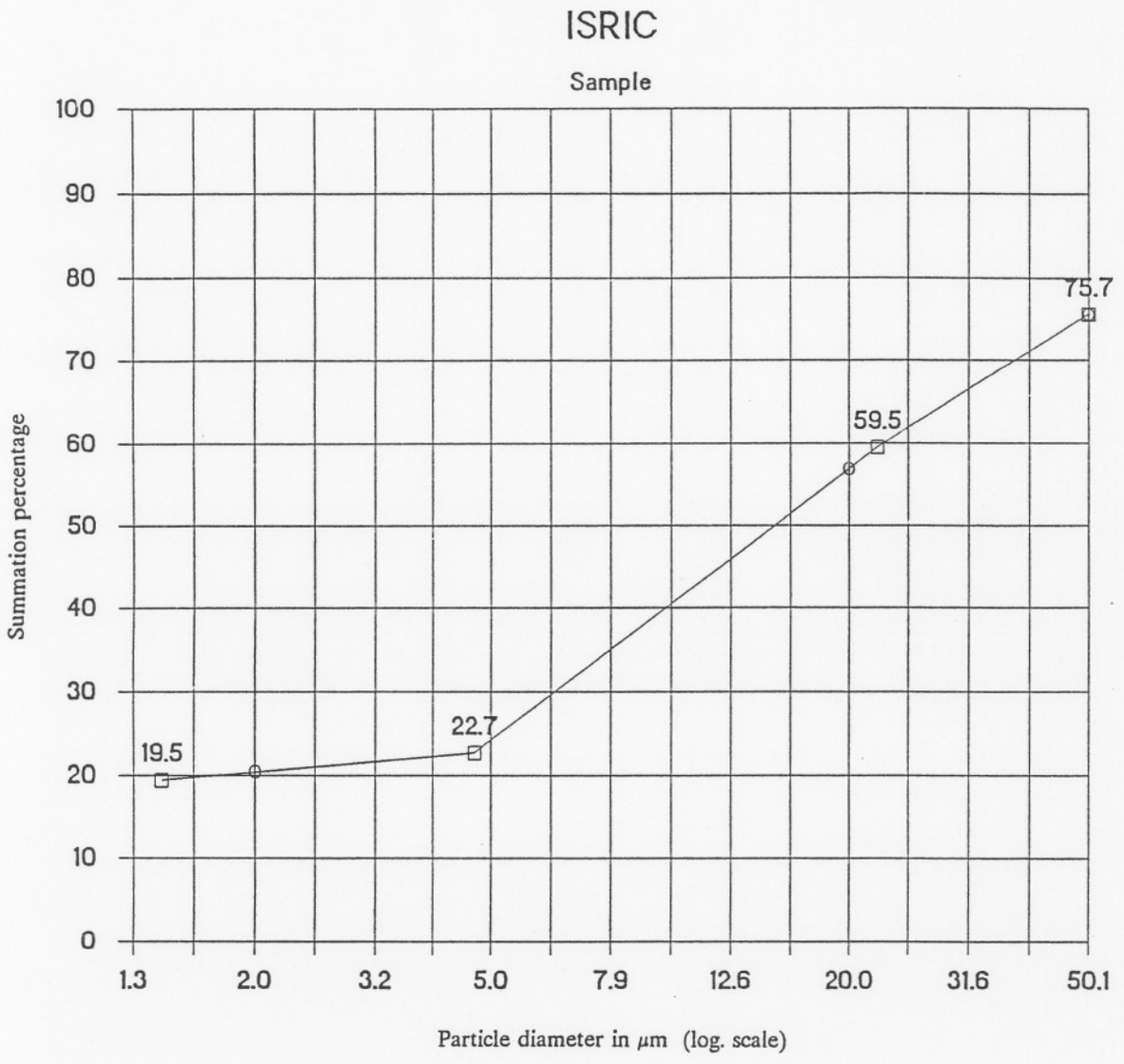

Fig. 3-1. Summation graph of an example particle-size analysis with the hydrometer (see text).

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.

