METHODS OF ANALYSIS FOR SOILS OF ARID AND SEMI-ARID REGIONS

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PREFACE

About one fourth of the land surface is in arid and semi-arid regions. Soils of these regions are generally characterized by their slightly alkaline reaction (pH 7.8 – 8.6), and elevated accumulation of calcium- and magnesium-carbonates, and sulphates. Because of low rainfall, high evaporation, and restricted leaching, soluble salts accumulate to some high levels in certain areas, which lead to saline conditions. Abundance of lime and gypsum, and the accumulation of soluble salts, markedly influence the physical and chemical properties and the fertility status of these soils. The surface layers of most of these soils, which contain various kinds of deposits, are coarse textured and low in organic matters. These factors make the management of these soils difficult, and demand studies based on rightly adapted methods of soil analysis. The saying "test and don't guess" is appropriate for the management of these soils, and the determination of the problems related to irrigation and drainage, salinity, sodicity, and gypsum content.

A number of books are available describing numerous alternative procedures for soil analysis, and users are often confused in selecting the appropriate methods. This publication aims to establish a middle ground between the so-called “cook-book” and the detailed comprehensive type of manual. In doing so, analytical methods, which have been developed and adapted specially to the particular conditions of these soils, are described.

It is believed that this publication will be of particular interest to students, teachers, researchers and chemists working in laboratories for providing soil testing and analytical services to farmers in arid and semi-arid regions. It is also hoped that this manual will be a valuable reference to organizations helping in agricultural development projects in these regions.

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INTRODUCTION

With growing dependence on agriculture production in arid and semi-arid regions, use of fertilizers has increased tremendously. Ironically, more fertilizers are being applied than before, but agriculture production problems are, in general, getting worse. An important reason, yet little understood, is the improper use of fertilizers when it comes to kind and application rate. The problem arises partly from the lack of proper methods of soil analysis that reflects the actual soil status, and partly from the misunderstanding of what a fertilizer really is, how it should be used, and for what purpose. Soils of the semi-arid and arid regions vary widely in their condition and texture that range from sandy to loamy to clayey. The sandy soils vary in their chemical composition, such as content of silica, calcium carbonate and gypsum. The soil clay fraction varies in its mineralogical composition, which is a range of combinations of kaolonite, montmorillonite, micas, chlorite and attapulgite (Aba-Husayn and Sayegh, 1974). In addition, the proportionate occurrence of calcium carbonate, gypsum and soluble salts vary from one soil to another. Thus, fertilizer requirements of crops differ from one soil to another. Yet, fertilizer practices, as followed today in the Middle East, are carried-out on a trial and error basis without regard to soil properties and its fertilizer needs.

A sound soil management programme should provide crops with an adequate amount and in balanced proportion of all essential nutrients for optimum production. Diagnosis of deficiency can be checked by analysis of plant tissues and by soil analysis that reflect the actual condition of the soil. However, it should be recognized that fertility is only one of the major factors affecting crop production. Crop yield, both quantity and quality, is a function of several factors, like the soil, water, crop variety, management practices, climate, etc.

It is difficult to successfully manage salt affected calcareous and gypsiferous soils due to their poor physical conditions. Because of poor structure, aeration is seriously hindered. So is water infiltration and movement because of poor porosity. The outcome would be water logging and poor aeration.

In addition to their poor physical conditions, soils of arid and semi-arid regions possess chemical properties that would set off certain nutritional problems, like:

- Nitrogen volatilisation losses of surface applied ammonium or ammonium-forming fertilizers due to alkaline soil reaction and high Ca^{2+} activity.
- Phosphorus retention/fixation (precipitation of available fertilizer-P into less available forms) due to alkaline soil reaction and high Ca^{2+} activity.
- Reduction in plant uptake of potassium due to poor aeration resulting from excessive soil moisture content.
- Micronutrient deficiencies due to reduced solubility of Fe, Zn, Mn and Cu under alkaline soil reaction.

