



SOIL SURVEY OF ENGLAND AND WALES.

This small handbook gives in detail the methods used in the laboratory of the Dartington Hall Trustees from 1940 to 1946 when the analysis of samples of characteristic profiles from soil series classified in the field by surveyors was done in one central laboratory for the first time.

Most of the methods are well known standard ones, but an attempt has been made to give practical details of manipulation where small points which are not usually described in the literature are of critical importance.

The setting down of all details of the organisation was considered to be worthwhile so that future development can be based upon what has already been found to be effective so far.

SOIL SURVEY OF ENGLAND AND WALES.

LABORATORY HANDBOOK.

Index.

Chapter I	<u>The Handling of Samples.</u>	page.
	Section 1.1. Profile sampling.	1
	1.2. Packing of samples.	1
	1.3. Labelling of samples.	2
	1.4. Recording of samples received at the Laboratory.	3
	1.5. Preparation of samples for analysis.	5
	1.6. Storage and labelling of samples	6
Chapter II	<u>The Scheme of Analysis.</u>	
	Section 2.1. Purpose of the analytical work	7
	2.2. The determinations made in the Soil Survey of England & Wales	7
	2.3. Determinations which may be added when possible	8
	2.4. Method of reporting results	8
	2.5. Basis of calculation	9
	2.6. Order of determinations and drawing of subsamples	9
Chapter III	<u>Analytical Methods: Preliminary.</u>	
	Section 3.1. Moisture	11
	3.2. Calcium Carbonate	11
	3.3. Loss on ignition	12
Chapter IV	<u>Analytical Methods: Chemical.</u>	
	Section 4.1. Carbon	13
	4.2. Nitrogen	13
	4.3. Exchangeable bases	15

## Chapter IV (Continued)

page

Section 4.31	Removal of Iron, Aluminium and Manganese prior to determination of Calcium and Magnesium	16
4.32	Determination of Calcium	16
4.33	Determination of Magnesium	16
4.34	Determination of Potassium	17
4.35	Determination of Manganese	18
4.4	Clay Analysis	19
4.41	Separation of Clay	19
4.42	Fusion	20
4.43	Determination of Silica	21
4.44	Total Oxides	22
4.45	Determination of Calcium	23
4.46	Determination of Magnesium and Manganese	23
4.461	Determination of Manganese	24
4.462	Determination of Magnesium	25
4.47	Determination of Titanium	25
4.48	Determination of Iron	25
4.49	Determination of Phosphorus	26
4.410	Calculation of Ratios	26
4.5	Total Phosphorus	26
4.6	Citric-soluble Phosphorus	27

Chapter V Analytical Methods: Physical.

Section 5.10	Mechanical Analysis	30
5.11	Determination of dissolved sesquioxides in the filtrate	31
5.12	Determination of Silt, Clay and Sand	32
5.13	Silt plus clay	32
5.14	Clay	33
5.15	Fine sand	34
5.16	Coarse sand	34
5.17	General Technique	35

Chapter V (Continued)			page
Section	5.2	pH Glass and Quinhydrone electrodes	36
	5.3	Sticky-point moisture	36
	5.4	Keen-Raczkowski Measurements	37
	5.5	Midway Colours	39

Chapter VI Other Analyses:

Section	6.1	Available Cobalt in Soils	40
	6.11	Extraction and preparation of solution	40
	6.12	Development of colour	41
	6.13	Reagents and apparatus required.	41
		Recommended procedure	42

Chapter I.

The Handling of Samples.

1. 1. Profile Sampling.

The description of the profile should preferably be done according to some standard procedure, such as that given in G.R. Clarke's Field Handbook (O.U.P. 1940), for uniformity and ease of reference. For the most satisfactory interpretation and correlation of analytical results the Laboratory Staff must have a copy of the description of every profile of which samples have been sent in.

The sampling is done by the field surveyor and the location of the profile is chosen by him to give a generally typical specimen profile of the soil series upon which information is required. Each sample taken from a pit must correspond to one horizon described in the surveyor's field notebook or field soil description sheet.

For the Survey of England and Wales at least two, and preferably up to four, pounds of sample of each horizon should be taken. This, when air dried and sieved to remove stones above 2 m.m. diameter, will give sufficient soil for a full analysis, leaving enough stock sample for any further examinations which may be desirable later.

1. 2. Packing of samples.

The sample should be enclosed in a close mesh cloth bag. Ordinary hessian bags are too open and allow loss of the finer particles during transit to the laboratory. Cardboard boxes come to pieces easily in contact with damp soil. The type of bag used up to now in the Survey measures  $9\frac{1}{2}$  ins. by  $13\frac{1}{2}$  ins. when flat and is made of close-weave cotton. If a tape is fastened on for tying it is preferably fastened by sewing at one point to the outside of the bag at one to one and a half inches below the top edge. Threaded draw tapes in a hem at the top of the bag do not give a satisfactory close fastening and are unnecessarily expensive.

For transport by rail or road to the Laboratory these bags are packed in specially made cases with divisions to hold ten samples. The cases are made of one inch thick timber, strengthened by cross battens on the outside, and measure externally 2 ft 9 ins long by 1 ft 7 ins wide by ten ins. deep. Rope handles are fitted at the ends for ease of handling. The boxes are similar to ammunition boxes in design and weigh about 40 lb. empty. They are deliberately made of stout material to stand rough handling, and of sufficient weight to ensure fairly handling. The lids are fastened on by fourteen wooden screws.

The boxes are provided with stout reversible cardboard labels 6 ins. by 4 ins. bearing the following details:-

<u>SOIL SAMPLES.</u>	
To: THE LABORATORY, DARTINGTON HALL TRUSTEES, TOTNES, S. DEVON.	
Station: Totnes G.W.R.	BY GOODS TRAIN.
Name and Address of Sender.....	
.....	
Date of Dispatch.....	

<u>EMPTY CASE.</u>	
To:.....	
.....	
.....	
Station:.....	Rly:.....
Sender: THE LABORATORY, DARTINGTON HALL TRUSTEES, TOTNES, S. DEVON.	
Date:.....	
REVERSE LABEL WHEN RETURNING.	

1.3. Labelling of Samples.

Careful labelling of samples is essential if easily made mistakes are to be avoided. If the greatest care is not taken it is fatally easy

to mix up samples and stultify all the field work and laboratory analyses.

The Survey system is to classify all samples under the name of the county from which they come and the profile and horizon numbers (given by the Sampler) corresponding to the profile description.

Ordinary tie-on luggage labels are used, which have printed on them twice the above three headings.

The diagram shows a rectangular luggage label with a trapezoidal top section. At the top center of the trapezoid is a small circle containing the number '6'. Below this, the label is divided into two identical sections by a horizontal dashed line. Each section contains three lines of text, each followed by a dotted line for writing: 'COUNTY.....', 'PROFILE No.....', and 'HORIZON No.....'.

The details are filled in by the Surveyor at the time of sampling and the two halves are torn apart at the perforations. The lower half is folded to protect the writing from being defaced by damp soil and is put into the bag with the sample. The top half is tied to the outside of the bag by the closing string or tape. The Surveyor, on sending off to the Laboratory a consignment of samples, posts off a letter of advice with a list of the details of the samples, with or without the corresponding profile description sheets. A useful farther precaution is the enclosure in the case of a copy of the full list which has been sent by post.

1.4. Recording of Samples received at the Laboratory.

On arrival of the case at the Laboratory the contents are sorted out according to profile and horizon numbers and checked with the lists received by post and/or in the case. Each sample is then entered in a register under the following headings:-

- (1) Date of receipt.
- (2) Consecutive laboratory number.
- (3) Centre letter.
- (4) Centre consecutive number.
- (5) Profile number.
- (6) Horizon number.
- (7) Series name (if known)
- (8) Details of site.
- (9) Initials of Surveyor.

(1) and (2) are obvious routine identification particulars.

(3) is a reference to the province in which the sample pit is situated.

The letters used at present [1946] are:

A	ABERYSTWYTH	Merioneth, Montgomery, Cardigan, Radnor, Brecknock, Carmarthen, Pembroke.
B	BANGOR	Gaernarvon, Denbigh, Flint, Anglesey.
C	CAMBRIDGE	Norfolk, Suffolk, Hertford, Bedford, Cambridge, Huntingdon.
D	DARTINGTON	Devon, Cornwall, Lundy and Scilly Isles.
G	GLAMORGAN	Glamorgan, Monmouth.
H	HARPER ADAMS	Shropshire, Warwick, Stafford.
L	LONG ASHTON	Somerset, Wiltshire, Gloucester, Worcester, Hereford.
M	MIDLAND	Leicester, Derby, Nottingham, Rutland, Lincoln.
N	NEWCASTLE	Northumberland, Durham, Westmorland, Cumberland.
Q	MANCHESTER	Lancashire, Cheshire.
R	READING	Dorset, Hampshire, Berkshire, Buckingham, Oxford, Northampton Isle of Wight, Middlesex.
W	WYE	Sussex, Surrey, Kent.
Y	YORK	Yorkshire.
X		Scotland and other special purposes.

(4) is an identification detail complementary to (3)

(5) and (6) are given by the Sampler on the label enclosed in the sample and connect the sample directly with the profile description.

(7) is taken from the profile description sheet, if given by the Surveyor.

(8) is also furnished by the surveyor and acts as a further check on (3)

The most satisfactory site reference is an Ordnance grid number on the 5th relief edition 1" Ordnance Series.

(9) assists in obtaining supplementary information later if desired.

Examples are:

(a) 1495 6.11.44 Y.79 12/2 Kirkby Overblow. F.F.K. Kirkby Overblow  
(O.S. 47/46 S.W.  
904/688)

The full description is:

1495th sample received at the Laboratory. It arrived on 6th November 1944, and is the 79th sample from the Yorkshire province. It was taken from the second horizon of profile 12 and is classified by Dr. F.F. Kay as an example of the Kirkby Overblow series. The pit from which it was taken is at co-ordinates 904/688 on Ordnance sheet 47/46 S.W. at Kirkby Overblow.

