AG : BOT/85/011
FIELD DOCUMENT 3

Soil Mapping and Advisory Services

Botswana

# SOIL TESTING PROCEDURES FOR SOIL SURVEY

## Part 1
## Theoretical background and modifications of standard procedures

FOOD & AGRICULTURE ORGANIZATION OF THE UNITED NATIONS

UNITED NATIONS DEVELOPMENT PROGRAMME

REPUBLIC OF BOTSWANA

GABORONE, 1988

AG: BOT/85/011

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Soil Mapping and Advisory Services

Botswana

# SOIL TESTING PROCEDURES FOR SOIL SURVEY

## Part 1 : Theoretical background and modification of standard procedures

by

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Food and Agricultural Organization Of The United Nations
United Nations Development Programme

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# INTRODUCTION

In view of the increasing rate of population and severe drought conditions over the last years the Government of Botswana has given high priority to measures improving self-reliance in food production.

To develop optimal land use systems sound knowledge of soil characteristics is imperative. As early as 1979 the Government of Botswana requested technical assistance from UNDP/FAO in soil classification and land evaluation.

A full scale project, 'Soil Mapping and Advisory services', was implemented as BOT/80/003 phase I and phase II in 1981.

The overall Government objective has been that the project should help improve the basis for medium and long term planning of agricultural and rural development.

The immediate objectives for the project are:

Establishment of an effective soil survey section and a soil analytical laboratory.

Training of national staff for these sections.

Initiation of a systematic national soil mapping programme at reconnaissance level to identify the most suitable areas for arable farming.

Phase III started in 1985 as BOT/85/011. Additional immediate objectives are semi-detailed and detailed scale soil surveys according to the needs of Government.

The FAO soil chemist (associate expert) arrived in the country in March 1982.

From 1982 till January 1985 the laboratory was accomodated in the plants analytical section of the Agricultural Research station at Sebele. The available working space was two laboratory benches or about 20 $m^2$.

After redesigning the layout the laboratory was accomodated together with the Agricultural Research soils laboratory. The total available space for the soil survey laboratory now is about 35 $m^2$.

The laboratory was designed to serve exclusively soil survey and related activities. Analysis for soil fertility recommendations are carried out by the Agricultural Research laboratories.

Minimum staff requirements for the laboratory are:

One counterpart with a BSc in chemistry or environmental science with a minor in chemistry.

One senior laboratory technician with a Diploma in science laboratory technology.

Six to eight junior laboratory technicians.

Two cleaners for laboratory glassware.

The two most critical factors in the laboratory are lack of space and lack of professional and technical staff.

The first untrained laboratory technician started work only in October 1982., the second in January 1983. Until to date the number of junior laboratory staff never exceeded five. The post of senior laboratory technician has only been filled in November 1987 by a United Nations Volunteer, a suitable counterpart has not been identified yet.

Junior laboratory staff are recruited as trainees. After two years in service on the job and, if possible, successful participation in a part time laboratory assistants course at Botswana polytechnic they are promotied to technical assistant. After two further years of probation the technicians are fully integrated into the Botswana Government system. Depending on their qualifications they then can be sent abroad for Diploma and Higher Diploma courses.

The relative long period of four years before getting the opportunity for full time training distracts many applicants and also results in staff quitting when they see faster ways for promotion or training. This is one of the reasons why it is difficult to maintain permanently the required minimum staff of 6 junior technicians.

The above mentioned constraints required tailoring of the programme to the absolute minimum. Determination of a number of important soil properties had to be put aside until new facilities are made available, the staff situation has improved and/or the amount of samples coming to the laboratory for standard analysis is reduced.

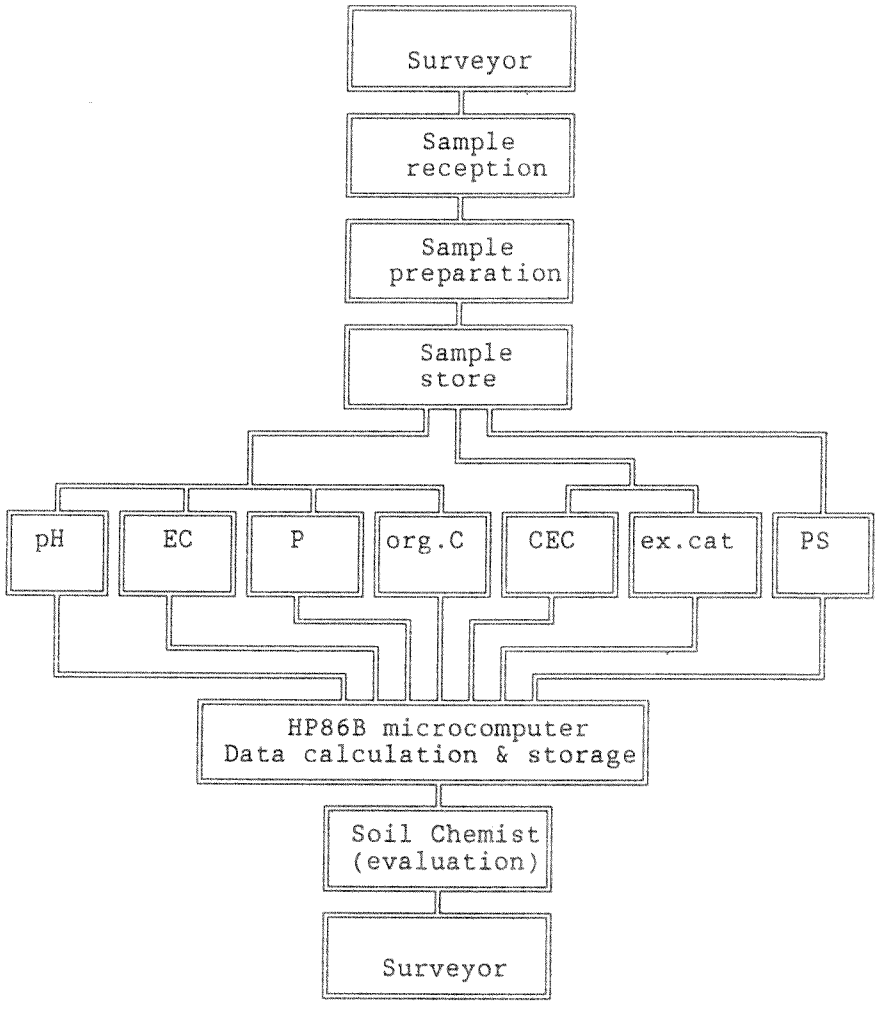
The report has been divided into three parts:

Part I gives a short introduction to the theortical background of the different determinations their relevance for soil classification and the principles of the methodes applied.

Part II is the laboratory procedures manual to be used by the laboratory technicians. It describes in detail the procedures presently performed in the standard analytical programme.

Part III is a statistical analysis of the reproducibility and repeatability of laboratory data. It gives an indication of the magnitude of the error each determination is subjected to. A knowledge of these limitations should help the surveyors in interpretation and correlation of their field observations with analytical data since it can often be observed that once figures have been noted down they are seen as the absolute which may easily lead to misinterpretations and wrong classifications.

ORGANIZATION FLOWCHART OF THE LABORATORY



## 1. SOIL REACTION (PH-DETERMINATION)

### 1.1. Soil reaction and soil properties:

The determination of pH values is one of the essenytial and most relevant chemical measurements made in soils.

(pH = negative logarithm of the $H^+$-ion activity.)

Soil pH affects many soil properties such as the availability of plant nutrients or the occurrence of toxic ions like aluminum (see figures 1 and 2).

### 1.2. Conclusions to be drawn from pH measurements:

From the measurement of the soil pH the following general conclusions can be drawn (Buol, 1980):

pH < 3.5: Acid sulfates may be present

pH < 4.5: A significant amount of exchangeable hydrogen and exchangeable aluminum is most probably present.

Sources of the hydrogen could be:

a. Dissociation from strong acid functional groups in the organic fraction. (Likely to occur only in intergrades to Histosols)

b. Free acid produced by oxidation of sulfur and sulfides to sulfates.

pH 4.5 to 5.2: Sufficient exchangeable aluminum may be present to affect plant growth significantly. Percent base saturation is low.

pH 5.8 to 6.5: A base saturation of 70 to 90%, depending on the clay minerals, can be expected.

pH 6.5 to 8.0: The soil is fully base saturated. No exchangeable aluminum is present. Free $CaCO_3$ may be present.

pH 8.0 to 8.5:The soil is fully base saturated and free $CaCO_3$ is present in the system. The exchangeable cations are mainly Ca and Mg.

pH 8.5 to 10 : The soil contains significant amounts of soluble salts and conductivity is high. An appreciable amount of exchangeable sodium is present, which may be expressed by the occurrance of a natric horizon in the soil.

pH > 10 : The soil is highly sodium saturated - alkali soil.

## 1.3. Principles of pH determination:

Two pH-values are measured:

pH water (1:2.5 soil:distilled water)
pH $CaCl_2$ (1:2.5 soil:$CaCl_2$ solution, 0.01 molar)

pH-water values are usually about 0.5 to 1 units higher than pH-$CaCl_2$ due to the exchange of $H^+$- and/or Al-ions by Ca-ions.

With increasing dilution of the suspension pH values will increase.

In 1930 the International Soil Science Society has adopted a ratio of
1 : 2.5

After two hours shaking samples are allowed to settle for one hour.

pH is measured with a glass electrode and a digital pH-meter. To avoid too long equilibration times the electrode is inserted into the supernatant solution just above the sediment without stirring the soil particles up.

A constant reading is defined when the reading changes less than 0.02 units in 10 seconds.

## 1.4. Drifting of pH-readings in soil suspensions:

Electrodes bathed in a heterogeneous system of a solution plus suspended solid particles are exposed to a considerable density gradient in the vertical direction due to sedimentation. It can be observed that an electrode first placed in the clearest upper part of the supernatant liquid and then lowered into the sediment subsequently gives changing pH-readings - usually from higher to lower values.

This pH-change has been termed **suspension effect.** It can be explained in terms of a diffusion potential at the liquid junction between a concentrated KCl-solution (inside the electrode) and a sediment containing charged surfaces. For a detailed discussion of this phenomenon refer to Bolt and Bruggenwert, 1978.

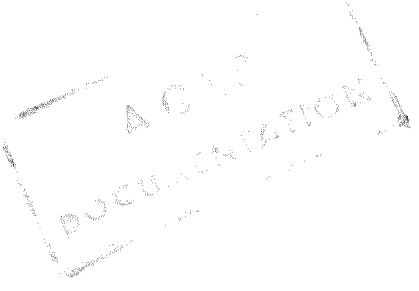


Fig. 1: Solubility of Fe-, Al- and Si- hydroxides in relation to pH values.