- Restricted root development due to poor structure and hard pan.

Consequently, the need and motivation for this publication grew out of the need to establish the use of soil and plant analyses as a guide to fertilizer recommendations. The scope of this publication has been kept limited to soil testing methods. Similar publication on methods of plant analysis will be considered at a future date.

GENERAL LABORATORY GUIDELINES

In chemical laboratories, the use of acids, alkalis and some hazardous and explosive chemicals is inescapable. Apart from this, some chemical reactions during the process of analysis may release toxic gases and if not handled well, may cause explosion. Inflammable gases are also used as a fuel/heating source. Thus safe working in a chemical laboratory needs special care, both in terms of design and construction of the laboratory building, and handling and use of chemicals. For chemical operations special chambers also need to be provided.

Air temperature of the laboratory and working rooms should be maintained at a constant level between 20-25^0 C. Humidity should be kept at about 50%. Soil samples are often affected by the temperature and humidity. The temperature influences even some chemical operations. Hence, maintenance of temperature and humidity as specified is critical.

Proper air circulation is also important so as hazardous and toxic fumes and gases do not stay in the laboratory for long. The release of gases and fumes in some specific analytical operation are controlled through fume hood, trapped in acidic/alkaline solutions and washed through flowing water. Maintenance of clean and hygienic environment in the laboratory is essential for the good health of the workers.

Care is needed to be taken to store acids and hazardous chemicals in separate and safe racks. An inventory of all the equipment, chemicals, glassware and miscellaneous items in a laboratory should be maintained. A safe laboratory building should have suitable separate rooms for different purposes and for performing different operations.

Laboratory Safety Measures

Special Care is required while operating equipment, handling the chemicals and in waste disposal.

Equipment

Electrical cables, plugs and tubing need proper check to avoid accident. Various types of gas cylinders needed in the laboratory like acetylene, nitrous oxide and LPG may be kept under watch and properly sealed/capped and may be stored in ventilated cupboards.

Chemical Reagents

Hazardous chemicals may be stored in plastic bottles. While working with chemicals such as perchloric acid, fume hood may be used. Chemicals may be properly labelled indicating their hazardous nature.

Bottles with inflammable substances need to be stored in stainless steel containers.

Waste Disposal

Each country has special rules and methods for disposal of hazardous waste. Cyanides, chromates, arsenic, selenium, cobalt and molybdate are very commonly used but hazardous chemicals and should never be disposed off in the laboratory sink but collected in a metal container for proper disposal at the specified places and in the manner as described in the country's law for waste disposal.

General Rules and Required Care

- Learn safety rules and use of first aid kits. Keep the first aid kit handy at a conspicuous working place in the laboratory.
- Personal safety aids such as laboratory coat, hand protection gloves, safety glasses, face shield and proper footwear should be used while working in the laboratory.
- Observe normal laboratory safety practice in connecting equipment with power supply, in handling chemicals and preparing solutions of reagents. All electrical work must be done by qualified personnel.
- Maintain instrument manual and logbook for each equipment to avoid mishandling, accident and damage to equipment.
- Keep the working tables/space clean. Clean up spillage immediately.
- Wash hands after handling toxic / hazardous chemical.
- Never suck the chemicals with mouth but use automatic pipetting device.
- Use forceps / tongs to remove containers from the hot plates/ovens/furnaces.
- Do not use laboratory glassware for eating/drinking.
- Use fume hood while handling concentrated acids, bases and hazardous chemicals.
- Never open a centrifuge cover until the machine has stopped.
- Add acid to water and not water to acid while diluting the acid.
- Always put labels on bottles, vessels and wash bottles containing reagents, solutions, samples and water.
- Handle perchloric acid in fume hoods. Avoid direct contact with organic matter/rubber. In wet oxidation method of sample digestion, destroy organic matter first with nitric acid.
- Read the labels of the bottles before opening them.