(b) 1889 4.9.45 H.435 119/1 - K.L.R. High Dell Farm, Bighton,  
Alresford, Hants.

This sample was the 1889th received at the Laboratory. It arrived on 4th September 1945, and is the 435th from the Reading province. It was taken by K.L. Robinson from the surface horizon of profile 119 of an, as yet, unnamed series at High Dell Farm, Bighton, Alresford, Hants.

Between the surveyor (who is usually also the sampler) and the Laboratory the details recorded should enable the position of the sampling pit to be fixed, and definite identification of any sample to be made. The surveyor gives details five to nine inclusive and the Laboratory the remainder.

For safety's sake the register is made out in duplicate. One copy is kept at the Laboratory and the other is sent to the Director of the Survey. The use of a loose leaf system enables the latter's copy to be kept up to date at approximately monthly intervals.

#### 1.5. Preparation of samples for analysis.

If no samples are missing and there is no doubt about any of the details given, the Consecutive laboratory number (2), Centre consecutive number (4) and Series name (7) are written on the labels tied to the outsides of the bags. The bags are then opened one at a time and the label inside is compared with that tied on to the outside. If the inscriptions correspond the details (2), (4) and (7) are written on the inside label also. Both halves are then placed with the soil which is spread out thinly on a clean metal tray to dry in the air in a room protected from dust and chemical fumes, especially ammonia.

The material on the tray is broken up roughly with the fingers as far as possible and is allowed to dry over several days with or without artificial heat at a temperature not exceeding 40°C, with occasional breaking down. It is then ground down with a wooden pestle in a porcelain, wood or rubber-lined

iron mortar until all the friable material will pass through a sieve having circular holes of 2 mm. diameter. All pieces of plants, roots and wood are removed and care is taken not to break up any pieces of rock or stone by the use of undue pressure. Special care must be taken with soils derived from chalk or similar easily broken material to avoid grinding down the particles larger than 2 m.m.

The inorganic material retained on the 2 m.m. sieve is roughly weighed, washed free of soil particles, dried and separated from any vegetable matter and weighed. The weight expressed as a percentage of the total weight of the whole soil sample is reported as "Stones".

The soil passing the 2 m.m. sieve is well mixed and stored for future analysis.

1.6. Storage and labelling of samples.

To avoid repeated drying of samples which will, as air-dried soil, take up or lose moisture according to the relative humidity of their surroundings, it is advisable to use strong moisture-proof containers, such as tins, waxed cartons or lined paper bags. In the Survey we have found most suitable round slip cover tins  $4\frac{1}{2}$  inch diameter by  $4\frac{3}{4}$  ins. high. These hold about 3 lb. air dry 2 m.m. soil. For the most economical use of storage space square tins would be preferable, but are not obtainable at present. The push-on type of lid is better than the lever-lid pattern as there are no dead spots in the container covered by the flange.

In each tin are placed both portions of the label enclosed with the original sample, on which portions the registrar has added the Laboratory Consecutive number, the Centre letter and number and the Series name. On the outside of the tin and of the lid are written with black paint the Laboratory Consecutive number, the Centre letter and the Centre Consecutive number.

The tins are stored on shelves in order of Laboratory Consecutive number. It might be preferable, if greater shelf space were available, to keep in separate bays the samples from each of the Centres.

Chapter II.

The Scheme of Analysis.

2.1. Purpose of the analytical work.

Soil analysis for the Soil Survey is done for reasons different from those underlying the examination of samples received for farm advisory purposes. The purpose is to determine numerically such physical and chemical characteristics as will enable an accurate description and definition of each soil series to be made and correlated with field observations and classification. In the examination of farm advisory samples the determinations are made chiefly on the plant nutrient status and acidity of a general sample representative of a whole field so that advice may be given on the steps to be taken to assist in the production of a satisfactory crop in one year or on the tracing of causes of unsatisfactory soil conditions. Profile samples, on the other hand, are taken in order to measure and define more fundamental and less readily altered characteristics of a particular specimen of a given soil series.

2.2. The Determinations made in the Soil Survey of England and Wales.

Those made at present (1946) are:

(A) Physical.

- (a) Mechanical analysis including stones.
- (b) Free Calcium Carbonate.
- (c) Loss on Ignition.
- (d) Moisture determination at 100°C.- 105°C. on soil:
  - (i) air-dry.
  - (ii) at sticky point.
  - (iii) at saturation point.
- (e) Single value constants.
  - (i) True density.
  - (ii) Apparent density.
  - (iii) Pore space.
  - (iv) Volume expansion.
- (f) pH.
  - (i) by glass electrode.
  - (ii) by quinhydrone electrode.
- (g) Colour (Ridgway)
  - (i) on air-dry soil

(ii) on peroxidised soil

(iii) at sticky point of soil

(B) Chemical.

(i) Nitrogen )  
                  ) for C/N ratio.

(ii) Carbon )

(iii) "Total"  $P_2O_5$

(iv) Exchangeable bases

(a) CaO

(b) MgO

(c)  $K_2O$

(d) MnO

(v) Clay fraction analysis for  $SiO_2/Al_2O_3$ ,  $SiO_2/R_2O_3$  and  $Al_2O_3/Fe_2O_3$  ratios.

2.3. Determinations which may be added when possible,

(A) Physical.

(a) Moisture equivalent at  $pF_3$ .

(B) Chemical.

(a) Base exchange capacity.

(b) Total exchangeable bases (S value).

(c) Trace elements - copper, cobalt, molybdenum, zinc.

2.4. Method of reporting results.

Results are reported on a foolscap size printed form on which the physical determinations are set out on one side and chemical determinations on the reverse. Each sheet is designed for the reporting of one profile with spaces for figures on six horizons.

Six copies are made of each sheet and are distributed as follows:-

(1) The Director of Soil Surveys.

(2) The Soil Science Museum, Oxford.

(3) Master copy. Laboratory strong room.

(4) Institute to which Surveyor is attached.

(5) Institute of Province in which sample site is situated (if different from (4)).

(6) Laboratory (working copy).

2.5. Basis of Calculation.

To ensure uniformity of results all percentage figures are calculated to the basis of oven-dry weight. The figure for loss on ignition is compensated for loss of carbon dioxide from carbonates, by calculation from the "free" calcium carbonate figure. Exchangeable bases are expressed as milligram equivalents per 100 grams of oven-dry soil unless otherwise stated.

2.6. Order of Determinations and drawing of subsamples.

As one or two of the determinations made affect the procedure on other determinations these are done as a routine first.

About 200 grams of soil are required for the routine examination. This is drawn by quartering down from the well-mixed bulk of soil ground to pass the 2 m.m. round-hole sieve. A sub-sample of 10 grams is taken and put into a separate bottle carefully labelled.

The 200 g. working sample is dried at 100°C - 105°C for two days and then stored in an air-tight bottle, containing one half of the original label from the main tin. All analyses, except for nitrogen and carbon and pH, are done on this material.

The 10 g. sub-sample is ground to pass a 70 I.M.M. sieve, dried overnight at 100°C - 105°C and stored in an airtight bottle. This is used for nitrogen and carbon determinations.

Preliminary determinations.

(a) Moisture.

This figure is needed for calculation of all results to the standard basis. The use of a large bulk (200 g.) dried and kept in an airtight bottle saves frequent redeterminations of the moisture content of small individual samples.

(b) Free Calcium Carbonate.

A knowledge of the percentage of free calcium carbonate is needed for correction of the results of Loss on Ignition or choosing the procedure for determination of exchangeable bases, mechanical analysis and citric-soluble constituents (if done), and as a check and guide in pH determinations.

(c) Loss on Ignition.

This figure is also used for obtaining an idea of the quantity of organic matter present which will affect the oxidation processes in mechanical analysis.

The most convenient order in which to do analyses is:-

1. Preliminaries.
2. Carbon.
3. Mechanical analysis.
4. pH.
5. Nitrogen
6. Exchangeable bases.

All other determinations may be done in any convenient order.

Chapter III.

Analytical Methods.

Preliminary.

3.1. Moisture.

Weigh accurately 10 g. 2 m.m. air-dry soil into a weighed aluminium tin. Dry overnight in a thermostatically controlled oven at 100°-105°C. Allow the tin and contents to cool in a desiccator and re-weigh. The loss in weight X 10 = percentage moisture in air-dry soil.

3.2 Calcium carbonate.

The apparatus and method devised by Collins (J.S.C.I. 1906. 25. 518 - 522., and Wright. Soil Analysis. 2nd. edition. 1939. Pub. Harby. pp 150 - 153) are used.

Weigh 5 g. 2 m.m. oven-dry soil into the special 150 ml. wide-mouthed conical flask and add the celluloid acid measure containing 18 ml. 1:3 hydrochloric acid - water mixture, care being taken to avoid acid being spilt on to the soil.

Attach the flask to the apparatus and immerse it in the water jacket. Open all the glass taps and blow air through the water to mix it thoroughly and bring the whole apparatus to an even temperature. Read the thermometer immersed in the water. Adjust the level of the water in the gas measuring tube to the zero mark at atmospheric pressure, so that the meniscus of the water in the levelling tube is at the same height as that in the gas measuring tube. Turn off the tap at the top of the measuring tube and allow the water in the levelling tube to run back into the reservoir.

Remove the flask containing the soil and acid from the water jacket and tilt it so that the acid mixes with the soil to react with the free calcium carbonate in the soil. Shake it well for about thirty seconds and put it back into the water jacket. Blow air through the water jacket to even the temperature of the whole apparatus. When all reaction has ceased and the carbon dioxide produced has been collected in the gas measuring tube, the volume of it at atmospheric pressure is read after the meniscus in the levelling tube has again been adjusted to the same height as that in the gas measuring tube. Repeat the shaking of the flask and contents and the reading of gas volume until constant readings of volume are obtained. The temperature

of the water in the jacket is read again and the barometric pressure in m.m. is found.