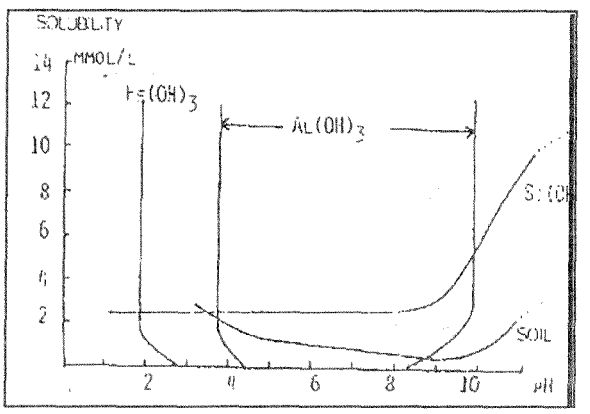
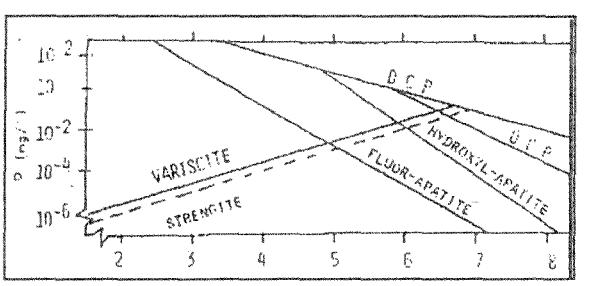



Fig. 2: Solubility of different phosphorus minerals in relation to pH at 25° C (Scheffer and Schachtschabel, 1979).



## 2. ELECTRICAL CONDUCTIVITY

### 2.1. Soluble salts in soils:

Most soils contain some salts in soluble form. These salts are usually chlorides and sulfates, to some extend carbonates, bicarbonates and nitrates.

The salts are mainly formed by weathering of primary minerals and deposited by water. Under arid and semiarid conditions where evapotranspiration is higher than precipitation they are not removed by leaching. In the opposite, due to capillary action they can move upwards and be deposited at the surface. Salt accumulation is preferential in depressions with high clay content and low permeability with reduced leaching.

Plants have different levels of tolerance to salinity. Plant growth can be affected significantly and even completely inhibited.

Electrical conductivity measurements in saturated paste extracts are a relatively fast and accurate method to estimate the concentration of soluble salts in soils as a parameter which can be correlated with plant growth. (Scofield, 1942)

### 2.2. Principles of electrical conductivity determination:

The current in amperes flowing through a conductor is proportional to the electromotive force U [Volts] and inversely proportional to the resistance R [Ohms]

The reciprocal of the resistance is called conductance. It is measured in reciprocal ohms [$ohms^{-1}$] or Siemens S (formerly referred to as mhos).

The conductance of a one meter cube of a substance is called conductivity K or specific conductance and has the unit S/m.

The conductivity of an electrolytic solution is the conductance at 25°C between electrodes 1 cm square and 1 cm apart [S/cm]. In soil solutions the conductivity usually is so low that it is expressed in millisiemens per cm [mS/cm] (previously millimho per cm).

> The conductivity of a salt solution is proportional to its concentration and it increases about 2 percent for every degree Celsius increase in temperature. All values are therefore standardized by converting to equivalent values at a reference temperature of 25° Celsius.

Relations between electrical conductivity and the salt content of various solutions are shown in figure 4. The curves for chlorides and $Na_2SO_4$ almost coincide, $MgSO_4$, $CaSO_4$ and $NaHCO_3$ have a lower conductivity than the others. (US. Salinity Laboratory Staff, 1954)

For good estimation of the concentration of soluble salts from the conductivity of saturated paste extracts figure 5 can be used. (US. Salinity Laboratory Staff, 1954)

For calculation of exchangeable sodium percentage ESP or sodium absorption ratio SAR a quantitative analysis of the soluble cations in the saturated paste extract has to be carried out. Relations between ESP and SAR will be discussed later.

2.3. Method adopted for the laboratory:

Saturated pastes for electric conductivity determinations are extracted with the automatic extractor described in chapter 3.8.

12 samples can be extracted at a time. Saturated pastes are left standing over night for the case that gypsum is present. The extraction time is set to one hour.

Figure 3 shows the configuration of the extractor used when extracting from soil paste. One extraction cup takes the saturated paste prepared from about 200 g of sample.

Fig. 3: Configuration of automatic extrator extracting from saturated soil paste.

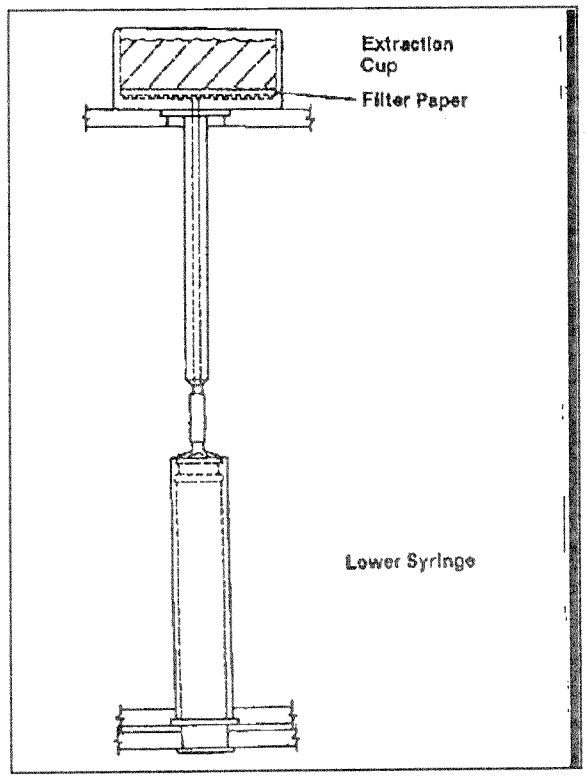


Fig. 4: Relation of concentration of single salt solutions to electrical conductivity. (US. Salinity Laboratory Staff, 1954)

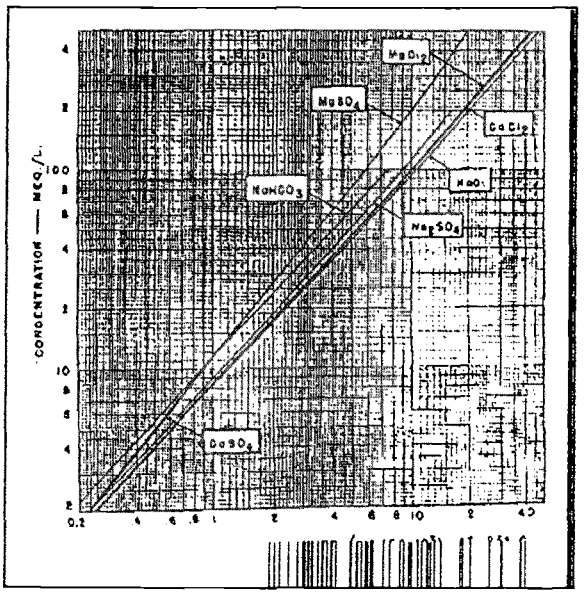
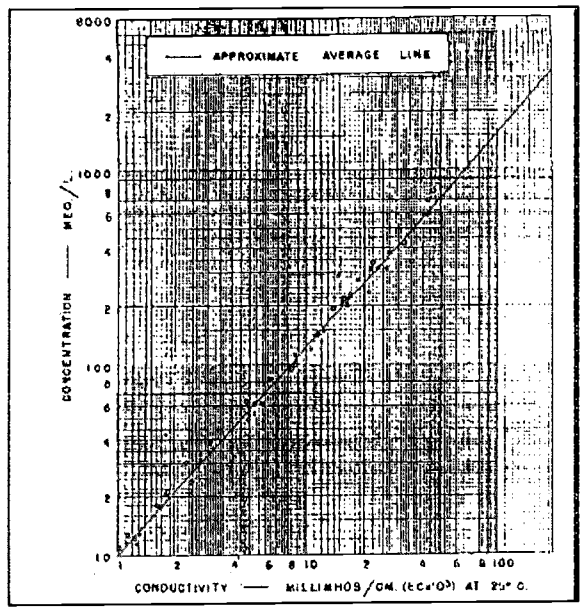


Fig. 5: Concentration of saturated paste extracts of soils in milliequivalent per litre as related to electrical conductivity.

(US. Salinity Laboratory Staff, 1954)



## 3. CATION EXCHANGE CAPACITY AND EXCHANGEABLE CATIONS

The capacity of a soil to adsorb or hold cations and to exchange species of cations in reversible chemical reactions is a quality most important in soil fertility and soil genesis studies. Exchangeable cations influence characteristics like soil structure, water and oxygen balance, biological activity and soil reaction (pH). This is why these data are widely used in soil classification. (Buol, 1980)

Solid soil particles adsorb at their surfaces molecules and ions from the soil solution. Adsorption of ions is always combined with desorption of other ions which then go into the soil solution.

The sum of exchangeable cations, including exchangeable hydrogen, is called **cation exchange capacity.**

In soil science exchangeable calcium, magnesium, potassium and sodium are called **exchangeable bases**, because soils saturated with these cations react alkaline.

The quantity of these bases in percent is called **percent base saturation (PBS).**

### 3.1. Cation exchange capacity:

The measurement of this soil property is rather empirical and a large number of analytical procedures have been proposed which all yield different results. Main factors of the various methods which lead to a diversity in results are:

**Differences in pH:**

The reactivity of the various exchangers in soil systems - clay minerals, organic matter, hydrous oxides and amorphous material - differs considerably with the pH. Variations become quite large in highly weathered soils rich in kaolinite and hydrous oxides.

**Differences in the exchanging or displacing solutions:**

Certain species of ions are more readily displaced or exchanged than others. Some species (especially potassium) may be trapped or fixed by certain types of clay minerals.

Cation exchange capacity of a soil can be partitioned into two components, the 'permanent charge' and the 'pH dependent charge'.

The **permanent charge** results from a net negative charge in the crystalline structure of the clay minerals due to substitution of cations of higher valence by cations of lower valence.

The **pH dependent charge** results from ionization of certain functional groups of organic matter or $OH^-$groups at the surfaces of Al- and Fe-hydrous-oxides and broken edges of clay minerals.

Apart from the negative charge the amount of exchangeable cations depends on the surface area of the different clay minerals.

The FAO classification has adopted the ammonium acetate method at pH 7.0 as standard procedure.

Table 1: Range of cation exchange capacities for different clay minerals measured with ammonium acetate method pH 7.0. (Grim, 1968)

| | CEC [meq/100 g clay] |
|---|---|
| Kaolinite | 3 - 15 |
| Smectite group (inc. montmorillonite) | 80 - 150 |
| Illite | 10 - 40 |
| Vermiculite (non interlayered) | 100 - 150 |
| Chlorite | 10 - 40 |

Some interpretations of CEC data are:

1. Degree of weathering of soils: Low CEC indicate low amounts or absence of primary weatherable minerals and accumulation of secondary clay minerals like kaolinite due to extensive weathering. High CEC is normally associated with soils having appreciable amounts of weatherable primary minerals as nutrient reserve.