---

[*] 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 = $50 \times 10^{-3} \times 10 \times 100\%$ (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-$H_2O \leq 6.5$ 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.

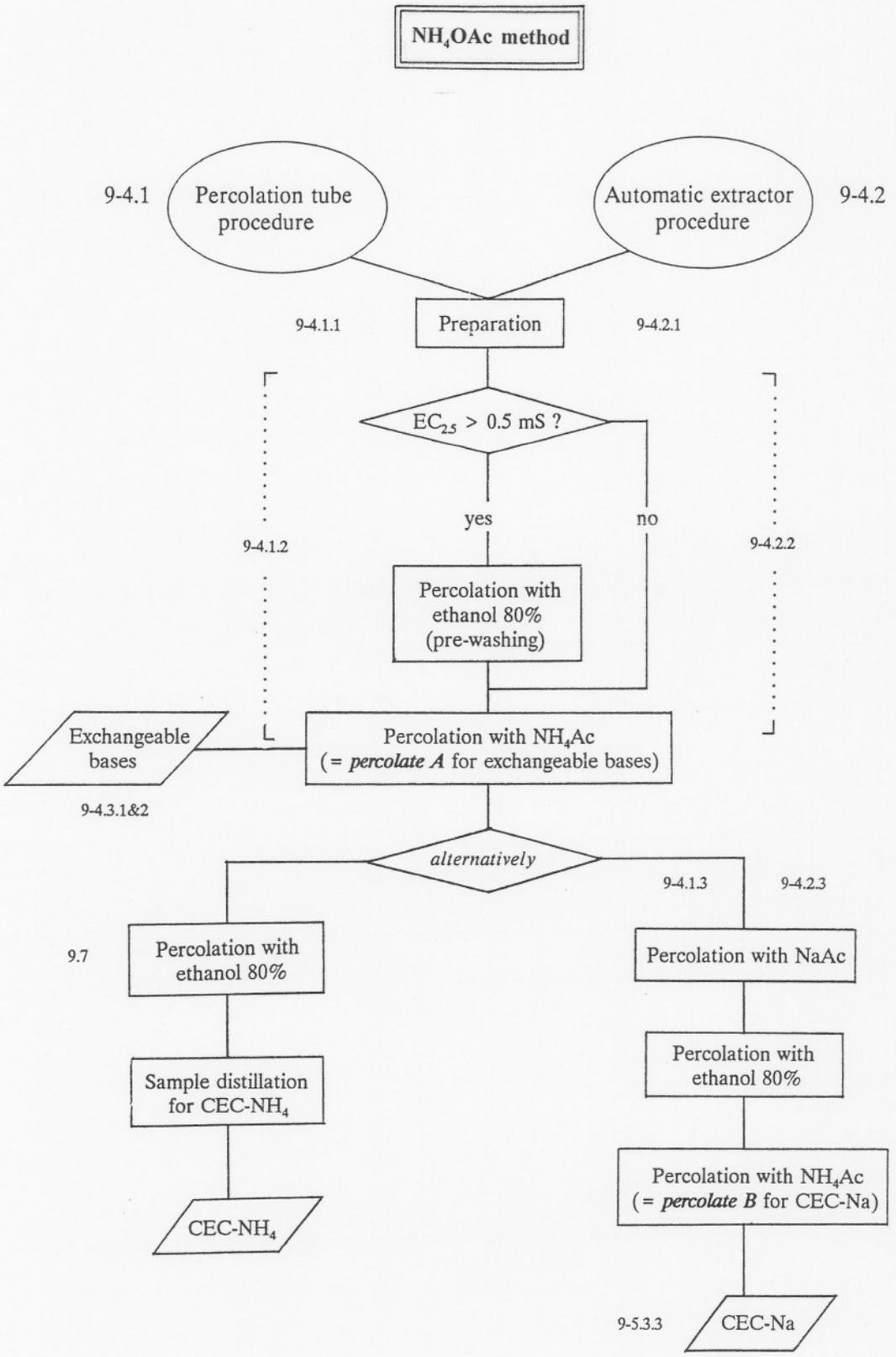

Diagram 9-1. Flow diagram of ammonium acetate method for exchangeable bases and CEC.