For full details of corrections and calculations the references given should be consulted.

3.3. Loss on Ignition.

Carefully transfer the soil used for the moisture determination to a weighed crucible. Ignite for  $\frac{1}{2}$  to 1 hour in a muffle furnace at  $850^{\circ}$  -  $900^{\circ}$ C. If the temperature is too high silicates may fuse and  $Fe_2O_3$  will be oxidised to  $Fe_3O_4$ . Allow the crucible and contents to cool in a desiccator, and weigh.

$$\frac{\text{Loss of weight} \times 100}{\text{Oven dry weight of soil}} = \text{percentage loss on}$$

ignition on oven dry soil.

If free calcium carbonate is present, the above figure will be too high as it will include loss of carbon dioxide. Therefore, from the percentage total Loss on Ignition subtract 44% of the calcium carbonate percentage to obtain the true Loss on Ignition.

If it is not possible to reach a temperature ( $850^{\circ}$ C) high enough completely to decompose calcium carbonate after ignition, moisten the ash with 5% ammonium carbonate solution and ignite at a low temperature to drive off excess ammonium carbonate. Cool and weigh. Repeat until constant weight is obtained. In this way any partially decomposed calcium carbonate is reconstituted and no correction is required.

If the percentage of clay is high the loss-on-ignition figure will be too high by inclusion of combined water in the colloidal fraction.

Chapter IV

Analytical Methods.

Chemical.

4.1. Carbon.

Weigh 0.5 to 1.0 g. soil ground to pass a 70 I.M.M. sieve into a 200 ml. beaker-flask. Add 10 ml. N/1 potassium dichromate followed by 20 ml. concentrated sulphuric acid added quickly to make the solution boil. This is important as the method is based on making use of the heat of dilution for the oxidation of carbon. Leave to stand for 5 minutes with occasional shaking. Dilute with about 100 ml. distilled water and stand the beaker in running water to cool the contents. Add about 5 g. neutral sodium fluoride and 1 ml. diphenylamine indicator. Titrate to a green end-point with N/2 ferrous ammonium sulphate. The amount of soil should be so adjusted as to react with between 2.5 and 7.5 ml. N/1 potassium dichromate, equivalent to 5 - 15 ml. N/2 ferrous ammonium sulphate. When the carbon content is low and large amounts of soil have been used, the soil colour masks the end point. Such samples should be filtered rapidly through an 11 cms. No. 4 Whatman filter paper before titration.

1 ml. N/1 potassium dichromate = 0.0036 g. carbon.

Reagents required:

Sulphuric acid. Concentrated. Analar.  
N/1 Potassium dichromate  
N/2 Ferrous ammonium sulphate  
Sodium fluoride (neutral)  
Diphenylamine Indicator. Dissolve 0.5 g. in 20 ml. distilled water and add 100 ml. concentrated sulphuric acid.

4.2. Nitrogen.

Weigh 4 g. oven dry soil, ground to pass a 70 I.M.M. sieve, into a 300 ml. or 500 ml. Kjeldahl flask. Moisten it with small amount of water to prevent caking. Add 15 ml. concentrated sulphuric acid and heat gently at first to avoid frothing over, then strongly until the contents become brown (approximately  $\frac{1}{2}$  hour). Then add 10 g. sodium sulphate and 0.1 g. copper sulphate (or mercuric sulphate and selenium) and continue digestion until the contents of the flask are white or grey, or until no further change of colour is noted for  $\frac{1}{2}$  hour. Heat for a further 60 minutes, then allow to cool. Dilute to about 40 ml., wash all into a 100 ml. measuring

flask, cool and make the volume up to the mark.

Shake the suspension, and pipette 5 ml. ( $\bar{=}$  0.2 g. soil) into any type of micro-Kjeldahl distillation apparatus. Place a 100 ml. conical flask containing 5 - 10 ml. N/70 hydrochloric acid with Tashiro's indicator under the condenser, with the tip of the tube under the surface of the acid. Add 7 ml. 40% sodium hydroxide containing 5% sodium thiosulphate and about 5 ml. distilled water. Close the apparatus with a stopper or clip, open the steam tap and steam distil for 4 minutes. Lower the receiving flask so that the condenser tube is clear of the distillate and distil for a further 1 minute. Turn off the steam, wash the liquid on the outside of the condenser tube into the receiving flask and remove the flask containing the distillate. Meanwhile the apparatus will have cooled and siphoned the residue into the steam jacket. Remove the stopper and wash it with cold water and allow / <sup>the washings</sup> to siphon over so as to clean the apparatus for the next distillation. Back titrate the distillate with N/70 sodium hydroxide to pH 4.8 (green with Tashiro's indicator). When large batches are being run together, each titration can be done while the next one is distilling. Two micro-distillation units can conveniently run off one steam generator and will just keep one person occupied.

Calculation. When 0.2 g. soil is used for distillation 1 ml. N/70 HCl  $\bar{=}$  0.1% Nitrogen.

Note: allowing the soil to stand with water for some time before addition of sulphuric acid gives a higher figure than if the acid is added immediately before heating. (Bal. J. Agric. Sci. 1925. 15. 454 and Srinivasan. Indian J. Agric. Sci. 1932. 2. 525). Walkley (J. Agric. Sci. 1935. 25. 598) finds that fine grinding of the sample has the same effect as preliminary digestion with water.

Reagents required:

Concentrated sulphuric acid, Analar.  
Anhydrous sodium sulphate, Analar.  
Copper sulphate, Analar.  
40% sodium hydroxide containing 5% sodium thiosulphate.  
N/70 hydrochloric acid in 20% alcohol containing Tashiro's indicator (10 ml. Tashiro's indicator, 200 ml. absolute alcohol, 133.2 ml. N/10 hydrochloric acid made to 1 litre with distilled water). Store in a Pyrex bottle.

Tashiro's indicator. To 200 ml. 0.1% alcoholic solution of methyl red add 50 ml. 0.1% alcoholic methylene blue. This keeps indefinitely in a brown bottle. (Ref: E.J. Conway, Micro Diffusion Analysis and Volumetric Error, 1939. Pub. Crosby Lockwood. Pp. 79 - 80.)  
Run blanks on all reagents with each batch.

Notes.

- (1) We have found most satisfactory the type of all-glass micro-Kjeldahl distillation apparatus described by Markham. (Biochem. J. 1942, 36, 790)
- (2) As a timer for the distillation a sand-glass of the small egg-boiler type (4 minutes) is useful and can be fixed, on a backboard which can rotate on a horizontal pivot, to the retort stand supporting the distillation apparatus.

4.3. EXCHANGEABLE BASES.

Weigh 25 g. soil, (2 m.m. oven dry) into a 600 ml. beaker. Add 200 ml. N/2 acetic acid plus extra acetic acid to neutralise any free calcium carbonate present (1 ml. 5 N acetic acid for each 1% free calcium carbonate when 25 g. soil is used) and leave to stand overnight. Filter the solution into a 1 litre conical pyrex flask through 27 cms. No. 2 Whatman paper using a fluted funnel. Pour back the first 50 - 100 ml. of filtrate into the beaker as this is usually cloudy and then leach the soil on the filter with eight 100 ml. portions of N/2 acetic acid, allowing each portion to pass completely through the filter before adding the next. Heat the filtrate almost to boiling and evaporate gently, taking precautions against dust, to a final volume of about 100 ml. which will take about 70 hours - that is from a Friday evening to Monday morning. Add 25 ml. concentrated nitric acid and evaporate the solution down to about 20 ml. Wash it into a 70 ml. vitreosil basin, evaporate to dryness, and ignite the solids at 500°C. for  $\frac{1}{2}$  hour. Allow to cool. If the soil contains much organic matter add a further 5 ml. nitric acid, evaporate to dryness and ignite again. (The contents of the basin should be white or yellow; if brown, add more nitric acid, evaporate to dryness and ignite again). Add 5 ml. 1:1 hydrochloric acid, rotate the basin to wet the whole residue and evaporate it to dryness on a water bath. Heat for half an hour in an oven at 100°-150°C to dehydrate silica. Cool it and at once add 10 ml. N/10 nitric acid and 10 ml. water. Extract the solids on a water bath for 15 minutes; filter through a 9 cms. No. 32 Whatman paper into a 50 ml. measuring flask,

wash the residue with hot water, cool and make the solution up to the mark.

4.31 Removal of Iron, Aluminium and Manganese prior to determination of Calcium and magnesium.

Pipette 5 ml. of extract into a 15 ml. centrifuge tube, add 2 ml. 10% sodium acetate and 1 ml. saturated bromine water. Spin the tube between the palms of the hands to mix the contents, place it in a water bath held at 90°C. and fitted with a rack to hold 2 dozen tubes. Heat the water-bath to 95°C - 100°C and hold it at this temperature for 1 - 1½ hours until excess bromine has volatilised. Add 2 ml. 25% ammonium chloride, mix by spinning, and heat for a further 15 minutes. Remove the tube from the water bath and add 3 drops 50% ammonium hydroxide. Spin the tube between the palms of the hands to mix the contents and heat for 5 minutes at 80°C. Centrifuge the suspension for 15 minutes at 2,500-3,000 r.p.m., carefully pour off the supernatant liquid into a clean 100 ml. tall beaker, and wash the centrifuge tube once with 10 ml. 1% ammonium hydroxide. Centrifuge again at 2,500-3,000 r.p.m., add this washing to the original beaker and discard the centrifuge tube with the precipitate.

4.32 Determination of calcium.

To the solution in the beaker add 1 drop methyl red and 50% acetic acid drop by drop until the solution is just neutral, i.e. pink. Heat it to boiling and add 3 ml. 3.5% ammonium oxalate to precipitate calcium. Leave to stand overnight. Filter the solution with suction through a Gooch crucible fitted with an asbestos pad into a 100 ml. filter flask. Wash the filter six times with hot water. Place the Gooch crucible in the same beaker and add 2 ml. 50% sulphuric acid and 50 ml. hot water. Heat the mixture to 70°C and titrate with approximately N/50 potassium permanganate to determine calcium.