2. High CEC indicates high nutrient storage capacity. However, in combination with low pH large amounts of exchangeable aluminum are likely to be present and affect plant growth.

3.2. CEC clay:

According to Soil Taxonomy and the FAO soil classification system CEC is calculated as CEC per 100 g clay. In the FAO-classification as used in Botswana the contribution of organic matter to the CEC of the soil is corrected.

The correction is based on the assumption of a CEC of 4 meq per gram organic carbon. This is generally considered as a mean value for soils. However, it can vary considerably between different soil types and also with the clay contents of a soil. High clay contents lower the CEC of organic matter (Scheffer and Schachtschabel 1979).

Sand and silt, especially when coated with iron oxides and related minerals, also contribute to the CEC. The average value is estimated to be in the range of 1 meq/100 g sand. In sandy soils, especially fine sandy soils, with a low CEC this contribution should not be neglected because the resulting CEC clay values will be far too high. However, no correction is applied as a routine procedure.

### 3.3. Exchangeable cations:

The composition of exchangeable cations vary in a wide range depending on the soil pH. They can be placed into two groups:

- exchangeable bases: mainly calcium, magnesium, potassium and sodium
- exchangeable acid generating cations: hydrogen (more properly hydronium) and aluminum.

The more acid a soil is the more hydrogen and aluminum and the less Ca and Mg are present in the exchange complex. If exchangeable aluminum occupies more than about 60% of the CEC, levels of aluminum in soil solution result which are toxic to plants.

In soils with pH >7 Ca+Mg levels are more than 90% of the CEC, except in sodic soils. These high levels can be explained with the good weatherability of Ca/Mg containing minerals and the higher bond energy of the bivalent cations compared to monovalent cations.

For soil classification the following terms are of importance:

- **Percent Base Saturation PBS**
- **Exchangeable Sodium Percentage ESP**
- **Sodium Adsorption Ratio SAR**

### 3.4. Percent base saturation:

Percent base saturation is calculated by summing the exchangeable bases multiply with 100 and divide by CEC.

The value indicates the degree of leaching - the extend to which exchangeable bases have been replaced by exchange acidity.

### 3.5. Exchangeable sodium percentage:

ESP is defined as:

$$ESP = [\text{exch. } Na^+] \times 100 / CEC$$

Accurate determination of ESP requires extraction of **all** soluble **and** exchangeable sodium from the soil with an appropriate salt solution (i.e. ammonium acetate), and subsequent subtraction of soluble sodium determined in the saturated paste extract. In addition, a cation exchange capacity determination is required.

Three different procedures with all their inaccuracies and pitfalls make the determination of ESP in a routine laboratory time consuming and difficult.

The seemingly easiest procedure, prewashing the sample with 50% ethanol and carrying out a normal CEC and exchangeable cations determination leads to wrong results due to effects of dilution and hydrolysis. ESP values obtained with this method are 20-30 % too low. (Table 2)

Possible sources of errors during the CEC determination which tend to decrease the apparent CEC (increase the ESP):

Displacement of the index cation ($NH_4^+$) by divalent cations from slightly soluble salts (e.g. $CaCO_3$).

Removal of index cation from exchange sites by hydrolysis due to excessive washing.

Incomplete initial saturation with index cation.

Reverse effects, leading to low values for the apparent ESP might be:

Incomplete washing to remove excess of index cation.

Salt retention on surfaces or fixation in interlayers of clay minerals.

Possible sources of error during exchangeable cations determination in the presence of high concentrations of sodium may be:

Incomplete extraction due to low permeability of soil.

Errors diluting extracts to measurable concentration range.

In table 2 ESP values of 11 samples have been determined with both methods to demonstrate the effect of hydrolysis.

Table 2: Effect of hydrolysis due to prewashing samples with 50% ethanol.

Exchangeable cations determined by subtracting concentration of soluble salts in saturated paste extract from total analysis.

Samples measured in: meq/100 g soil

| No | labno | CEC | Ca | Mg | K | Na | ESP |
|---|---|---|---|---|---|---|---|
| 1 | 4121 | 13.69 | 22.98 | 2.72 | 1.92 | 3.34 | 24 |
| 2 | 4176 | 8.63 | 4.88 | 1.69 | 1.01 | 5.62 | 65 |
| 3 | 4179 | 9.14 | 0.49 | 1.46 | 0.75 | 9.23 | 101 |
| 4 | 4301 | 17.62 | 11.15 | 2.12 | 1.71 | 9.72 | 55 |
| 5 | 4302 | 25.62 | 12.44 | 1.60 | 2.34 | 34.80 | 136 |
| 6 | 4355 | 17.25 | 10.82 | 0.99 | 1.49 | 21.38 | 124 |
| 7 | 3756 | 43.16 | 24.38 | 5.88 | 1.97 | 1.26 | 3 |
| 8 | 2810 | 20.95 | 2.01 | 1.17 | 1.75 | 36.28 | 173 |
| 9 | 2987 | 5.84 | 6.51 | 0.77 | 1.71 | 9.21 | 158 |
| 10 | 4177 | 11.95 | 4.17 | 1.74 | 1.28 | 16.83 | 141 |
| 11 | 4178 | 15.05 | 1.40 | 1.32 | 1.39 | 19.40 | 129 |

Table 2 continued: Samples prewashed with 50% ethanol

| No | labno | CEC | Ca | Mg | K | Na | ESP |
|---|---|---|---|---|---|---|---|
| 1 | 4121 | 14.42 | 22.70 | 3.31 | 1.89 | 2.78 | 19 |
| 2 | 4176 | 9.34 | 5.07 | 1.65 | 0.95 | 5.44 | 58 |
| 3 | 4179 | 8.58 | 1.65 | 1.14 | 0.65 | 7.36 | 86 |
| 4 | 4301 | 18.03 | 11.64 | 2.02 | 1.70 | 9.28 | 51 |
| 5 | 4302 | 24.88 | 13.42 | 1.60 | 2.33 | 23.84 | 96 |
| 6 | 4355 | 17.80 | 9.91 | 1.05 | 1.54 | 19.94 | 112 |
| 7 | 3756 | 42.36 | 28.44 | 6.83 | 1.80 | 0.66 | 2 |
| 8 | 2810 | 19.81 | 2.36 | 1.67 | 1.73 | 27.38 | 130 |
| 9 | 2987 | 5.72 | 6.93 | 0.98 | 1.58 | 5.48 | 96 |
| 10 | 4177 | 14.42 | 2.71 | 1.96 | 1.38 | 9.50 | 66 |
| 11 | 4178 | 16.18 | 3.08 | 1.71 | 1.45 | 15.52 | 96 |

Comparing these figures shows that the CEC determination is not affected by prewashing. The variations are within the error range of the determination.

The same applies for calcium, magnesium and potassium.

Sodium values of the batch prewashed with 50% ethanol are in most cases considerably lower which is explained by the hydrolysis of part of the exchangeable sodium.

In table 3 linear regressions have been calculated using the data of the batch not prewashed for the independent X-parameter and the prewashed batch for the Y-parameter.

(For more detailed explanations about linear regression analysis see part 3 of this report.)

The X-coefficient of 0.75 for sodium indicates that an average of about 25% exchangeable sodium is washed out due to hydrolysis.

Table 3: Linear regression analysis of the two methods to determine exchangeable sodium to show the effect of hydrolysis due to prewashing samples with 50% alcohol.

| Regression Output: | CEC | Na | ESP |
|---|---|---|---|
| Constant | 0 | 0 | 0 |
| Std Err of Y Est | 1.05 | 1.88 | 15.13 |
| R Squared | 0.99 | 0.94 | 0.87 |
| No. of Observations | 11 | 11 | 11 |
| Degrees of Freedom | 10 | 10 | 10 |
| X Coefficient | 1.00 | 0.75 | 0.70 |
| Std Err of Coef. | 0.02 | 0.04 | 0.04 |

### 3.6. Sodium absorption ratio:

SAR is defined as:

$$SAR = [\text{soluble } Na^{+}] / [(\text{sol. } Ca^{2+} + \text{sol. } Mg^{2+}) / 2]^{1/2}$$

The concentration of soluble cations is determined in the saturated paste extract prepared for electric conductivity determination.

In a soil:water system the concentrations of soluble and exchangeable (adsorbed) cations form an equilibrium. A theoretical calculation of satisfactory equilibrium constants is subjected to a number of constraints because a soil is composed of cations of unequal valences and different kinds of cation exchange materials.

SAR is expressed in terms of ion concentrations rather than in terms of activities (which would consider ionic concentration of a salt solution). Furthermore the calculation does not take into account reductions in free ion concentrations due to ion-pair or complex formation.

Most effects have opposing trends or exclude each other, which accounts for the widespread success using SAR for making ion exchange predictions.

Further reasons for giving preference to SAR determinations over ESP are its relative simplicity and the fact that it generally works. (Bresler, 1982)

A relationship between SAR and ESR (exchangeable sodium ratio) is given in Figure 6. Figure 7 is a nomogram to determine SAR values of a saturation extract and for estimating the corresponding ESP.