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.

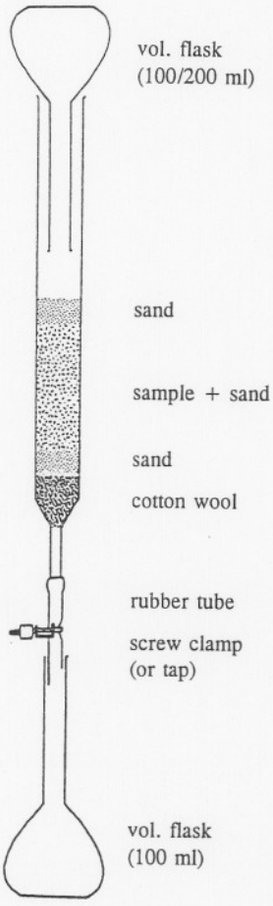

Fig. 9-1. Percolation assembly

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.

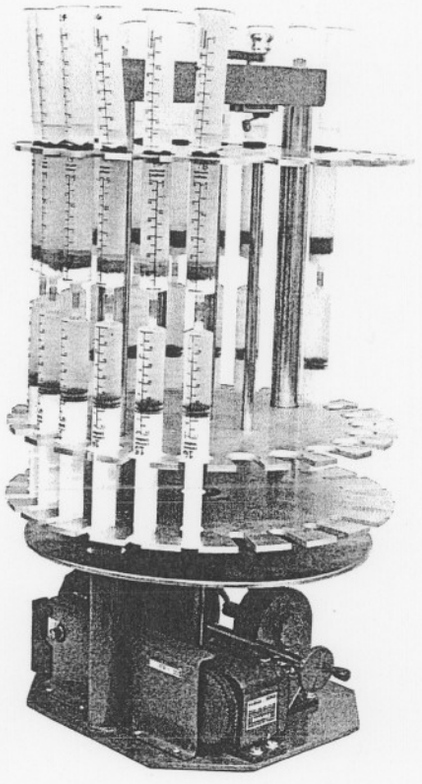

Fig. 9-2. Mechanical extractor.

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

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

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

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

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

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

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:

$$\text{Effective CEC (ECEC)} = \text{exchangeable bases} + \text{exchangeable acidity}$$ (see Chapter 11)

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

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

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)

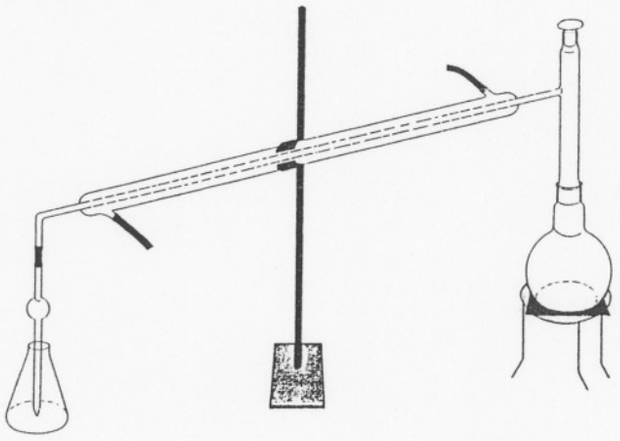

Fig. 9-3. A simple distillation assembly.

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.

---

* 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.

---

*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

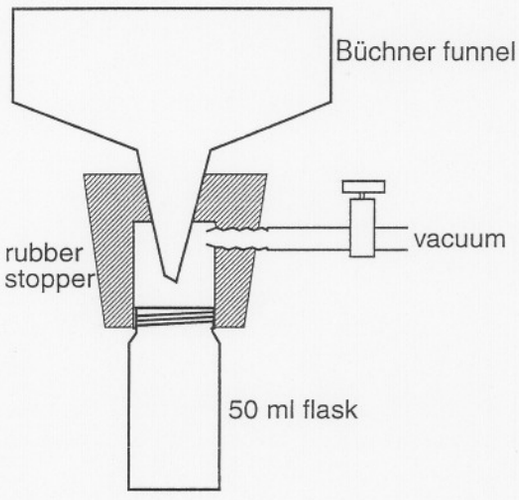

Fig. 13-1. Suction device for obtaining saturation extract (after a model by Dr. P.M. Driessen). The rubber stopper can be prepared with different gauges of cork-borers. The assembly is placed in a stand or a rack.