4.33 Determination of magnesium.

To determine magnesium, transfer the filtrate to a 125 ml. conical flask and evaporate it at low heat to about 10-15 ml. Add 25 ml. concentrated nitric acid and continue heating till nitrous fumes are evolved. This drives off most of the excess ammonium salts. After cooling transfer the solution to a Pyrex evaporating basin (30 ml. size) and take just to

dryness on low heat. Cool again, add 2 ml. 2-N hydrochloric acid, warm slightly and rotate the dish to assist solution of the salts. Pour the solution into a clean 15 ml. centrifuge tube, wash the basin 4 times with about 1 ml. hot water and add the washings to the tube, keeping the total volume to 8 ml. Add 1 ml. 10% ammonium phosphate, stir with a glass plunger and then add 1 ml. 50% ammonium hydroxide. Stir the mixture with a plunger for about  $\frac{1}{2}$  minute, wash the solution on the plunger into the tube with a small quantity of water, and leave to stand over-night. Centrifuge the tube and contents for 10 minutes at 2,500-3,000 r.p.m. Pour off the supernatant liquor without disturbing the precipitate and drain the tube for 10 minutes by inverting it at an angle of  $45^\circ$ , with the base resting on a clean filter paper. Detach the precipitate from the bottom of the tube by adding 2 drops of 1% ammonium hydroxide and tapping the end of the tube against the palm of the hand. Then add 5 ml. 1% ammonium hydroxide around the sides and finally blow into the tube to mix the contents well. Centrifuge again, pour off the solution and drain as before. Wash and centrifuge the precipitate twice more, each time detaching it from the bottom of the tube with 2 drops of 95% alcohol. Add 5 ml. N/100 sulphuric acid and place the tube in a water bath at  $75^\circ\text{C}$  until the precipitate has dissolved. Mix the contents with a plunger to assist solution. Add 1 drop mixed indicator, consisting of equal quantities of freshly mixed 0.2% Bromo-cresol Green and 0.02% Neutral Red, each in 50% alcohol, (achromatic end point at pH 4.5) and back titrate with N/100 sodium hydroxide. (Ref: Marsden, J. Soc. Chem. Ind. (Trans) Jan. 1941, p.20)

4.34

Determination of Potassium.

Pipette 5 ml. of extract into a 15 ml. centrifuge tube graduated at 13 ml. Add 0.2 ml. N/1 nitric acid and evaporate to about 3 ml. in a boiling water bath. Add 1 ml. 25% sodium cobaltinitrite freshly prepared. Spin the tube between the palms of the hands to mix the contents, and place it in a refrigerator for 1 hour. Add 3 ml. 70% alcohol, mix the contents of the tube with a plunger and wash the plunger with about 1 ml. 70% alcohol directed into the tube. Centrifuge the tube for 10 minutes at 2,500-3,000 r.p.m. Pour off the supernatant liquid and drain the tube for 10 minutes at an angle of  $45^\circ$  with the base resting on filter paper. Wash the precipitate three times with 5 ml. 70% alcohol, detaching it at each washing as described for magnesium above,

centrifuging for ten minutes and draining for ten minutes between washings. After the third washing add 5 ml. N sulphuric acid, then fill the tube to the mark with hot distilled water. Place the tube in a water bath at 70°C until the precipitate is dissolved; then make up to 13 ml. with water. Cork it and mix the contents by shaking. Take 1 ml. of this solution in a 50 ml. test tube graduated at 20 ml., add 1 ml. 5% sodium pyrophosphate and 1 ml. 2.5% sodium acetate, make the volume up to 20 ml. with water, add 2 ml. Nitroso R-Salt (1%) to each of the range of tubes at 1 minute intervals and read on Spekker Absorptiometer after 30 minutes, using an Ilford Spectrum Green filter (No. 604) and 1 cm. cells.

Prepare a set of standards to run through with the unknowns. Pipette quantities of standard solution containing from 0.1 mg. to 1.0 mg.  $K_2O$  into centrifuge tubes, make the volume of each up to 3 ml., add 0.3 ml. N/1 nitric acid and treat as for soil extracts. Plot a standard curve and read off the unknowns.

4.35 Determination of manganese.

Pipette 2-5 ml. of the extract into a test tube graduated at 10 or 11 ml. Add 1 ml. ortho-phosphoric acid and make the volume up to the mark. Place the tube in a water bath at 95°C, add (approximately) 50 mg. sodium periodate, mix all together with a plunger and leave the tube in the water bath at 95°C for one hour. Remove the tube, cool it and make the volume up to the mark. Read in a Spekker Absorptiometer using Ilford Spectrum Green filter No. 604 and 1 cm. cells.

Run a series of standards 0.05 - 1 mg/10 ml. at the same time. Plot the curve and read off the unknowns.

The above method is suitable for soils with low calcium contents, that is, up to 5% free calcium carbonate. In soils containing more than this the heavy calcium precipitate is undesirable and is removed from the original acetate extract, thus: After leaching, evaporate the extract to about 500 ml. To the hot solution add 20 g. ammonium chloride and sufficient ammonia (S.G. .880) to make the solution neutral to methyl red and 1.5 g. ammonium oxalate for each 1 g. of calcium carbonate present. Heat the solution nearly to boiling and allow it to stand 2-3 hours. Filter it through a Buchner funnel using a

No. 5 Whatman filter paper, wash the paper and precipitate well with hot water, transfer the filtrate to a clean 1 litre conical flask and evaporate it as for soils containing a small amount of calcium carbonate. The precipitation of calcium will be done as usual to remove last traces of calcium before determining magnesium.

Reagents required:

Methyl red.  
Mixed Indicator - equal volumes freshly mixed 0.2% Brom-cresol Green and 0.02% Neutral Red in 50% alcohol.  
2.5 N sodium acetate.  
2-N sulphuric acid.  
N/2 acetic acid = 30 ml. Glacial/litre.  
N/10 nitric acid.  
N/50 sulphuric acid.  
N/50 sodium hydroxide.  
N/50 potassium permanganate.  
2-N hydrochloric acid.  
Concentrated nitric acid.  
1:1 hydrochloric acid.  
10% sodium acetate.  
Saturated bromine water.  
25% ammonium chloride.  
1% ammonium hydroxide.  
3.5% ammonium oxalate.  
50% ammonium hydroxide.  
95% alcohol.  
25% sodium cobaltinitrite (freshly prepared each day)  
5% sodium pyrophosphate.  
1% nitroso-R-salt.  
Ortho-phosphoric acid.  
Sodium periodate.

Stock Solutions:

6.1133 g.  $MgSO_4 \cdot 7H_2O$  per litre = 1 mg.  $MgO$  per ml.  
1.5830 g.  $KCl$  " " = 1 mg.  $K_2O$  per ml.  
3.1446 g.  $MnSO_4 \cdot 4H_2O$  " " = 1 mg.  $MnO$  per ml.  
1.7847 g.  $CaCO_3$  (+HCl to dissolve it) per litre = 1 mg.  $CaO$  per ml.

4.4 CLAY ANALYSIS.  $SiO_2$ ;  $Fe_2O_3$ ;  $Al_2O_3$ ;  $TiO_2$ ;  $MgO$ ;  $CaO$ ;  $P_2O_5$ ;  $MnO$ .

4.41 Separation of Clay.

Weigh sufficient air-dried soil to yield approximately 5 g. clay into a numbered squat beaker (600 ml.). Add about 100 ml. hydrogen peroxide (20 volumes) and allow to stand overnight. Evaporate the suspension nearly to dryness on a steambath, add more hydrogen peroxide and repeat until oxidation of organic matter is complete. If the soil contains not more than 1% of organic matter oxidation with hydrogen peroxide is unnecessary. Most samples of hydrogen peroxide contain appreciable quantities of phosphorous. Allowance is made for

the effect of this on the precipitation of Group 3 metals by determination of the percentage of phosphorus present.

If the soil contains manganese dioxide, digestion with sodium bisulphite will be necessary.

Boil the liquid in the beaker briskly for about half an hour or until the volume is about 25 ml, cool, add 50 ml. N. sodium acetate solution and allow to stand overnight.

Filter through a Whatman No.50 filter paper on a Buchner funnel, and wash the soil retained on the paper with 500 ml. N. sodium chloride solution in 100 ml. portions, followed by at least 500 ml. hot distilled water, or until all chlorides have been removed as shown by silver nitrate test.

Wash the residue on the filter paper into a numbered bottle - a 1 pint milk bottle is very suitable -, add N. sodium hydroxide until the liquid is alkaline and make up the liquid with distilled water to a mark of 5 cms. from the mouth of the bottle. Shake the bottle and contents overnight in a rotary shaker.

Allow the suspension to settle for 24 hours and, using a tube with a tip bent sharply upwards, siphon off the clay suspension to a depth of 8.6 cms. into a numbered 600 ml. beaker or basin. Again fill the shaking bottle to the mark with 0.005 N. sodium hydroxide, shake by hand for one minute, allow to stand for 24 hours and siphon off as before to a depth of 8.6 cms. Repeat this process until the liquid in the bottle is clear to a depth of 8.6cms. after standing 24 hours. Evaporate all the suspensions siphoned off to dryness, transfer the clay to a numbered porcelain crucible and ignite in a muffle at 800°C. for 30 - 60 minutes. It is important that all free sodium chloride shall have been removed by washing on the Buchner funnel or else the traces of sodium chloride will act as a flux during the ignition and will cause part of the clay to fuse into the glaze of the crucible.

Grind the ignited clay in an agate mortar to pass a 70 I.M.M. sieve. Mix thoroughly and transfer to a labelled specimen tube.

Twelve extractions may be conveniently carried out at one time.