Fig. 6: Exchangeable sodium ratio (ESR) as related to the sodium adsorption ratio of the saturation extract. (U.S. Salinity Laboratory Staff 1954)

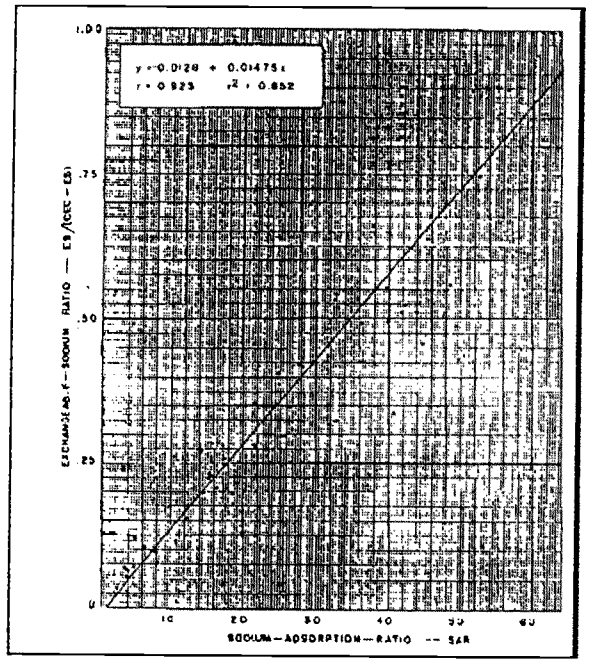
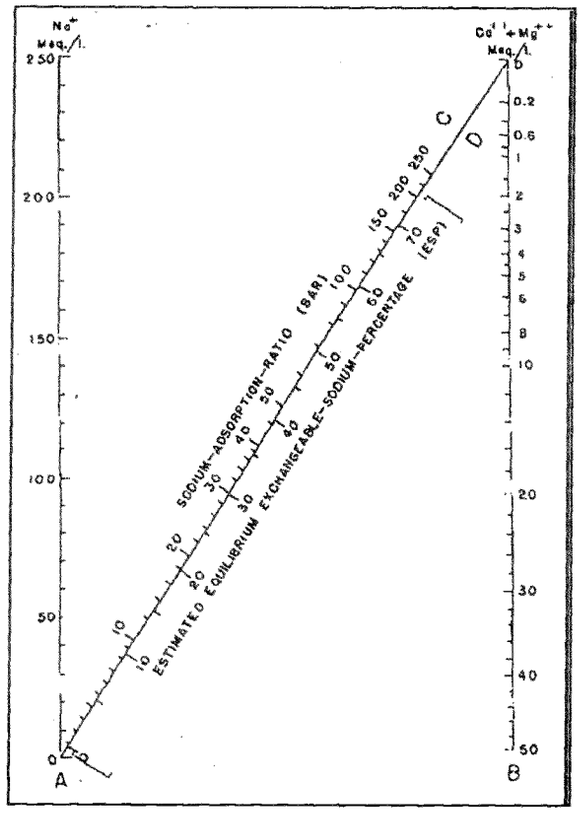


Fig. 7: Nomogram for determining the SAR value of a saturated paste extract and for estimating the corresponding ESP value of soil at equilibrium with extract



3.7. Principles of CEC determination with ammonium acetate method pH 7.0:

Samples are percolated with a 1 normal ammonium acetate solution with pH adjusted to 7.0. $NH_4$-ions replace the other cations adsorbed on the surfaces - the soil is $NH_4$-saturated.

Adsorbed $NH_4^+$ is determined with a **Kjeldahl distillation** and the resulting ammonia solution **titrated** with acid of known concentration. (Kjeldahl J., 1883)

The Kjeldahl distillation is based on the reaction:

$$NH_4^+ + NaOH \rightarrow Na^+ + NH_3 + H_2O$$

The weak base $NH_4^+$ is driven out by concentrated sodium hydroxide solution as ammonia ($NH_3$) which is 'steam'-distilled and dissolved in a dilute solution of boric acid.

3.8. Advantages of extractor method adopted for the laboratory:

Advantages of the automatic extractor method to the percolation procedure with Buchner funnels:

1. Extraction time can be set precisely.
2. Extraction time is exactly the same for every sample.
3. Volume of extracting solution above sample is kept constant throughout extraction. Therefore also the solution:soil ratio is constant which reduces the chances for hydrolysis.
4. During the extraction no attention from technician is required.
5. The space requirement of an automatic extractor is far less than for the set up of percolation method with Buchner funnels for the same amount of samples.

Fig. 8: Automatic extractor.

For the ammonium acetate extraction an automatic extractor, developed at the USDA Soil Survey Laboratory in Lincoln, Nebraska, USA, is used. The principle method has also been developed at the same laboratory. 24 samples can be extracted simultaneously

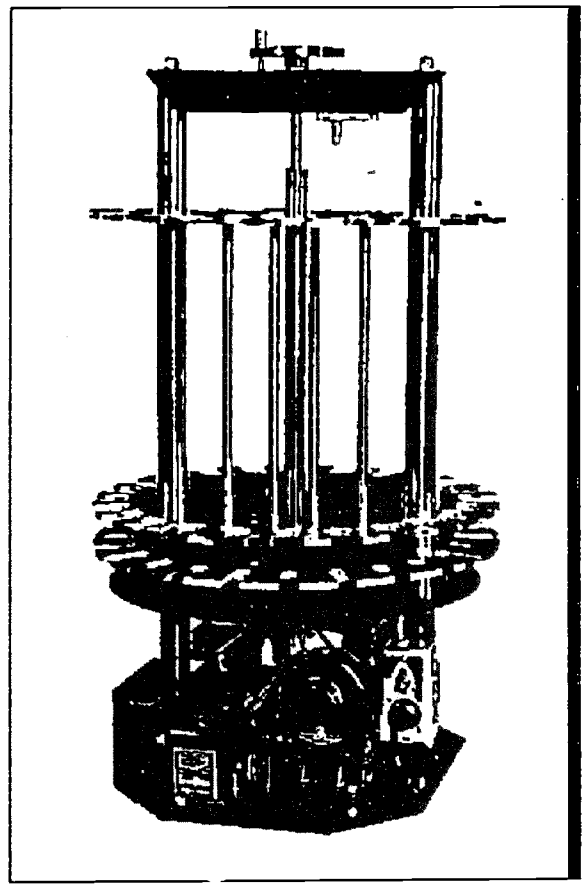
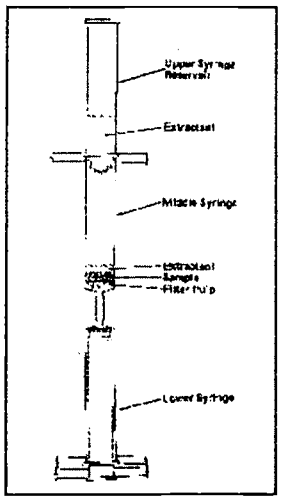


Fig. 9: Automatic extractor:

Configuration of syringes when extracting samples for CEC determination.



### 3.9. Distillation and titration:

A Kjeltec automatic distiller and an automatic titrator are used for the Kjeldahl analysis (ammonia determination). Each distillation takes about 4 minutes during which the previous sample is titrated.

Distillation and titration have a high degree of efficiency and accuracy. The automatic endpoint titration prevents overshooting even if samples have very much differing values.

Space requirement for the whole set up is about two meters bench space. The possible weekly production is 88 CEC analyses (plus one standard sample per batch and blank). The determination is carried out by one technician.

### 3.10. Method adopted for the laboratory:

Exchangeable cations (Ca, Mg, K, Na) are determined in the ammonium acetate extract with an atomic absorption spectrometer.

The AAS is equipped with an automatic sample changer and connected to the Hewlett Packart HP 86B microcomputer. The computer controls the measuring protocol, checks the quality of the standard curve, calculates the concentration of the elements measured and stores them in the laboratory data base.

If a standard reading is more than 10% off the expected value the programm goes into a loop and the operator can not continue. The introduction of this step has improved the quality of the determination significantly because this forces the technicians to prepare the determination with great care.

# 4. ORGANIC MATTER

## 4.1. Organic matter in soils:

Soil organic matter normally consists of small amounts of non or slightly transformed materials like carbohydrates and others. The major part are dark colored humic acids with different degrees of polymerization.

For plant growth the nutrient storage capacity of the organic matter is important (high CEC), especially in clay poor soils.

In clay rich soils it enables the formation of aggregates with large pores and improves therefore water and air availability.

Organic matter has a high water holding capacity of 3 to 5 times its own weight. This is especially of importance for sandy soils, because the field capacity of these soils mainly depends on the organic matter content.

Organic matter contents indicate the extent of accumulation under different environmental conditions as influenced especially by climate.

Soils rich in clay usually have a higher organic matter content than sandy soils because of adsorption on the surfaces of clay minerals as well as Al- and Fe-oxides and amorphous Al-silicates (organo-mineral complexes).

Nitrogen is not determined in the standard analysis program because of the usually very low organic matter contents of the soils in Botswana. However, it can be determined using the 'macro Kjeldahl method'.

The ratio carbon:nitrogen is an indication for the decomposition of the organic matter because it narrows with increasing modification.

## 4.2. Methods for determination of organic matter:

Organic carbon is determined by either dry combustion (800-950°C) and measuring the carbon dioxide or wet combustion by measuring the degree of reduction of a strong oxidizing agent.

Most commonly used is wet digestion by the Walkley and Black method in which soil organic carbon is oxidized in chromic acid. Since some assumptions and approximations are involved in this method it is less accurate than dry combustion, but it requires less time and less complicated and expensive laboratory apparatus.

Organic matter is calculated by multiplying the organic carbon concentration with a factor.

A factor of 1.724 has been used assuming a mean carbon contents of 58% in organic matter. Allison (1965), points out that organic matter:organic carbon ratios vary considerably in different soils and also among horizons of the same soil.

A factor of about 1.9 is more appropriate for surface horizons. For subsurface horizons the factor is about 2.5. (Broadbent (1953))

4.3. Principles of organic carbon determination by wet digestion:

The principle of this determination is oxidation of organic carbon to carbon dioxide with dichromate in concentrated sulfuric acid:

$$2\ Cr_2O_7^- + 8\ H_2SO_4 + 3\ C = 2\ SO_4^- + 2\ Cr_2(SO_4)_3 + 8\ H_2O + 3\ CO_2$$

$$4\ Cr^{6+} + 12\ e^- = 4\ Cr^{3+} \qquad \text{reduction}$$

$$3\ C = 3\ C^{4+} + 12\ e^- \qquad \text{oxidation}$$

The Walkley and Black method and also the modified method are similarly affected by the presence of oxidizable substances other than carbon. (However, no influence of $Cl^-$ was detected mixing two different soils with 1 to 10% sodium chloride and determining the amount of $Cr^{3+}$ with a spectrophotometer.)

4.4. Comparison of original Walkley and Black method with modified method adopted for the laboratory:

| Original method: | Modified method: |
|---|---|
| Digestion: | |
| 10 ml 1 normal potassium dichromate is dispensed to the sample and 20 ml concentrated sulfuric acid are added. | A solution of about 3.4 normal sodium dichromate in 10 normal sulfuric acid is dispensed to the sample. (Sodium dichromate is preferred because of better solubility than potassium dichromate.) |
| The reaction is facilitated by the heat of dilution of sulfuric acid. The maximum temperature is about 126°C and keeps only for a few seconds. | Organic matter is digested heating the samples in an oven at 140°C for 30 minutes. Water, containing a flocculent is added with an 'AD 1-3' dispenser. After particles are settled an aliquot is taken and diluted by factor 1:8 with a 'SD-1' diluter. (Figure 10) |
| Determination: | |
| The amount of dichromate not used up by the organic carbon is determined by back titrating with iron (II) sulfate using barium diphenylamine sulfonate or ortho-phenanthroline-ferrous complex indicator (ferroin). | The $Cr^{3+}$-ion formed during the reaction has a green color with an absorbance maximum at 578 nm. This is determined with a spectrophotometer using glucose standards digested in the same way as the samples. |

The modified method is based on a method developped at the 'Control Laboratory International Soil Fertility Evaluation and Improvement (ISFEI)' by Arvel Hunter, Director, North Carolina State University, Releigh. (Reference unknown.)