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.

* 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)

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* 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
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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.

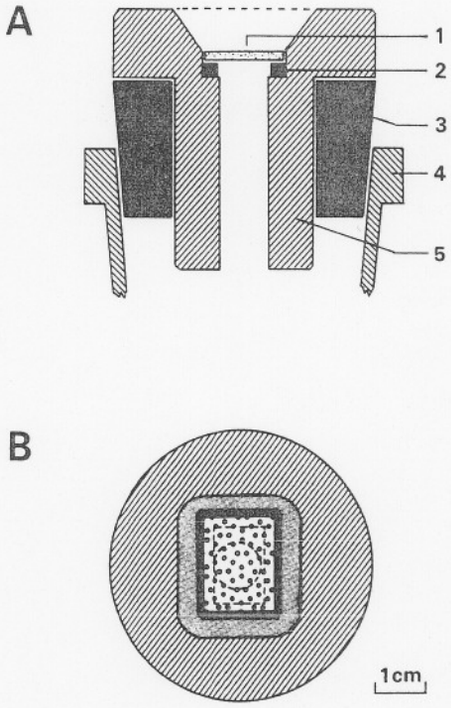
16-4.2.4 Formamide test for halloysite

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.

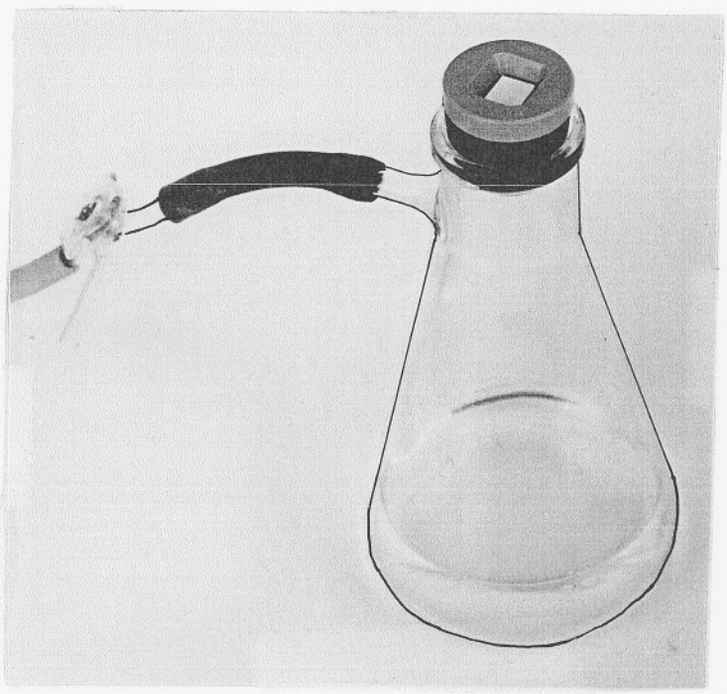
1. Make Mg-saturated specimen as indicated for *General Run* (16-4.2.1) or wash glycerol-treated specimen as indicated in 16-4.2.3 Step 1 (if no K-treatment is applied).
2. If no *General Run* is made, run *XRD* between 3° and 16° 2Θ.
3. Spray the specimen with formamide with a spray-bottle.
4. Allow 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.