#### 4.42 Fusion.

Weigh into a 30 ml. platinum crucible 0.5 g. ignited clay ground to pass a 70 I.M.M. sieve. Add (approximately) 5 g. fusion mixture, mix with a platinum spatula and place the cover on the crucible. Heat it gently until fusion begins (about 30 minutes) over a bunsen burner turned up full, with the top of the burner about 10 cms. below the bottom of the crucible. Then raise the burner

to about 1 cm. below the crucible and heat for  $1\frac{1}{2}$  hours. Place the crucible and lid with contents after cooling in a 250 ml. porcelain evaporating basin and add about 20 ml. water. Cover the basin with a watch glass, run 25 ml. concentrated hydrochloric acid down the side of the basin and leave until effervescence has ceased. Rock the basin occasionally to rotate the crucible and bring any undissolved melt into contact with the acid. When effervescence has stopped remove the watch glass and wash any drops on its underside into the basin. If appreciable quantities of manganese are present, or shown by a green colour in the melt, the addition of hydrochloric acid to the water for dissolving the melt may produce free chlorine which will attack the platinum. It is better under these circumstances to detach the melt by warming with water and to remove the crucible from the evaporating basin before the addition of hydrochloric acid to the water. All the usual precautions of washing the crucible thoroughly and collecting the washings in the basin will be necessary. Make swabs from quarters of 9 cms. No. 42 Whatman filter papers. Remove the crucible and lid from the basin and wash any adhering solution into the basin. Rub off adhering silica with the filter paper swabs held in platinum tongs. Wash the crucible and lid thoroughly with warm water and discard them. Drop the swabs into the basin, wash down the sides of the basin and wash the tongs, collecting the washings in the basin.

#### 4.43 Determination of silica.

Evaporate the solution to dryness, place the basin in an oven at  $110^{\circ}\text{C}$  for 30 minutes to dehydrate the silica, and add 10 ml. concentrated hydrochloric acid and 50 ml. water. Heat the basin until salts dissolve, and filter the solution through an 11 cms. No. 41 Whatman paper into a 250 ml. conical flask, using  $1\frac{1}{2}$  hydrochloric acid as a wash liquid. Return the filtrate to the basin and evaporate it again to dryness. Treat it as before and filter the solution into a 250 ml. measuring flask through a 9 cms. No. 42 Whatman fluted filter paper. Wash the precipitate with hot  $1\frac{1}{2}$  hydrochloric acid until it is free from ferric chloride. Rub the inside of the basin with a policeman to remove any adhering silica. Set the filtrate aside in the flask without making it up to the mark (Solution A). Place both filter papers and contents in a platinum basin (5 cm. diameter and ignite for 1 to 2 hours at  $800^{\circ}\text{C}$  in a muffle furnace. Alternatively, the burning off of the filter paper may be done over a bunsen flame so that the carbon is charred and smoulders away without bursting into flame

Cool and weigh the basin and silica. Add a few drops of 50% sulphuric acid and 5 to 10 ml. hydrofluoric acid (Analar). Drive off fluorsilicic acid by the heat of a bunsen burner and ignite the basin and contents in a furnace at 300°C for half hour. Reweigh the basin and contents after cooling. The difference in weight from the first weighing gives the weight of silica. Fuse the residue in the basin with a small lump of sodium bisulphate (Analar) by holding the basin over a low flame in platinum tipped tongs. When all the residue is in solution allow the basin to cool and dissolve the melt in hot water and wash it into the 250 ml. flask containing the filtrate (Solution A). Cool, and make the filtrate up to 250 ml. in a standard flask. The solution is now ready for determination of the other constituents.

#### 4.44 TOTAL OXIDES

Pipette 100 ml. of the filtrate from the silica determination (Solution A) into a 250 ml. Griffin beaker and evaporate it to about 30-40 ml. Add 5 ml. concentrated hydrochloric acid. Bring it nearly to the boil, run in 50% ammonia from a burette until a precipitate starts to form; then add more ammonia cautiously, one drop at a time, until ammonia can just be detected when the nose is held over the top of the beaker, after free ammonia gas has been blown out of it. Alternatively methyl red may be added and ammonia solution run in until the red colour just changes to yellow at pH 4.5 (approximately). Boil the solution for 2 minutes to coagulate the precipitate. Remove the beaker and contents from the heaters and allow the precipitate to settle. If, when methyl red has been used, the supernatant liquid is red, add 1 or 2 drops of ammonia to turn it yellow. When the beaker is cool enough to handle, filter the solution through a 9 cms. No. 41 Whatman filter paper into a 300 ml. conical beaker and wash the precipitate with hot 2% ammonium nitrate. Any precipitate adhering to the beaker need not be removed at this stage. Continue washing until about 80 ml. of filtrate and washings have been collected, remove the funnel from the beaker, and, without removing the filter paper, hold it over the beaker used for the precipitation and wash the precipitate back into the beaker, using a hot wash bottle with a medium jet. Care must be taken to avoid damaging the filter paper by blowing just hard enough to get a gentle jet directed on to the threefold side

of the folded filter paper. With practice this can be accomplished, using about 30 ml. water, without damaging the paper. Replace the funnel in the filtration beaker and dissolve the precipitate in 7 ml. concentrated hydrochloric acid run around the sides. Bring the solution to the boil again and re-precipitate as before. This time the sides of the beaker must be rubbed with a policeman during washing. When washing is complete the total volume will be about 170 - 200 ml. Ignite the filter paper and precipitate in a tared porcelain crucible in a muffle furnace at 800°-900°C to constant weight (approximately 2 hours). Cool and weigh. The weight of the ignited precipitate (consisting of  $\text{Fe}_2\text{O}_3$  plus  $\text{Al}_2\text{O}_3$  and  $\frac{1}{2} \text{TiO}_2$  and  $\text{P}_2\text{O}_5$ ) is reported as weight of total oxides.

The filtrate in the conical flask contains calcium, magnesium and manganese. Heat this nearly to boiling, and evaporate gently to about 100 ml.

#### 4.45 Determination of Calcium.

Add 1 ml. acetic acid, 10 drops Bromo-Cresol green and 5 ml. 20% oxalic acid. Run 50% ammonium hydroxide into the boiling solution until the colour changes to greenish blue, at pH 4.2. Keep the solution warm at a low heat for  $\frac{1}{2}$  hour and leave it to cool overnight. Filter it through asbestos in a Gooch crucible into a 500 ml. conical flask, using an adaptor and suction tube fitted to a rubber bung which fits the 500 ml. flask. Use only gentle suction as the flask is thin. This method saves time in transferring the filtrate from the filter flask to the evaporating flask which is used for the next operation. Wash the precipitate six times with hot water. Place the Gooch crucible in the same beaker, add 2 ml. 50% sulphuric acid and 50 ml. water. Heat to 70°C and titrate with N/100 potassium permanganate.

1 ml. N/100 potassium permanganate = 0.23 mg. CaO.

#### 4.46 Determination of magnesium and manganese.

To the 500 ml. conical flask containing the filtrate from the calcium determination add hydrochloric acid until the colour changes to yellow, followed by 20 ml. nitric acid. Boil the solution until nitrous fumes are evolved (this removes excess ammonium salts). Evaporate the solution gently to complete dryness and fuse the salts on the bottom of the flask. Remove the flask from the heaters, cool it and dissolve the salts in 5 ml. concentrated hydrochloric acid and about 10 ml. water. Warm to assist solution. Wash the solution into a 300 ml. conical beaker, keeping the volume to about 70 ml, add 2 drops bromo-

A standard curve prepared from standard solutions containing 0.05 to 0.50 mg. of iron, neutralise with 50% ammonia, and add 1 drop concentrated hydrochloric acid to turn it just acid. Add 10 ml. 20% microcosmic salt ( $\text{NH}_4\text{NaHPO}_4 \cdot 4\text{H}_2\text{O}$ ), stir and add 10 ml. concentrated ammonium hydroxide. Boil and allow to stand overnight. Filter off the precipitate through a 9 cms. No. 32 Whatman filter paper and wash it with 0.5 N ammonium hydroxide. Discard the filtrate and place the filter paper with the precipitated magnesium and manganese ammonium phosphate in the original beaker used for the precipitation. Leave them overnight in a warm room, so that by morning all free ammonia will have volatilized. Spread the paper on the side of the beaker by means of a glass rod, run in 10 ml. N/20 sulphuric acid, and by rotation of the beaker assist the solution of the precipitate from the paper. Wash down the paper and the sides of the beaker with hot distilled water and warm, if necessary, to dissolve the precipitate. When all is dissolved, push the paper down into the solution, add eight drops brom-cresol green indicator and back-titrate with N/20 sodium hydroxide to determine the sum of magnesium and manganese ammonium phosphates.

4.45. Determination of Iron.

4.461. Determination of manganese.

To the solution, after titration with sodium hydroxide, add a few drops of concentrated sulphuric acid and filter it through an 11 cms. No. 4 Whatman filter paper into a 150 ml. porcelain evaporating basin. Wash the paper with hot distilled water and collect the washings in the same basin. Evaporate the solution to dryness at a low temperature and leave until blackening indicates destruction of the indicator. Cool and add 20 ml. 50% sulphuric acid, 10 ml. orthophosphoric acid and about 30 ml. distilled water. Warm for 15 - 20 minutes and filter the solution into a 300 ml. conical beaker through a 9 cms. No. 32 Whatman filter paper. Wash the paper with hot water until the volume of filtrate and washings is about 30 ml. and add about 0.2 g. potassium periodate. Boil for one minute, keep hot for 5 - 10 minutes and after cooling, make the solution up to 100 ml. in a standard flask. Read the depth of colour in a Spekker Absorbometer, using 4 cms. cells and Ilford spectrum Green filters No. 604. and convert to percentages by use of

in the flask is white or grey. Cool and dilute the bulk to about 70 ml. with cold water, cool again and filter it through an 11 cms. No. 2 fluted Whatman filter paper into a 500 ml. Pyrex beaker. Wash the residue well with hot water - about 150 ml. - and neutralise the solution with concentrated ammonium hydroxide - about 20 ml. Dissolve any ferric hydroxide precipitated with a few drops of nitric acid, add 50 ml. ammonium nitrate (50% w/v containing 20% concentrated nitric acid), heat the mixture to 70°C and run in 50 ml. ammonium molybdate-nitric acid solution made by dissolving 150 g. ammonium molybdate in one litre of distilled water and pouring the solution into 1 litre of nitric acid S.G. 1.20. Stir the mixture when its temperature has fallen to 55°C and leave it to stand overnight. The ammonium phosphomolybdate should be precipitated rapidly in a granular state. If precipitation is too slow or the state of division is too fine the solutions should be thrown away and the determination done again from the beginning.