Recovery factors for various wet combustion methods:

None of the wet combustion methods oxidizes the total organic carbon, present in soils.

The relatively low temperature and short digestion time in the Walkley and Black method is sufficient to oxidize the active forms of organic carbon but not the more inert forms.

In a study by Allison (1960), recovery of carbon varied between 59% and 94%, depending on the soil group. Walkley and Black (1934), report a recovery factor of 1.30 and a recovery range of 60% to 86%.

With the application of external heat the oxidation is more complete and the degree of oxidation is more consistent than in the original method. The recovery range is narrower. External heating was proposed by Schollenberger (1927 and 1945).

Allison (1935), obtained recoveries of 85% to 90% using Schollenberger's method and found that a recovery factor of 1.15 was satisfactory to adjust carbon values to dry combustion data.

(In Schollenberger's method soil is mixed with dry Potassium dichromate. Concentrated sulfuric acid is added and heated up to 175° C within 90 seconds.)

Due to lack of equipment no dry combustion data have been obtained in the Botswana laboratory. However, to get some idea about the recovery factor for the modified method 40 samples of different soil types and texture classes have been analyzed with the original Walkley and Black method and the modified method. (The modified method was carried out at two different temperatures, 140° and 170° Celsius.)

Table 5: Organic carbon contents of 40 soils measured with original Walkley and Black and modified methods.

| Sample no. | clay% | org. carbon [wt%] orig. | modif. 140°C | modif. 170°C |
|---|---|---|---|---|
| 4149 | 8 | 0.04 | 0.00 | 0.00 |
| 2760 | 8 | 0.13 | 0.25 | 0.26 |
| 2726 | 8 | 0.21 | 0.25 | 0.26 |
| 2765 | 4 | 0.32 | 0.38 | 0.36 |
| 4360 | 6 | 0.43 | 0.38 | 0.32 |
| 2901 | 6 | 0.77 | 1.12 | 0.79 |
| 2530 | 9 | 0.83 | 1.00 | 0.84 |
| 2980 | 9 | 1.20 | 1.29 | 1.12 |
| 2925 | 6 | 1.81 | 1.35 | 1.24 |
| 2959 | 10 | 1.35 | 1.47 | 1.47 |
| 4319 | 10 | 5.95 | 6.82 | 7.88 |
| 2936 | 16 | 0.13 | 0.19 | 0.42 |
| 2847 | 11 | 0.23 | 0.38 | 0.32 |
| 2990 | 16 | 0.74 | 0.81 | 1.41 |
| 3026 | 11 | 0.98 | 1.00 | 1.29 |
| 2742 | 16 | 2.19 | 2.52 | 3.38 |
| 3070 | 16 | 2.48 | 2.26 | 2.63 |
| 2533 | 11 | 0.15 | 0.19 | 0.32 |
| 3046 | 17 | 4.05 | 4.00 | 5.00 |
| 4177 | 27 | 0.16 | 0.19 | 0.26 |
| 2735 | 30 | 0.24 | 0.31 | 0.79 |
| 4110 | 21 | 0.60 | 0.69 | 0.84 |
| 4122 | 29 | 0.80 | 1.12 | 1.53 |
| 4317 | 30 | 0.66 | 0.75 | 0.84 |
| 2549 | 22 | 1.02 | 1.24 | 1.53 |
| 2519 | 37 | 0.14 | 0.13 | 0.11 |
| 2050 | 31 | 0.22 | 0.31 | 0.26 |
| 2529 | 37 | 0.36 | 0.50 | 0.63 |
| 2718 | 37 | 0.45 | 0.44 | 0.47 |
| 2419 | 33 | 0.59 | 0.81 | 0.68 |
| 4184 | 37 | 0.53 | 1.41 | 1.82 |
| 3018 | 31 | 2.05 | 2.58 | 2.81 |
| 2859 | 32 | 2.83 | 3.35 | 3.31 |
| 4311 | 47 | 1.54 | 2.06 | 3.06 |
| 3763 | 66 | 0.51 | 0.81 | 1.00 |
| 2407 | 73 | 0.61 | 1.00 | 0.84 |
| 2404 | 78 | 0.31 | 0.50 | 0.42 |
| 2409 | 81 | 0.30 | 0.69 | 0.53 |
| 2474 | 83 | 0.71 | 1.06 | 1.12 |
| 3696 | 88 | 2.16 | 3.48 | 3.69 |

Linear Regression Output:

Table 6:Modified versus original Walkley and Black organic carbon determination:

| Regression Output: | orig./140 | orig./170 | 140/170 |
|---|---|---|---|
| Constant | 0.12 | 0.10 | -0.03 |
| Std Err of Y Est | 0.30 | 0.42 | 0.28 |
| R Squared | 0.95 | 0.93 | 0.97 |
| No. of Observations | 40 | 40 | 40 |
| Degrees of Freedom | 38 | 38 | 38 |
| X Coefficient | 1.09 | 1.27 | 1.16 |
| Std Err of Coef. | 0.04 | 0.06 | 0.03 |

Abbreviations:

orig./140 : Regression analysis original Walkley&Black as independent (X) variable and modified method at 140°C as dependent (Y) variable.
orig./170 : Regression analysis original Walkley&Black as independent (X) variable and modified method at 170°C as dependent (Y) variable.
140/170 : Regression analysis modified method at 140°C as independent (X) variable and modified method at 170°C as dependent (Y) variable.

Constant : Intersect with Y-axis.
R Squared : Correlation coefficient.
X Coefficient: Recovery factor.

Conclusions:

Recovery factors of 1.27 for 'orig./170' and 1.16 for '140/170' are close to the factors proposed by Walkley and Black ,1934, for their method and Allison, 1965 for the method with external heating compared to data from dry combustion.

This suggests that alomost complete digestion of organic matter is achieved with the modified method, heating the samples for about 30 minutes to 170° Celsius.

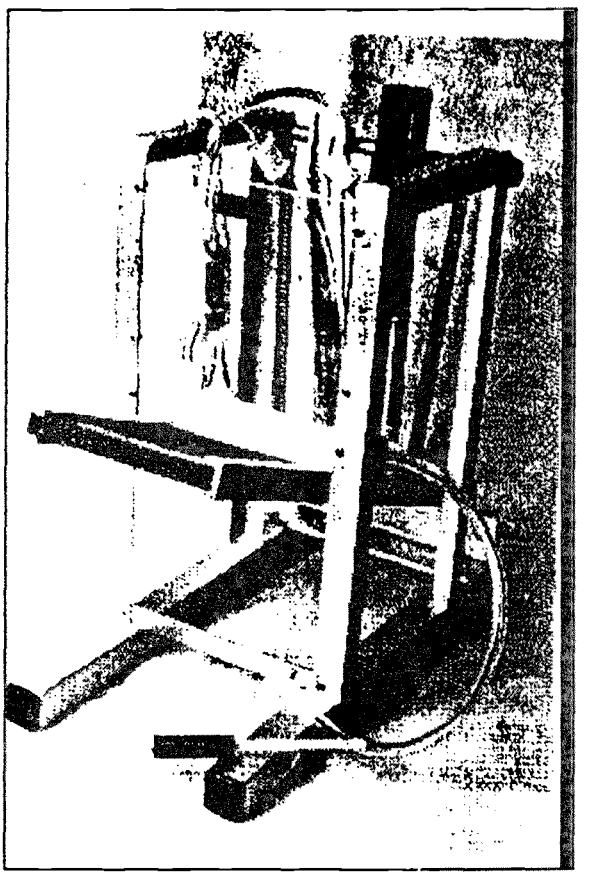
The variation of recovery, depending on soil type (Allison, 1960) for the Walkley and Black method is indicated by the correlation coefficient of 0.93 (orig./170) and the relatively large scatter of data points in figure 11.

In figure 12 values are compared from digestion at 140°C with data from digestion at 170°C. The points are clustered closely around the regression line, which is also expressed by a correlation coefficient of 0.97 in table 6 (140/170). This is in concordance with Allison (1935) who reports recoveries of 85% to 90% applying external heat.

Digestion at 140° Celsius and correction with a recovery factor of 1.15 is found a more suitable procedure for the conditions in the laboratory than digestion at 170°C.

During digestion at 170°C samples fall completely dry. Errors easily occur when technicians do not take great care to redissolve all crystallized salts what might happen under routine conditions, working with large amounts of samples.

Figure 10 : SD-1 diluter / AD 1-3 'one aliquot three volume' dispenser.



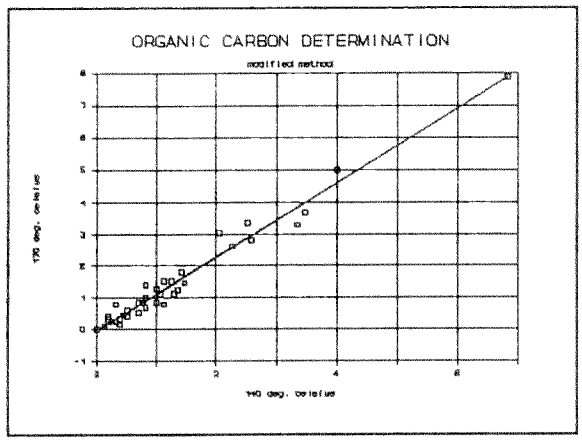
The SD-1 diluter and AD 1-3 dispenser are part of a system specifically designed for the needs of routine soil analysis laboratories. They are hand operated to avoid mechanical failures. Aliquot and diluent volumes are controlled by the size of the syringes and the stroke of the plunger. The stroke is controlled by the movement of the diluter handle through a constant distance and by varying the position of the plunger along the stroke control rod on the handle.

By simple changes in the hookup of the flow control valves, the diluter can be changed into a dispenser.

Each syringe position will accommodate sizes 1 ml to 50 ml which permits a wide range of dilutions and volumes to be set.

Precision and accuracy are excellent for the purposes these instruments are used for. The operation is fast and efficient.

Fig. 11 and 12: Comparison of modified with original Walkley and Black method for organic matter determination in 40 different soil samples from Botswana. The second diagram shows the correlation of data from the modified method digested at two different temperatures.