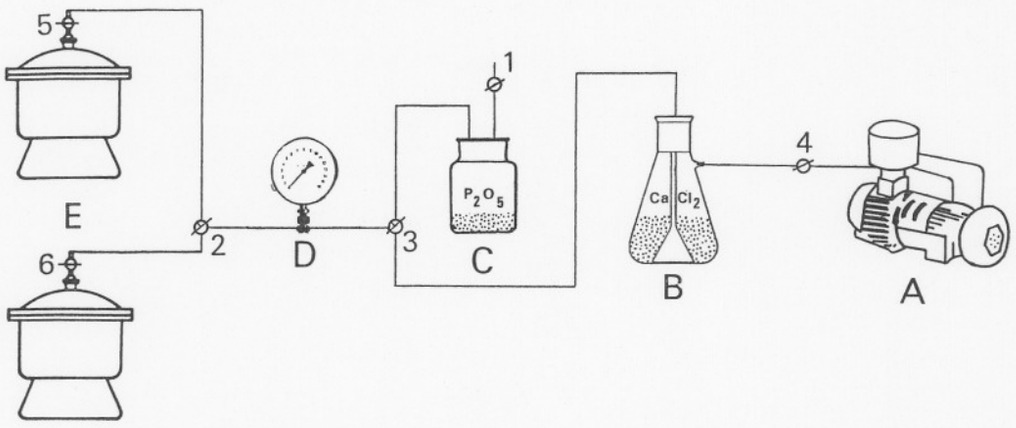


Fig. 17-1. Schematic assembly of apparatus for the determination of specific surface area with *EGME*. A. vacuum pump; B. *EGME*-trap; C. air-inlet; D. manometer; E. desiccators.

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

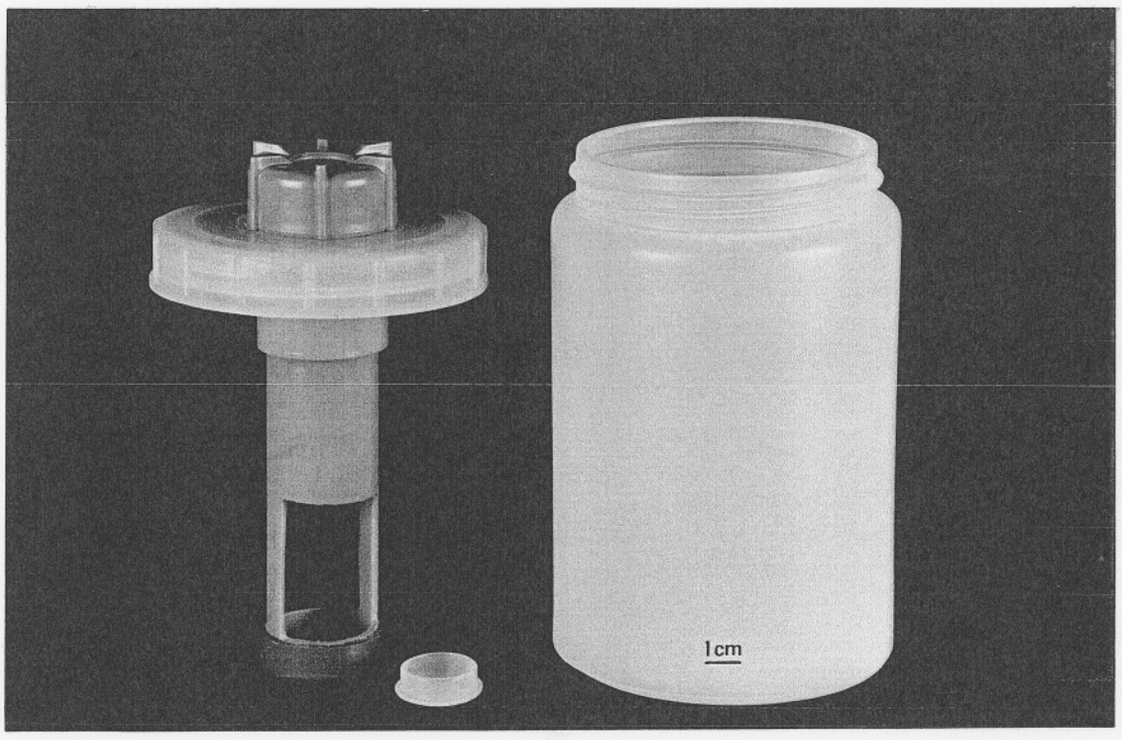

Fig. 19-1. Etching assembly.

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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