Filter the precipitate off through a Gooch crucible fitted with a No. 1 Whatman filter paper covered by a small amount of asbestos. Wash it six times with 2% sodium nitrate. Remove the paper and precipitate from the Gooch crucible with a glass rod and put them in the beaker in which the precipitation was done. Wash any precipitate still adhering to the Gooch crucible into the beaker with distilled water, directing the stream into the bottom of the crucible in order to overcome capillary attraction. Dissolve the ammonium phosphomolybdate in an excess (10 - 20 ml.) of N/10 sodium hydroxide and back-titrate with N/10 hydrochloric acid, using thymol blue (sodium salt) as an indicator.

1 ml. N/10 sodium hydroxide  $\equiv$  0.0005 g.  $P_2O_5$ .

#### 4.6 Citric-soluble Phosphorus.

This determination is not usually done, but, if desired, may be made by the following method:-

Weigh 10 g. 2 mm. oven-dry soil into a pint milk bottle. Add 100 ml. 1% citric acid plus sufficient extra 50% citric acid to neutralise

any free calcium carbonate (already determined by the method given in section 3.2.). Cork the bottle and shake it over night in an end-over-end shaker. Filter the contents into a dry 100 ml. conical flask through a dry 9 cms. No. 2 Whatman filter paper. Discard the first few ml. of filtrate. Only about 10 ml. need be filtered as only 2.5 ml. are required for the estimation.

Pipette 2.5 ml. ( $\pm$  0.25 g.) into a small porcelain evaporating basin. Add 0.4 ml. N/1 magnesium nitrate to oxidise phosphorus to orthophosphate. Evaporate the solution to dryness on a water bath at a low temperature. Care is required at this stage. Increase the heat slowly until the magnesium nitrate is decomposed. If the heat is increased too quickly a minor explosion occurs and the residue is blown away. When the gentle reaction has taken place, place the basin in a muffle at 500°C for half an hour. Cool, and extract the residue, which should be light in colour, with 10 ml. water and 2 ml. N/1 sulphuric acid. Warm it for 15 - 20 minutes on a water bath, break up any lumps with a glass rod and filter it through a 9 cms. No. 32 Whatman filter paper into a 100 ml. measuring flask, and wash the residue on the filter paper with hot water until the volume of filtrate is about 70 ml. Add 1 drop of phenolphthalein and add N/1 sodium hydroxide until a pink colour appears. Just discharge the pink colour with 1 or 2 drops of 2N sulphuric acid and add 1 ml. ammonium molybdate solution. Shake, make the solution up to the mark with distilled water, add 0.4 ml. stannous chloride solution, shake and stand for 15 minutes and read the depth of colour in a Spekker Absorptiometer, using 1 cm. cells and red filter No. 608 Ilford Spectrum. Read off the quantity of  $P_2O_5$  from a standard curve, prepared the same day, covering a range from 0.01 to 0.20 mg.  $P_2O_5$  per 100 ml.

When large batches are being examined, the following procedure is used. The shaker will hold 20 bottles. Sixty soils can be done by one person in one week of five days.

First day: Prepare reagents and apparatus. Weigh out the first batch and put it on the shaker.

Second day: Filter, pipette, evaporate, ash and extract. Wash the shaker

bottles and weigh out a fresh batch and put them on the shaker. Continue this procedure for four days. A set of standards and blanks are pipetted into basins, all reagents are added and the standards are put through as soil extracts. On the fifth day neutralise the extracts, add 1 ml. ammonium molybdate and make the solutions up to the mark. Add 0.4 ml. stannous chloride at  $1\frac{1}{2}$  minute intervals to 10 samples at a time; the first will be ready to read in the Spekker Absorptionmeter when the last one has had stannous chloride added. Continue this procedure until the solutions have all been read. (An assistant to develop colours will speed the operation; stannous chloride being added to one sample each time one is read off after the first ten have been read). Plot the standard curve and read off the unknowns.

Reagents required:

Stock solution = 1.9168 g.  $\text{KH}_2\text{PO}_4$ /litre = 1 mg.  $\text{P}_2\text{O}_5$ /ml.

Dilute solution = 5 ml. stock solution made to 500 ml. = 0.01 mg  $\text{P}_2\text{O}_5$ /ml.

Use 1 ml. to 20 ml. for the standard curve determinations.

Ammonium molybdate:

Add 100 ml. 10% aqueous ammonium molybdate to 300 ml. 1-1 sulphuric acid. If it is stored in a dark bottle it will keep for 1 - 2 months.

Stannous chloride:

Prepare the solution freshly each day. 0.1 g. tin foil is dissolved in 2 ml. concentrated hydrochloric acid and made up to 10 ml. with water.

For soils containing free calcium carbonate add 0.28 ml. 50% citric acid for each 1% calcium carbonate before shaking.

CHAPTER V.

Analytical Methods.

Physical.

5.10. Mechanical Analysis.

The International Soda Method of Robinson and Richardson (Imp. Bureau of Soil Science., Tech. Comm. No. 26. 1933. 27-28. and Wright. Soil Analysis. 2nd. edition 1939. pp. 39-46. Pub. Murby) is used.

Weigh 10 g. soil passing a 2 mm. sieve into a 600 ml. beaker. Add 60-100 ml. of 20 volume hydrogen peroxide to oxidise organic matter. If manganese dioxide is present in large quantities, the soil should first be boiled with 50 ml. water and about 1 g. sodium bisulphite until evaporated to about half the original bulk. Then add 60 - 100 ml. 20 volume hydrogen peroxide and heat the mixture on a water bath until frothing has subsided. Gently bring the contents of the beaker to the boil and continue boiling for 30 minutes with a watch glass covering the beaker. Remove the watch glass and evaporate the water off to leave a final volume of about 30 ml. If much organic matter is present a further addition of 60 ml. hydrogen peroxide (20 volume) and repetition of the process until all organic matter is oxidised may be required. Finally, boil the liquid down to about 30 ml., add 200 ml. water and sufficient 2 N hydrochloric acid to decompose any free calcium carbonate, (1% calcium carbonate requires 1 ml. 2-N hydrochloric acid when 10 g. soil is taken), followed by an excess of 20 ml. 2 N hydrochloric acid. Stir and leave the mixture to stand overnight.

Filter the solution through a 9 cms. Whatman filter paper on a Buchner funnel into a 500 ml. filter flask. It may be necessary to stick the edges of the filter paper to the funnel with Durofix. Wash the solids on the paper with hot water until they are free from chlorides. Rub the beaker with a policeman to remove any soil adhering to the sides. Pour the filtrate into a beaker and evaporate to about 50 ml. for determination of dissolved sesquioxides, or "Loss by Solution". Wash the soil while still damp from the Buchner funnel into a 1 pint milk bottle through a 70 I.M.M. sieve which is placed in a suitable size ordinary funnel. Use a hot-water bottle with a fine jet thus: First run a glass

rod with a policeman attached around the outside of the soil in the Buchner funnel to expose the edge of the filter paper. Wash the rod and direct the washings into the sieve, and with a thin spatula or section lifter lift the filter paper and soil out of the Buchner funnel, holding the funnel and paper over the sieve so as to catch in the sieve any coarse particles which may be loosened in the process. Hold the paper containing the soil on the fingers and palm of the left hand and bend it into the shape of a trough directed downward towards the sieve. Direct a jet of hot water on to the bottom half of the paper and wash the soil on it into the sieve. When the bottom half of the paper is reasonably clean, rotate the paper and wash the other half likewise. Remove the last traces of soil from the paper with a strong jet and discard the filter paper. Now, holding the Buchner funnel over the sieve, wash off any adhering soil, using a policeman if necessary. Wash the soil on the sieve with a jet of hot water and rub it lightly with a policeman until it is free from silt and clay, leaving coarse sand on the sieve. (See Section 5.16.) The volume of water in the milk bottle after this operation should be about 400 ml. Add 4 ml. N. sodium hydroxide and place the bottle in an end-over-end shaker. Shake it overnight.

5.11. Determination of Dissolved Sesquioxides in the filtrate.

When the volume of the filtrate has been reduced by evaporation to about 50 ml. add 5 ml. concentrated nitric acid and boil it for about 5 minutes. Add 50% ammonia from a burette until hydroxides have been precipitated, avoiding adding a large excess of ammonia. Boil for 2 minutes to coagulate the precipitate. Filter the solution through an 11 cms. No. 31 Whatman filter paper and wash the precipitate free from chlorides with hot 5% ammonium nitrate. Place the filter paper and precipitate while still wet in a tared porcelain crucible and ignite for 1-2 hours at 800°C in a muffle furnace. There will be no loss by spluttering and the oxides will be left in a good granular state if the crucible and wet contents are placed directly in the hot muffle. The weight of oxides is reported as "loss by solution", or dissolved sesquioxides.

5.12. Determination of Silt, Clay and Sand.

After having been shaken overnight the soil suspension is washed into a 500 ml. measuring cylinder and the volume of liquid is made up to the mark.

5.13. Silt plus Clay.

The cylinder containing the suspension is closed by a rubber bung, inverted and all sediment on the bottom is loosened by vigorous shaking. The temperature of the suspension is taken and the whole is then thoroughly mixed for 1 minute by a reciprocating movement of the hand before being placed under the special 20 ml. pipette in the A.S.A. sampling apparatus. A stop watch is set in motion immediately. The two-way tap in the pipette is turned off and the attached long rubber tube is flattened by suction. The tip of the pipette is now lowered to touch the surface of the suspension. After consultation of the temperature and velocity tables the depth of sampling is ascertained, i.e. if the temperature is 20°C and depth of sampling to be = 10 cms. then the corresponding time of sedimentation is 4 mins. 48 secs.