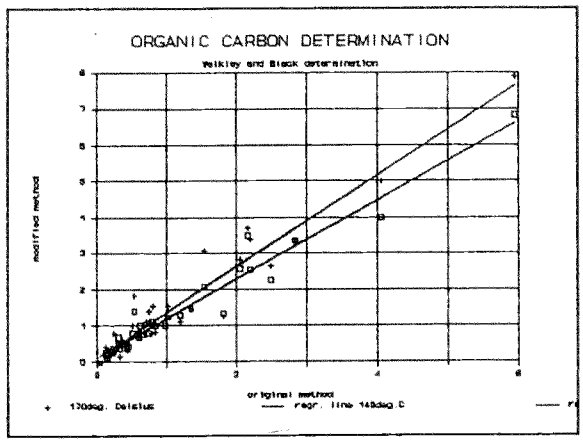
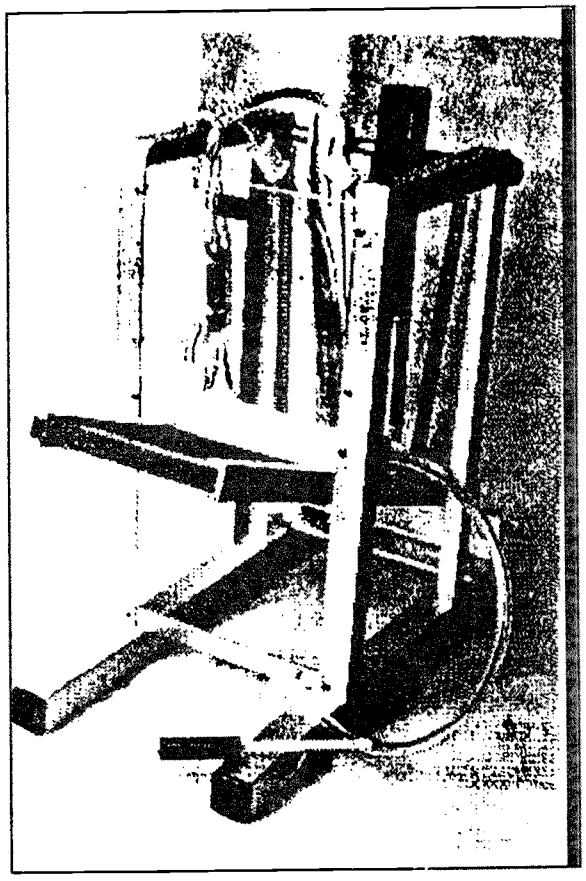



Figure 10 : SD-1 diluter / AD 1-3 'one aliquot three volume' dispenser.



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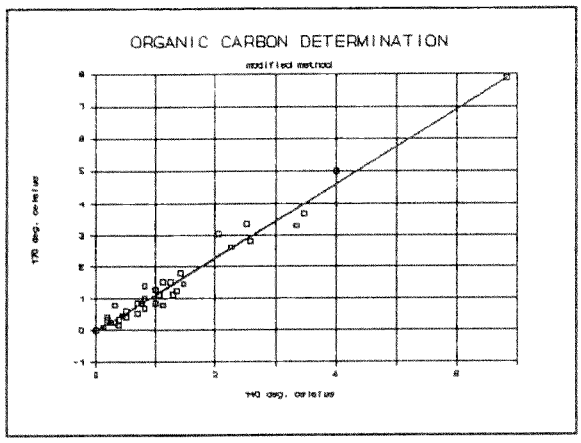
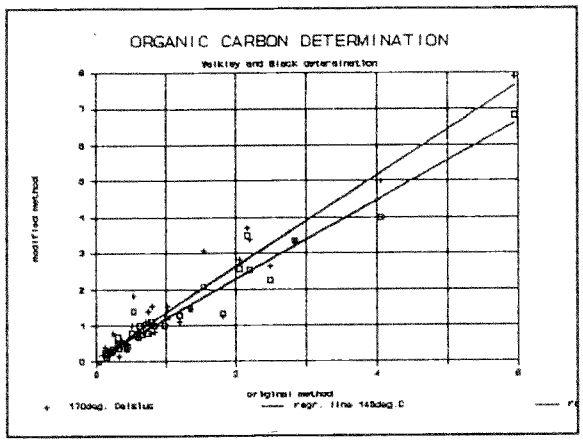


## 5. PHOSPHORUS

### 5.1. Phosphorus forms in soils:

In general Phosphorus together with nitrogen is considered the most critical plant nutrient. A lack of phosphorus is especially serious because it also may prevent other nutrients from being acquired by plants. The phosphates present in soils are predominantly derived from primary minerals.

P-forms in soils can be subdivided in:

- defined Ca-, Al-, Fe-phosphates (e.g. hydroxyapatite, fluorapatite, variscite, strengite, etc.)
- defined organic P forms (e.g. salts of the inosit-hexa-phosphoric acid)
- phosphates adsorbed to AlOH-, $AlOH_2$-, FeOH-, $FeOH_2$-groups of the exchange complex
- phosphates occluded in Fe-Mn concretions (often in tropical soils and gleysols)

### 5.2. Plant availability of phosphorus:

The solubility of soil phosphorus is a rather complicated subject because phosphate ions going into solution can derive from defined P-minerals but also from adsorbed forms with different bonding strengths. The solubility of different phosphorus forms also strongly depends on pH and redox potential of the soils (Figure 2).

At any one moment the amount of phosphorus in plant available forms is relatively low because the solubility of most phosphorus minerals is low.

Phosphorus moves from inorganic forms into organic forms and back via mineralization. This is called the 'phosphorus cycle'. The organic P-forms usually increase with the organic matter and it is evident that the organic proportion is higher in topsoil than in subsoils.

### 5.3. Methods for determination of available phosphorus:

Several methods are in use to determine the plant available phosphorus in soils. They all are based on extracting the soil with solutions which dissolve only the 'easy soluble' fraction of the occurring phosphorus forms, for example:

- various 'lactate' methods
- citrate extracts
- ammonium fluoride-hydrochloric acid extracts (Bray&Kurtz)
- sodium bicarbonate extracts for calcaric soils (Olsen)

Results obtained with the different methods vary considerably. The Botswana soil survey laboratory has adopted the Bray and Kurtz method as standard procedure.

5.4. *Principles of phosphorus determination with Bray and Kurtz method:*

The Bray and Kurtz determination of available phosphorus is based on the extraction of the soil with a dilute solution of ammonium fluoride in hydrochloric acid. The amount of phosphorus extracted is sensitive to shaking time (stirring time) and to soil:extractant ratio. In the laboratory the proposed parameters from Bray and Kurtz (1945) are used. (soil:extractant ratio 1:7, contact time 1 minute).

The amount of phosphorus in the extract is determined with the 'molybdenum blue' method:

> The molybdenum blue method is the most sensitive and therefore very suitable for soil analysis with small concentrations of phosphorus.
>
> The method is based on the principle that in an acid molybdate solution in presence of orthophosphate ions a phosphomolybdate complex is formed. Reducing this complex with stannous chloride or ascorbic acid a blue, colloidal solution of mixed oxides of four and six valent molybdedium forms.
>
> The intensity of the color depends on the concentration and is measured with a spectrophotometer.

5.5. Method adopted for laboratory:

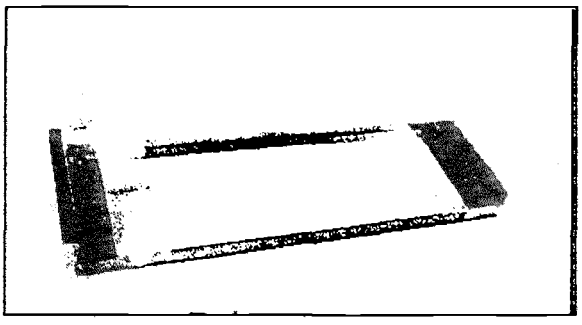
Using specially designed equipment large numbers of samples can be handled by one technician with little space requirements and satisfactory results:

> To thirty three samples, arranged on a tray in three blocks of bottle racks, extractant solution is added (Figures 13 and 14). The type of dispenser used dispenses three samples at a time by pushing a handle. It is connected to a 25 liter drum with extractant under the table (Figure 15).
>
> With a multi-sample stirrer all samples are stirred simultaneously for one minute (Figure 16).
>
> Eleven samples (one bottle rack) are filtered at a time through a multi-funnel rack.
>
> With a combination diluter/dispenser an aliquot of the filtrate is diluted and at the same time ammonium molybdate solution added (Figure 17). After thirty minutes the samples are measured with a Brinkmann spectrophotometer and a 'dip in probe'.

One technician, concentrating on this determination, can do four batches (132 samples) per day using about two meters of bench space.

The equipment illustrated in figures 13 to 17 belongs to the same routine soil analysis system as the diluter and dispenser described in figure 10.

Figure 13 and 14: Carry tray and bottle rack with 11 plastic bottles.



The carry trays are built so that three bottle racks will fit.

The bottle rack is made from styrofoam. Eleven bottle holes are spaced along the center and sized so that plastic bottles fit snugly in each hole. This permits the bottle racks to be inverted and shaken without bottles falling out.

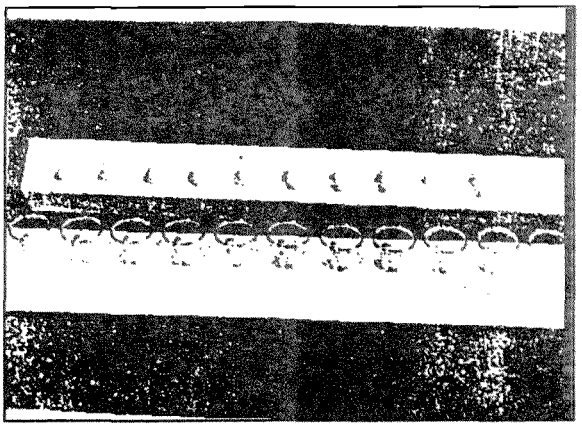


Figure 15: AD-3 'three volume' dispenser.

The three aliquot dispenser dispenses three equal size or different size aliquots of the same or of three different solutions at a time.

The functioning of the dispenser is based on the same principle as described in figure 10 - it is hand operated and the dispensing volume(s) is (are) controlled by the size of the syringes and the position of the plunger bracket along the stroke control rod.