Laboratory Quality Control

Quality control is an important part of quality assurance, which is defined by ISO as “the operational techniques and activities that are used to satisfy quality requirements”. Quality assessment or evaluation is necessary to see if the activities performed to verify the quality are effective. Thus, an effective check on all the activities and processes in a laboratory can only ensure that the results pronounced on a product quality are within the acceptable parameters of accuracy.

In quality control system, the following steps are involved, which when implemented properly, ensure that the results delivered are acceptable and verifiable by another laboratory.

- Check on the performance of the instruments.
- Calibration or standardization of instruments and chemicals.
- Adoption of sample-check system as a batch control within the laboratory.
- External check – inter-laboratory exchange programme.

To ensure obtaining accurate and acceptable results of analysis on a sample, the laboratory has to run in a well regulated manner where the equipment are properly calibrated and the methods and techniques employed are scientifically sound which will give reproducible results. For ensuring the high standards of quality, Good Laboratory Practice (GLP) has to be followed. The GLP can be defined as “the organizational process and the conditions under which laboratory studies are planned, performed, monitored, recorded and reported”. Thus, the GLP expects a laboratory to work according to a system of procedures and protocols whereas the procedures are also specified as the Standard Operating Procedure (SOP).

Standard Operating Procedure

A Standard Operating Procedure (SOP) is a document, which describes the regularly recurring operations relevant to the quality of the investigation. The purpose of a SOP is to carry out the operation correctly and always in the same manner. A SOP should be available at the place where the work is done. If, for justifiable reasons, any deviation is allowed from SOP, the deviated procedure may be fully documented.

In a laboratory, SOP may be prepared for:

- Safety precaution.
- Procedure for operating instruments.
- Analytical methods and preparation of reagents.
- Registration of samples.

To sum up, all the operations have to be properly documented so as no chance is left for adhocism in any manner.

Error, Precision, Accuracy and Detection Limit

Error

Error is an important component of the analysis. In any analysis, when the quantity is measured with the greatest exactness that the instrument, method and observer are capable of, it is found that the results of successive determination differ among themselves to a greater or lesser extent. The average value is accepted as most probable. This may not always be true value. In some cases, the difference in the successive values may be small, in some cases it may be large, and the reliability of the result depends upon the magnitude of this difference. There could be a number of factors responsible for this difference which is also referred as 'error'. The error in absolute terms is the difference between the observed or measured value and the true or most probable value of the quantity measured. The absolute-error is a measure of the accuracy of the measurement. The accuracy of a determination may, therefore, be defined as the concordance between it and the true or most probable value. The relative error is the absolute error divided by the true or most probable value.

The error may be caused due to any deviation from the prescribed steps required to be taken in analysis. The purity of chemicals, their concentration/strength and the accuracy of the instruments and the skill of the technician are important factors.

Precision and Accuracy

In analysis, other important terms to be understood are precision and accuracy. Precision is defined as the concordance of a series of measurements of the same quantity. The mean deviation or the relative mean deviation is a measure of precision. In quantitative analysis, the precision of a measurement rarely exceeds 1 to 2 parts per thousand.

Accuracy expresses the correctness of a measurement, while precision expresses the reproducibility of a measurement. Precision always accompanies accuracy, but a high degree of precision does not imply accuracy. In ensuring high accuracy in analysis, accurate preparation of reagents including their perfect standardization is critical. Not only this, even the purity of chemicals is important. For all estimation, where actual measurement of a constituent of the sample in terms of the "precipitate formation" or formation of "coloured compound" or "concentration in the solvent" is a part of steps in estimation, chemical reagents involved in such aspects must always be of high purity which is referred as AR-grade (Analytical Reagent).

Detection Limit

In the analysis for trace elements in soils, plants and fertilizers and for environmental monitoring, need arises to measure very low contents of analytes. Modern equipment is capable of such estimation. However, while selecting equipment and the testing method for such purpose, it is important to have information about the lowest limits up to which analytes can be detected or determined with sufficient confidence. Such limits are called as detection limits or lower limits of detection.