Temperature °C	Viscosity (cp.)	Times of Sedimentation			Depths of Sampling. cm.
		Clay hr. min.	Silt min. sec.		
10	1.310	10 23	6 14	7.7	
11	1.273	10 6	6 3	7.9	
12	1.239	9 49	5 54	8.1	
13	1.206	9 34	5 44	8.4	
14	1.175	9 19	5 35	8.6	
15	1.145	9 5	5 27	8.8	
16	1.116	8 51	5 19	9.0	
17	1.087	8 37	5 10	9.3	
18	1.060	8 24	5 3	9.5	
19	1.034	8 12	4 55	9.8	
20	1.009	8 0	4 48	10.0	
21	0.984	7 48	4 41	10.3	
22	0.961	7 37	4 34	10.5	
23	0.938	7 26	4 28	10.8	
24	0.916	7 16	4 22	11.0	
25	0.895	7 6	4 15	11.3	

Temperature °C	Viscosity (cp.)	Times of Sedimentation				Depths of Sampling. cm.
		Clay		Silt		
		hr.	min.	min.	sec.	
26	0.875	6	56	4	10	11.5
27	0.855	6	47	4	4	11.8
28	0.836	6	38	3	59	12.1
29	0.818	6	29	3	54	12.3
30	0.800	6	21	3	48	12.6

About 20 seconds before this time expires, the tip of the pipette is gently lowered to the required depth. When the time has expired the two-way tap of the pipette is turned and the vacuum in the rubber tube causes a sample of the suspension to be sucked up into the pipette. This must be done fairly slowly so as to avoid eddies in the suspension. When the level of the suspension in the pipette has risen just above the tap, the tap is turned off and the pipette raised to allow removal of the cylinder. The remaining vacuum is now released from the rubber suction tube, and the two-way tap turned to enable the excess suspension to be blown out into the cylinder. The contents of the pipette are now emptied into a tared Pyrex evaporating basin 5 cms. diameter, and the pipette is allowed to drain for 15 seconds. The suspension is dried in an oven at 100°-105°C and weighed. The difference between full and empty weights of the basin divided by 0.004 = percentage silt plus clay.

#### 5.14 Clay.

The procedure for clay is similar to that for silt plus clay, except that the suspension must stand for 8 hours at 20°C before a sample is taken. The room in which clays are determined should have a fairly constant temperature, that is, it should not vary by more than 5°F over a day, and it should also be free from vibration. Temperatures must be read at hourly intervals during the settling period, and the mean taken to determine the depth and time of sampling.

When a series of determinations are being run together, 5 minutes should be allowed between each shaking. If possible, the pipetting apparatus should be moved over each cylinder of suspension in turn to avoid disturbing the suspensions when sampling. If this is not possible, because of lack of space, great care must be exercised when the cylinder containing the suspension is being moved into position. Evaporate and weigh the sample as before.

$$\frac{\text{Weight}}{0.994} = \text{percentage of clay.}$$

The percentage of silt is obtained by subtracting the percentage of clay from the percentages of silt and clay.

5.15. Fine Sand.

The suspension is allowed to settle for about 1 hour, or overnight to allow the fine sand to settle on the bottom of the cylinder. The liquid is then carefully decanted, leaving the fine sand with some adhering silt and clay on the bottom. This is now washed into a 600 ml. tall beaker and the beaker filled with water up to a height of 10 cms. The suspension is stirred and allowed to settle for 4 minutes 48 seconds at 20°C or for any time corrected according to temperature. Cautiously pour off the suspension, leaving the fine sand on the bottom of the beaker; then make the liquid up to 10 cms. depth again with distilled or filtered tap water. This decantation is repeated until no silt or clay remains in suspension at the end of the settling period. If filtered tap water is used, a final sedimentation with distilled water should be done to avoid errors due to dissolved solids in the tap water. The fine sand is now washed into a medium-sized tared evaporating basin, taken to dryness on a water bath, dried in an oven for 1 hour at 100°C, and weighed. The weight X 10 = the percentage fine sand.

5.16. Coarse Sand.

The material retained on the sieve consists largely of coarse sand, but Beater (J. Agric. Sci. 1937. 27. 123-125) has shown that surface tension holds on the coarse sand particles and the sieve wires a proportion of fine sand which is considerable in soils containing more than about 50% total sands.

In order to obtain a more accurate determination of the proportion of the two sand fractions the 70 I.M.M. sieve with the wet retained material is placed on a clean clock glass and dried at 105°C in an oven. When the contents of the sieve are dry gentle tapping of the sieve will cause the fine sand particles to fall through on to the clock glass. These are weighed and the fine sand percentage found in the method given in section 5.15 is corrected to give the true percentage.

The coarse sand retained on the sieve is weighed and the weight in grams

multiplied by 10 gives the percentage coarse sand present in the soil sample.

The sum of coarse sand, fine sand, silt, clay and dissolved sesquioxides and free calcium carbonate should total 100% within about 2% except when there are large percentages of organic matter or calcium carbonate

5.2. present. Electrode and Quinhydrone Electrode.

5.17 General Technique.

The method of operation of the potentiometer is usually set out in a booklet supplied by the makers of the instrument. It is convenient to run mechanical analyses in batches of a dozen, which 10 g. 2 mm. air dry soil into a 50 ml. Pyrex beaker. Add 25 ml. glass-distilled water, stir and leave to stand overnight. In the morning stir continuous flow of work. The following method has proved satisfactory; the suspension and leave it for at least 30 minutes. Then stir again for 1 assuming one batch to be oxidised and standing over the weekend with minute and place the beaker so that the electrodes are immersed in the sus-hydrochloric acid.

Monday morning: start these filtering, weigh out a new batch of soils If a quinhydrone electrode reading is also required add 0.1 g. quinhydrone and hydrogen peroxide and leave standing in a warm place. Meanwhile filter hydrous, stir, immerse the electrodes in the suspension and read after 1 minute, and wash the first batch into shaking bottles and put them in the shaker.

The following technique is used for large batches. After the first weigh the coarse sands.

Tuesday: Transfer the dispersed suspension to cylinders. Dry and weigh electrodes with distilled water and place the second beaker containing the 12 Pyrex evaporating basins and sample the silts and clays. Leave then soil suspension, which has previously been stirred, under the glass electrode in the oven overnight to evaporate. Also place in the oven another 12 while waiting to take the second reading add quinhydrone to the first beaker, clean Pyrex evaporating basins for clay determination.

Wednesday: At 9.00 a.m. shake suspensions and leave them to stand 8 hours third soil suspension in preparation for glass electrode reading. Take the for clay determinations. Weigh the silt and clay samples and the basins glass electrode reading on the second soil at the end of 5 minutes and for clay samples. At 4.00 p.m. begin sampling the clays, placing the clay continue alternate glass electrode and quinhydrone readings throughout the samples in the oven to evaporate, together with twelve 50 ml. evaporating basins drying off for determination of fine sand.

5.3 Thursday: Weigh the clay samples and the basins for fine sands. Do the fine sand determinations, using an electrically driven stirring apparatus which takes 6 beakers at a time. Between the decantations stir for one minute. At the end of the minute reverse the direction of stirring for a few seconds to stop swirling of the suspension. Start the stop watch immediately after this occurs, and after 4 min. 43 secs. at 20°C (or equivalent time for other temperatures) pour off the suspension, leaving the fine sand on the bottom of the beaker. Add more water (1 ml.) well and read and test.

Friday: (or at odd times during the current week) A second batch of samples is heated with hydrogen peroxide and treated with hydrochloric acid ready

and knead again and test with the spatula.

The rolling and kneading should be done until the mixture of soil and water is homogeneous.

A small sample of the ball (at the correct sticky point) should be cut off and put on a numbered paper so that its sticky point colour may be determined from a colour chart. The rest is put into a small, numbered and weighed glass dish and weighed.

The glass dish and contents are placed in an oven (100 - 105°C) and dried overnight. The dish is then allowed to cool in a desiccator and weighed, and the percentage of moisture at the sticky point is calculated as a percentage of the air-dry soil.

5.4

Keen-Raczkowski Measurements.

These determinations give in one operation the following parameters:

- (a) Apparent density
- (b) Moisture in saturated soil
- (c) Pore space
- (d) Specific gravity of soil
- (e) Volume expansion of 100 ml.

The method and apparatus used are those of J.R.H. Coutts (J. Agric. Sci. 1930. 20. 407-13). The boxes consist of a one inch length of brass tubing 2 ins. in diameter having a flange fastened to one end. This circular flange fits flush on to a circular brass plate of the same diameter and the two are held together by four finger nuts and screws. The plate is perforated with 70 small holes. A 5.5 cms. diameter filter paper can be held tightly between the flange and the plate and this forms the bottom of a circular box 2 ins. diameter and 1 inch deep.

The technique is given by Wright (Soil Analysis. 2nd. edition. 1939. Pub. Murdy, pp. 13-15) as follows:

The air-dry soil under examination, which has passed a 1 mm. sieve, is sieved through a 100 mesh sieve in order to break up the compound particles; the portion passing the sieve is then remixed with the particles held by the 100 mesh sieve. After fitting a piece of filter paper in position the box is weighed. It is then filled with the soil sample in a systematic way, so that the method of packing may be as uniform as possible. From 8 to 10 gm. are added at a time, and the box is tapped on the bench after each addition.