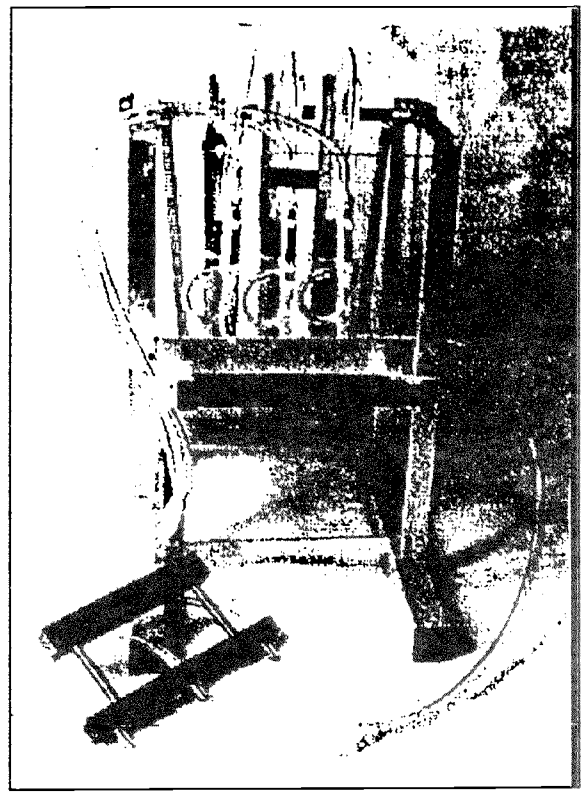
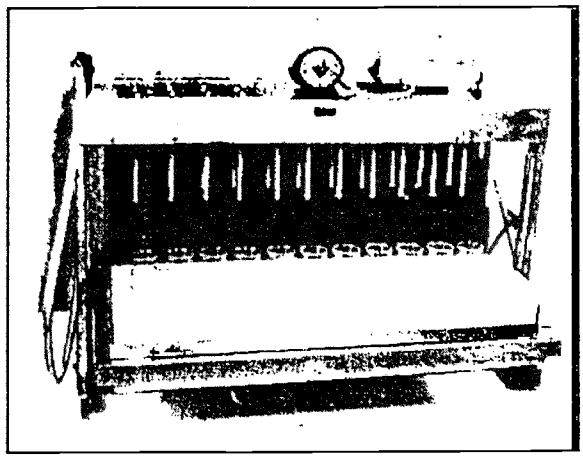


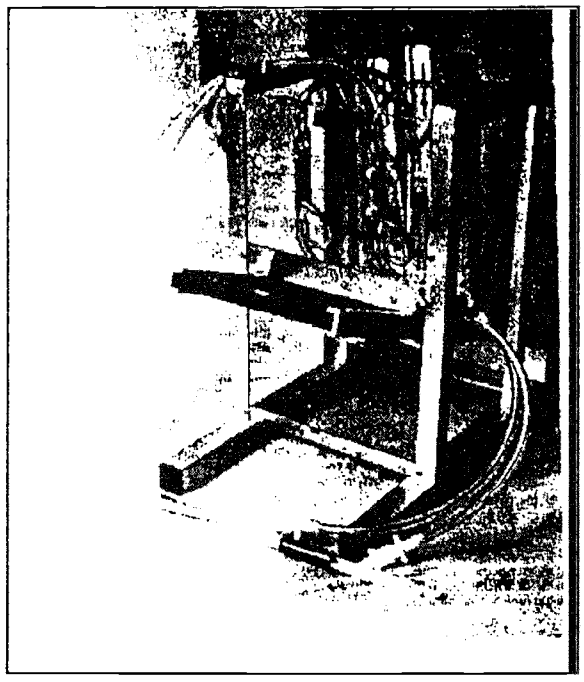
Figure 16: Multi sample stirrer



The multi sample stirrer is designed for uniform mixing of soil samples with extracting solutions. Each stirring rod turns at exactly the same rate as the others.

The stirrer has three rows of eleven rods which fit precisely the bottle racks described in the previous figure.

Figure 17: SCD-1 combination diluter-dispenser



The combination diluter-dispenser is in principle the same like the AD-3 dispenser in figure 14, with a different hookup of the flow control valve.

It takes up a chosen volume of sample to transfer it to another container while at the same time two exact volumes of different or the same diluents or reagents are added.

Three syringes are used for volume control and each position will accommodate sizes of 1 ml to 50 ml.

# 6. PARTICLE SIZE DETERMINATION

## 6.1. Soil texture and soil structure:

Physically, mineral soils are porous mixtures of mineral grains of different shapes and sizes, organic matter, air and water. Discrete grains do rarely occur in soils (e.g. in some sandy soils).

The particles, especially the fine particles, are usually aggregated into clods which is expressed as soil structure. Binding agents are mainly organic matter, but also carbonates and iron and aluminum hydrous oxides.

Soil texture in combination with soil structure determines the nutrient supplying ability of soil solids and also the air and water supply.

The different grain sizes of soil particles very often show strong relationship with the mineral sizes of the parent rock. The grain size of the newly formed soil particles also depends on the extend of physical and chemical weathering. Transport by wind and water causes further sorting of the grain size fractions.

Since the adsorption of water, nutrients, gas and the attraction of particles for each other are all surface phenomena, the significance of the specific surface of a soil and thus the particle size distribution analysis for soil characterization is obvious.

## 6.2. Nutrient supplying ability of soil solids:

With decreasing grain size grain number and total surface at same volume increases exponentially. Since in soils the proportion of sheet minerals increases (larger surface than rounded grains), the surface of clay minerals can be up to 400 $m^2$ / gram.

Swelling clay minerals have a so called 'inner surface'. The inner surface is between the silicate layers of the clay mineral crystals where molecules and ions can also be adsorbed. Among the clay minerals smectites and vermiculite have the largest specific surfaces with 600 - 800 $m^2$ / gram. (Scheffer and Schachtschnabel, 1979)

Table 7: Specific surfaces of grain size fractions in soils.

| | |
|---|---|
| Sand fraction | < 0.1 $m^2$/gram |
| Silt fraction | 0.1 - 1 $m^2$/gram |
| Clay fraction | 5 - 400 $m^2$/gram |
| Organic matter | 800 - 1000 $m^2$/gram |

## 6.3. Air and water holding capacity:

Soil texture and structure are the soil properties to which air and water holding capacity and hydraulic conductivity are most directly related to. The pore space ranges from 35 to 50 percent for sandy surface soils to about 40 to 60 percent for medium- to fine-textured soils. (Some compact subsoils drop as low as 25 to 30 percent.)

Pore size distribution also largely depends on texture and structure ('primary' pores mainly on texture, 'secondary' pores on structure). Water is held within the pore space with different potentials, depending on the pore size (capillary force). The pore system is subdivided into ranges:

Table 8:Pore size ranges in soils. (Scheffer and Schachtschabel, 1979)

| Range | Size [micro m] | Potential [mbar] | pF-value |
|---|---|---|---|
| coarse | > 50 | 0 - 60 | 0 - 1.8 |
| medium-coarse | 50 - 10 | 60 - 300 | 1.8 - 2.5 |
| medium | 10 - 0.2 | 300 - 15 000 | 2.5 - 4.2 |
| fine | < 0.2 | > 15 000 | > 4.2 |

(The pF-value is the logarithm of the potential in milli bar.)

Water in the coarse pore range cannot be held against gravity, it percolates through.

Water in the medium-coarse and medium range is held against gravity and is therefore reservoir for plants. (Water in the medium-coarse range actually is slowly draining but still can be considered plant available.)

Water in the fine pore range is held with such a high potential that it is not available for most plants. The pF value of 4.2 is therefore called 'permanent wilting point'.

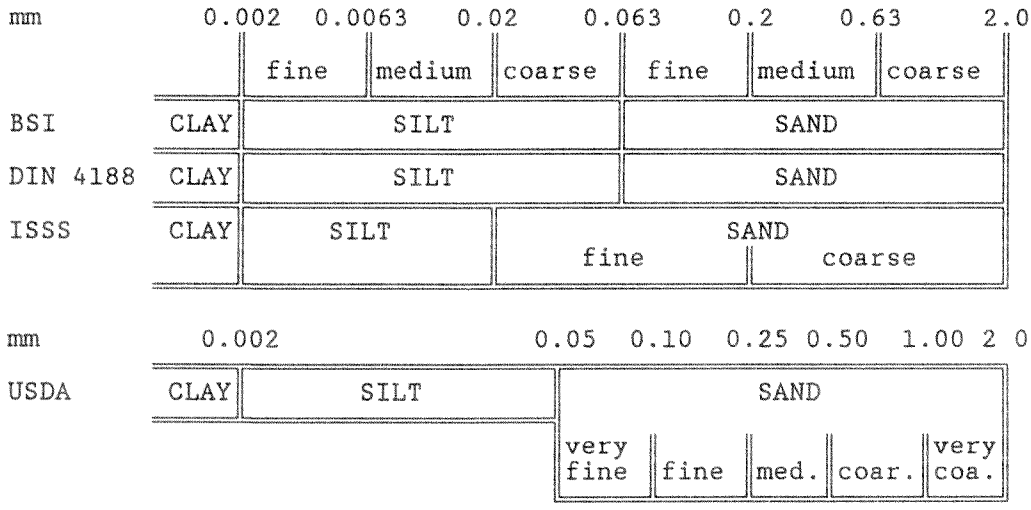
## 6.4. Classification of grain size ranges:

Because the size of particles in a soil is not subject to ready change soil texture is considered a basic property. The mineral grains are subdivided into grain size fractions. Depending on the quantity of the fractions soils are associated in grain size classes (e.g. sands, loams, clays, etc., see Figure 19: Soil texture classes).

To define the grain size ranges a number of classifications have been developped. The size classes of four system are shown in Figure 18.

The Botswana soil survey laboratory has adopted the USDA classification.

Fig. 18:Classification of soil particles according to size by four systems. (Particle diameter in logarithmic scale.) (Brady, 1974)




BSI: British Standards Institution
DIN 4188: German Industry Norm
ISSS: International Soil Science Society
USDA: United States Department of Agriculture

## 6.5. Mineralogic composition of different grain size ranges:

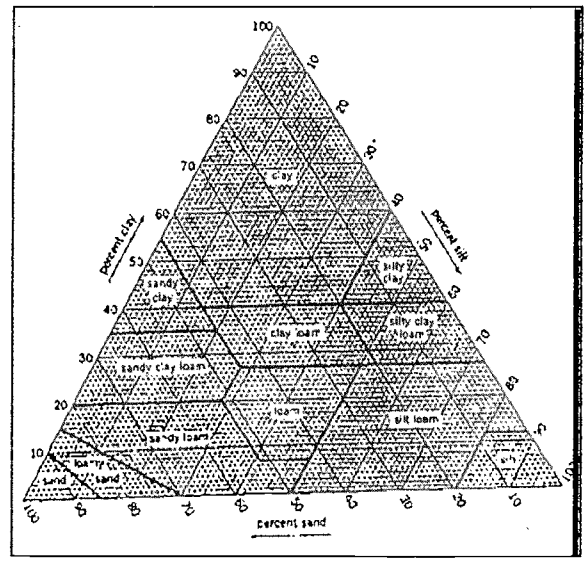
Although no specific investigations have been carried out some general remarks about the mineralogical makeup of soils may be allowed (Brady, 1974):

**Sand fraction:** The coarsest particles in the sand fraction often are fragments of parent rocks and minerals. Quartz usually dominates the finer grades of sand. Variable quantities of feldspars, mica and other primary minerals may also occur. Gibbsite, hematite, goethite and limonite minerals may occur as coatings on sand grains.

**Silt fraction:** The coarser silt fractions mainly consist of quartz. Other primary minerals like feldspars, hornblende and mica may be present but tend to disappear with progressing weathering. Secondary minerals such as the oxides of iron and aluminum, as well as kaolinite, may be prominent in the finer silt fractions.