When the box is nearly full, sufficient soil is added to allow the surface to be struck off flat with a spatula. The upper edge of the box is then tapped smartly with the edge of the spatula and more soil is added. This is struck off flat as before, and the process is repeated until very slight settling of the soil occurs, when the surface is finally struck off flat and the box and contents are weighed. The box and contents are then placed in a flat-bottomed dish containing about  $\frac{1}{2}$  in. depth of distilled water and left over-night. When a number of boxes are placed in the same dish, additions of water must be made at intervals to keep the level constant. During the wetting considerable movement takes place, the top of the block of soil retreating from the sides of the box, and at the same time rising in height. When the interstices are saturated the wet soil expands to the sides of the box, but the vertical expansion remains. The next morning the boxes are rapidly dried on the outside, weighed and replaced in the water for a few minutes. The portion of the soil which has expanded above the top of the box is then removed with a razor blade, which is held at a slight angle with the horizontal, placed on the edge of the box and then drawn across the top. The surplus soil is transferred from the razor blade to a glass dish and weighed. Any soil adhering to the under side of the razor blade should not be placed in the dish, but must be replaced in the box to which it belongs. The box and residual soil are weighed, and then placed, together with the dish containing the surplus soil, in an oven to be dried. When dry they are allowed to cool in a desiccator and weighed again.

In addition to these weighings it is necessary to determine in the usual way the moisture present in the air-dry soil used in the experiment, and to measure the weight of water taken up by the filter paper, which is best done by taking six pieces, saturating them with water, removing the surplus with a glass rod and finding the increase in weight.

the necessary weighings and measurements are:

Weight of box plus filter paper .. .. .	a gm.
" " plus " " plus air-dry soil .. .. .	b "
" " plus wet filter paper plus saturated soil .. .. .	c "
" " plus " " " plus saturated residual .. .. .	d "
" " plus dry " " Plus oven-dry residual .. .. .	e "
Weight of glass dish .. .. .	f "
" " plus saturated surplus soil . . . . .	g "
" " plus oven-dry " " . . . . .	h "
Percentage of moisture in air-dry soil .. .. .	x
Internal volume of box .. .. .	v c.c.

from these measurements the following results are obtained:

- (1) Apparent density =  $(b - a)/v$
- (2) The moisture content of the saturated soil, i.e., the weight of water taken up by 100 gm. of soil =

$$\frac{(c - a) - (b - a)}{(b - a)} \times 100$$

Correct  $(b - a)$  for the x per cent of water contained in the air-dry soil, and  $(c - a)$  for the water in the filter paper.

- (3) Pore space (per cent) =  $\frac{(d - a) - (a - a)}{v} \times 100$

Correct  $(d - a)$  for the water in the filter paper.

- (4) Specific gravity of soil =  $\frac{(g - a)}{v - (d - e)}$

- (5) Volume expansion of 100 c.c. of soil =

$$\frac{(g - h) \text{ plus } \frac{h - f}{\text{sp. gr.}}}{v} \times 100.$$

5.5. Ridgway colours.

Several methods of measuring and recording quantitatively the colours of soils are given in the literature and are conveniently summarised by Piper (Soil and Plant Analysis. 1942. Pub. Univ. Adelaide Press. pp. 112-116.)

The Ridgway Colour Atlas has been used for convenience in this work up to the present but will no doubt be superseded before long by some more accurate method. When comparing soil samples with the Ridgway Atlas it is convenient to view them through a rectangular aperture, of the same size as the colour specimens in the atlas, cut in a piece of grey card.

Chapter VI.

Other Analyses.

6.1 Available Cobalt in Soils.

Colorimetric Nitroso-R-salt method for soils containing from 0.05 - 1.00 p.p.m. cobalt.

6.11 Extraction and preparation of solution.

Weigh 12.5 g. 2 mm. soil into a shaking bottle, add 500 ml. 2.5% acetic acid and shake the mixture overnight in an end-over-end shaker. Filter the solution through a 27 cms. No.2. Whatman filter paper in a fluted funnel. Alternatively a fluted paper may be used in a plain funnel. The filtrate is collected in a clean, dry 500-ml. conical flask. Pour 400 ml. into a measuring cylinder, discard the remainder in the flask and return the 400 ml. to the flask, which will then contain a volume of extract corresponding to 10 g. soil.

Evaporate the contents of the flask gently overnight, taking precautions against the entry of dust, so that by the morning the volume will be sufficiently small to allow the solution to be boiled without risk of loss by splashing. Boil it until about 20 ml. are left, remove the flask from the source of heat, add 2 ml. concentrated nitric acid and bring the solution to the boil again. Cool it and wash it into a 70 ml. vitreosil evaporating basin. Evaporate the solution to dryness at a low temperature and ignite the residue for 30 minutes at 500°C in a muffle. Allow the basin and contents to cool, add 5 ml. 5.5% hydrochloric acid containing 1% nitric acid, and digest the mixture for 15 minutes on a water-bath, using a glass rod to loosen any solids adhering to the sides of the basin. Filter the extract through a 7 cms. No. 32 Whatman filter paper into a test-tube graduated at 20 ml. and wash the residue on the paper four times with approximately 4 ml. of hot distilled water. The volume of filtrate and washings collected should be between 20 and 25 ml. Stand the test-tube and contents in an oven at 100° - 105°C overnight to evaporate the contents to about 10 ml.

6.12 Development of Colour.

To the extract, whose volume must not exceed 14 ml., add 1 ml. 0.25% aqueous nitroso-S-salt, and 2 g. sodium acetate (hydrated). The latter may conveniently be measured out in a 2 ins. by  $\frac{1}{8}$  in. specimen tube. Stir the mixture with a glass plunger (made by heating one end of a length of glass rod to red-heat and pressing it vertically on an asbestos mat) until the salts are dissolved. With the plunger left in the tube make up the volume of the solution with distilled water to just under 20 ml. Place the tube and contents in a steam bath to heat for 5 minutes, remove it from the bath, add 2 ml. concentrated nitric acid and mix it in thoroughly with the plunger. Replace the tube and contents in the steam bath for a further two minutes. Remove them from the bath and allow them to cool screened from strong light. Lift the plunger above the solution, rinse it with cold water and make up the volume of solution to 20 ml. Mix it with the plunger again which may then be discarded. After 4 hours read the light absorbtive power of the solution in a Spekker Absorbtiometer, using rectangular 4 cms. cells of 20 ml. capacity and an Ilford spectrum Green filter No. 604. Compare the readings made with those shown on a standard curve made on the same day by the use of the same reagents on 5 ml. 5.5% hydrochloric acid and 1% nitric acid containing known quantities of cobalt.

The range is from 0.5 Y to 10.0 Y. Co.

Blank determinations should be run with each batch on 400 ml. of 2.5% acetic acid.

6.13. Reagents required:

Concentrated nitric acid     Analar.  
Concentrated hydrochloric acid     "  
2.5% acetic acid     "  
Sodium acetate hydrated.     "  
5.5% hydrochloric acid plus 1% nitric acid     Analar.  
0.25% nitroso-S-salt

Strong standard cobalt solution. 1.0 mg. Co/ml. = 2.0175 g  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  per 500 ml.

Dilute standard cobalt solution. = strong Co. solution diluted 1 - 1000 = 1 Y Co. per ml.

Apparatus required:

Shaking bottles (20)  
Moulded funnels 6 ins. diam. (20)  
500 ml. Pyrex conical flasks (20)  
Monax or Pyrex test-tubes 6"x $\frac{1}{8}$ " internal, graduated at 20 ml. (30)

Steam bath with stand to hold 30 test-tubes.  
Vitreosil evaporating basins 70 ml. (20)  
Glass plungers 7" x 5 mm. (30)

Recommended procedure.

It is most convenient to do 15 soils in a batch. A shaker which holds 20 bottles would include also 3 duplicates and 2 blanks in a series, making a total of 20 bottles. All blanks receive the same treatment as soils including all filtrations etc. Standards all contain 5 ml. 5.5% hydrochloric plus 1% nitric acid. Range as follows:

Y Co. 0 0.5 1.0 2.0 4.0 6.0 8.0 10.0 12.0 14.0 Y Co.

Calculation: 1.0 Y Co. in 10 g. soil.

**SOIL SURVEY OF ENGLAND AND WALES.**

Centre ..... Profile No. .... Series Name .....  
 County ..... Laboratory No. .... Date of Collection .....  
 Date of receipt of sample ..... Date of Report ..... Name of Collector .....

**NOTE:** 1. All percentages are calculated to oven-dry weight of samples (except for items 19-23 inclusive).  
 2. Soils are re-carbonated after ignition in 11.

**PHYSICAL DETERMINATIONS.**

	Horizon Number	1	2	3	4	5	6
1	Stones in bulk						
2	Moisture 100° - 105° C						
3	Coarse Sand						
4	Fine Sand						
5	Silt						
6	Clay						
7	CaCO <sub>3</sub>						
8	Sum of mechanical fractions						
9	Difference from 100%						
10	Dissolved R <sub>2</sub> O <sub>3</sub> included in (6)						
11	Loss on ignition						
12	Sticky-point moisture						
13	Moisture equivalent pF3						
14	True density						
15	Apparent density						
16	Pore space						
17	Moisture in saturated soil						
18	Volume expansion of 100 cc. soil						
19	pH glass electrode						
20	pH quinhydrone electrode						
21	Ridgway colour air-dry						
22	„ peroxidized						
23	„ at sticky-point						
24							
25							
26							
27							
28							



COUNTY .....  
PROFILE No. ....  
HORIZON No. ....

---

COUNTY .....  
PROFILE No. ....  
HORIZON No. ....

**EMPTY CASE.**

To.....

.....

.....

STATION..... RLY.....

SENDER:

**THE LABORATORY,  
DARTINGTON HALL TRUSTEES, TOTNES, S. DEVON.**

DATE.....  
REVERSE LABEL WHEN RETURNING.

COUNTRY .....  
 PROFILE No. ....  
 HORIZON No. ....

---

COUNTRY .....  
 PROFILE No. ....  
 HORIZON No. ....

**SOIL SAMPLES.**

TO: **THE LABORATORY,**

**DARTINGTON HALL TRUSTEES,  
 TOTNES, S. DEVON.**

STATION: **TOTNES G.W.R.**

**BY GOODS TRAIN.**

Name and Address of Sender.....

Date of Dispatch.....