**Clay fraction:** Secondary silicates such as kaolinite, illite and montmorillonite usually dominate the clay fraction. Quartz and other primary minerals may also occur.

Figure 19: Soil texture triangle



6.6. *Principles of particle size determination:*

Particle size determination consists of four steps:

- **Pretreatment**: Removal of organic matter, soluble salts, carbonates and iron oxides.
- **Dispersion**: Separation of soil particles into smallest discrete units by chemical and mechanical means.
- **Sedimentation**: Determination of clay and silt fraction using hydrometer or pipette method.
- **Sieving**: Determination of sand fractions by dry sieving.

**Pretreatment:**

Organic matter has a strong aggregating effect. For proper dispersion of samples removal of organic matter is absolute necessary.

Soils which contain considerable amounts of soluble salts or gypsum may be difficult or impossible to disperse and fractionate as a result of the flocculating action of the salts.

If the nature of the salts (including Ca-,Mg- carbonates) is such that the soil suspension is alkaline, hydrogen peroxide will decompose readily and removal of organic matter will be difficult.

Iron rich soils may require removal of free iron oxides to break down aggregates due to cementing action.

**Dispersion:**

Probably the most crucial step in particle size determination is the proper dispersion of soil particles.

A number of dispersing agents or various mixtures of them can be used, such as:

| | |
|---|---|
| Sodium hydroxide | NaOH |
| Sodium carbonate | $NaCO_3$ |
| Sodium oxalate | $NaC_2O_4$ |
| Sodium pyrophosphate | $Na_4P_2O_7$ |
| Sodium hexametaphosphat | $(NaPO_3)_6$ |

The effect of all these agents is that sodium is exchanged with other cations with the result of strong electrical repulsion forces between the soil particles.

Additionally the particles must be separated mechanically using 'end over end' or reciprocal shakers over several hours, usually over night. Electrical mixers cannot be recommended because of the risk loosing material due to splashing and also possible rupture of particles due to too vigorous action.

**Sedimentation:**

Clay and silt fractions are determined by sedimentation analysis. The determination is based on **Stroke's equation:**

'Small spherical particles of density $p_s$ and diameter X settle through a liquid of density $p_l$ and viscosity n at a velocity of:

$$v = X^2 * g * (p_s - p_l) / 18n$$

g = acceleration of gravity

Let: h = depth
t = time

$$v = h / t$$

Stroke's equation can be written then:

$$t = 18n * h / (g * (p_s - p_l) * X^2)$$

This equation means that after the time t all particles with a diameter bigger than X have sedimented through the depth h.

The relation between diameter and settling time of particles is the basis for two principle methods:

- **Pipette method**
- **Hydrometer method**

In pipette method a small sample is taken with a pipette at a certain time t and a certain depth h. In this sample all particles coarser than X have been eliminated.

The buoyant force of a hydrometer is determined directly by the density of the suspension. Hydrometer scales can be calibrated to read concentrations of suspended solids for particular values of $p_l$ and $p_s$, all in grams per liter. Soil hydrometers are calibrated for a particle density $p_s$ of 2.65 g/ml.

**Sieving:**

Particles coarser than 0.05 mm are segregated by sieving. The method seems to be simple and straight forward, but obtaining good reproducible results requires careful standardization of the procedure.

The probability of a particle passing a given sieve in a given time of shaking depends upon the nature of the particle and the properties of the sieve. A particle whose shape allows passage only in a certain direction only after prolonged shaking might have a chance of getting through.

Sieve openings usually are not of equal size and it might require extensive shaking before all particles had the opportunity approaching the largest openings.

6.7. Method adopted in the laboratory:

Tests have shown that differences between hydrometer method and pipette method for clay and silt determination are neglectable. Pipette method certainly is more precise but is also more complicated and requires much care and experience. Therefore the laboratory has adopted the hydrometer method as standard procedure.

In the literature it is mostly recommended to separate clay and silt fraction from the sand fraction by wet sieving before the actual determination. Under routine conditions it has been observed that the available amount of water (less than one liter to fill up the measuring cylinder) is not sufficient to wash all clay and silt through the sieve.

Performing the hydrometer analysis with the total sample and separating after determination avoids this risk because an unlimited amount of water is available then to wash out all clay and silt.

A constant temperature bath maintaining a temperature of 20° Celsius throughout the year is important for the hydrometer determination because the temperature differences in the laboratory are too big to be covered satisfactorily with a correction factor. (During winter often more than 10° difference between first reading in the morning and last reading in the afternoon and about 15-20° difference between summer and winter.)

As mentioned above, good dispersion is one of the most crucial steps in particle size analysis.

Good correlation with field estimates has been achieved for most samples using 27 g sodium hexametaphosphate plus 7 g sodium carbonate per liter as dispersant, adding 50 ml to each sample. Samples are shaken for about 16 hours (over night).

The few cases with poor correlation mostly can be solved through the application of special pretreatments like removal of iron oxides, carbonates or additional dispersion using ultrasound equipment.

# 7. DATA PROCESSING WITH HEWLETT PACKART MICRO COMPUTER

The Hewlett Packart HP86B micro computer serves two purposes:

- Interfacing with laboratory equipment
- Calculation, evaluation and storage of laboratory data

## 7.1 Interfacing with laboratory equipment:

The computer has been equipped with an additional IEEE-488 interface to control automatic operation of the atomic absorption spectrometer. A programm has been provided by the dealer which had to be debugged and modified to suit the requirements of the laboratory.

The IEEE bus has 31 unique adresses of which four are allocated for the AAS system control, one for a printer and one for an external computer.

The system is configured with the AAS as **system controller**. The computer, as all other accessories, is **non-controller**. When a device is ready with information it sends a **service request** to the **active contoller** (AAS). The controller determines who sent the request and the nature of it by performing a **serial poll**, querying the **status** of each device.

The computer can request to talk to any device in the system and has access to the majority of system keys.

The system controller acknowledges the service request and enables the required communications link, setting the computer **talker active** and the device, including itself if requested, **listener active**. After completion of the message transfer the service request bit is cleared and the bus is free for further operations.

An **interrupt mask** enables an **end-of-line** branch in the program when the bus is set talker active or listener active to go into a subroutine to either receive or transmit information.

All messages in the IEEE bus system have the structure:

[LDI] [MI] [MD] [MQ] [CSM]

[LDI]: Logical Device Identifier indicates the source of a message and will become talker active.

[MI] : Message Identifier indicates type of a message.

[MD] : Message Descriptor identifies which command is to be executed by receiving device or in case of a reply, which command has been executed.

[MQ] : Message Qualifier field is optional and depends on the content of numerical data.

[CSM]: Checksum is the binary value of each character in the message, including the checksum itself, added at the transfer time to provide a sum of zero. (The negative modulo of the sum is set into control register 16, which controls the end-of-line sequence. Bit 7 in this register is set which enables end-or-identify (EOI). Carriage-return (CR) and line-feed (LF) are disabled.)

All fields, except [CSM] are in ASCII code.

## 7.2 Laboratory data base:

The data base has been developed using the BASIC programming language version the computer is equipped with. The programm menu consists of a data input and a data output (print) programm, together with a variety of auxiliary programs.

Emphasis was put on user friendliness. A new user, without computer experience, should be able to learn how to input and retrieve data within a few hours.

A 'programm selection' menu is loaded automatically on switch on. From there the user is guided to what he wants to do by selecting from menus or answering simple questions with 'yes' or 'no'.

**Data input:**

The user selects the determination he wants to input from a menu. He is asked whether he wants to enter lab numbers first.

The next step are questions about parameters of the determination like sample weight, extract, temperature, etc.

Then, if applicable, the standard curve is entered, linear regression calculated and evaluated. Comments about the quality of the regression curve and single standards are displayed on monitor. Upon request a XY-diagram of the standard curve is displayed and printed.

The data are entered and calculated using the given parameters. Data and calculated results are displayed together with the lab numbers to check and eventually correct wrong inputs.

Finally, a hard copy is printed and the calculated results are stored on data disk, using lab number and type of determination as pointers to where a particular figure is to be placed.

**Data output:**

The print menu allows to print either results of single determinations or the full analysis. If full analysis is selected the operator has the choice between a plain and a commented printout.

The commented printout checks every profile for missing determinations and inconsistencies (for example whether organic carbon and/or phosphorus is irregular). It compares pH with percent base saturation and tests for large irregularities of CEC-clay values (if maximum CEC-clay differs more than 20% from minimum).

Analyses to print are selected either by lab numbers, profile numbers or area code.

**File structure:**

Each data disk stores 1200 full analyses.

Four files make up the data base:

DANO,SANO,DATA,MASTER

**DANO** contains a single number - the first lab number to be stored on the particular disk.

This is used to prevent data to be stored erroneously on wrong data disks. (The data input program checks each lab number whether it falls into the range DANO to DANO + 1199.)

**SANO** is a 'random access' file of 1200 records with a record size of 10 bits. It contains the sample numbers.

Each record contains the 2-digit area symbol, the 4-digit number of the profile plus the 1-digit sample symbol.

(for example MC 198A: the first two digits stand for Machaneng area, blank&198 = number of profile, A = first sample of profile)

Record number and lab number are connected through the algorithm:

recno = lab no - DANO + 1

**DATA** is a 'random access' file of 24000 records with a record size of 8 bits. It contains the analytical data.

Each sample occupies a cluster of 20 records, the 21$^{st}$ record is the beginning of the next sample.

In 18 records data of the different determinations are stored (1. = pH-$H_2O$ to 18. = clay).

The 19$^{th}$ record contains a decimal number which in binary form is coded for type of clay and silt determination, pretreatments applied and kind of extract for conductivity determination.

The 20$^{th}$ record is kept free for eventual additions.

PBS and CEC-clay are calculated by the print programm.

Lab number and record number for a specific determination of a sample are connected through the algorithm:

recno = (lab no - DANO) * 20 + N

N = number of determination (1 = pH-$H_2O$, 2 = pH-$CaCl_2$, 3 = el. conductivity, etc.)

**MASTER** is a 'random access' file containing record number and sample number of every first sample of a profile. It is used as an index file for faster search in the 'sample number' or 'area code' mode of the print programm.

## 7.3 Future aspects:

The data base serves its purpose very well and it is appreciated by the technicians because it reduces the amount of calculations and writing. However, it has its limitations, especially in flexibility, storage capacity and speed. Incorporation of new determinations into the standard programm and thus into the data base, would require major programming work restructuring the entire data set.

In the future it will be replaced by a modern, more sophisticated micro computer system. The new data base will be designed similarly user friendly like the existing one, but will take advantage of the flexibility and versatility of modern data base software and the enormous storage capacity of a hard disk system.

The Hewlett Packart computer will then be used controlling additional laboratory equipment, like a balance and the automatic titrator.

Data will be transferred as 'ASCII files' from one computer to the other and translated into the respective software file structure.

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