The capacity of the equipment and the method may be such that it can detect the traces of analyte in the sample. In quantitative terms, the lowest contents of such analyte may be decided through appropriate research as the values of interpretable significance. The service laboratories are generally provided with such limits.

Quality Control of Analytical Procedures

Independent Standards

The ultimate aim of the quality control measures is to ensure the production of analytical data with a minimum of error and with consistency. Once, an appropriate method is selected, its execution has to be done with utmost care. To check and verify the accuracy of analysis, independent standards are used in the system. The extent of deviation of analytical value on a standard sample indicates the accuracy of the analysis. Independent standard can be prepared in the laboratory from pure chemicals. When new standard is prepared, the remainder of the old ones always has to be measured as a mutual check. If the results are not within the acceptable levels of accuracy, the process of calibration, preparation of standard curve and the preparation of reagents may be repeated till acceptable results are obtained on the standard sample. After assuring this, analysis on unknown sample has to be started.

Apart from independent standard, certified reference samples can also be used as ‘standard’. Such samples are obtained from other selected laboratories where the analysis on a prepared standard is carried out by more than one laboratory and such samples along with the accompanied analytical values are used as a check to ensure the accuracy of analysis.

Use of blank

A blank determination is an analysis without the analyte or attribute or in other words, an analysis without a sample by going through all steps of the procedure with the reagents only. Use of blank accounts for any contamination in the chemicals used in actual analysis. The ‘estimate’ of the blank is subtracted from the estimates of the samples. The use of ‘sequence control’ samples is made in

long batches in automated analysis. Generally two samples, one with a low content of analyte and another with very high content of known analyte (but the contents falling within the working range of the method) are used as standards to monitor the accuracy of analysis.

Blind sample

A sample with known content of analyte. This sample is inserted by the head of the laboratory in batches and times unknown to the analyst. Various types of sample material may serve as blind samples such as control samples or sufficiently large leftover of test samples (analysed several times). It is essential that analyst is aware of the possible presence of a blind sample but is not able to recognize the material as such.

Validation of procedures of analysis

Validation is the process of determining the performance characteristics of a method / procedure. It is a pre-requisite for judgement of the suitability of produced analytical data for the intended use. This implies that a method may be valid in one situation and invalid in another. If a method is very precise and accurate but expensive for adoption, it may be used only when the data with that order of precision are needed. The data may be inadequate, if the method is less accurate than required. Two types of validation are followed.

Validation of own procedure

In-house validation of method or procedure by individual user laboratory is a common practice. Many laboratories use their own version of even well established method for reasons of efficiency, cost and convenience. A change in liquid solid ratio in extraction procedures for available soil nutrients and shaking time etc. result in changed value, hence needs validation. Such changes are often introduced to consider local conditions, cost of analysis, required accuracy and efficiency.

Validation of such changes is the part of quality control in the laboratory. It is also a kind of research project, hence all types of the laboratories may not be in a position to modify the standard method. They should follow the given method as accepted and practised by most other laboratories.

Internal quality control

Apart from validation of methods, a system of internal quality control is required to be followed by the laboratories to ensure that they are capable of producing reliable analytical data with minimum of error. This requires continuous monitoring of the operation and systematic day to day checking of the produced data to decide whether these are reliable enough to be released.

Following steps need to be taken for internal quality control:

- Use a blank and a control (standard) sample of known composition along with the samples under analysis.
- Round off the analytical values to the 2^{nd} decimal place. The value of 3^{rd} decimal place may be omitted if less than 5. If it is more than 5, the value of second decimal may be raised by 1.

Since the quality control systems rely heavily on control samples, the sample preparation may be done with great care to ensure that the:

- Sample is homogenous.
- Sample material is stable.
- Material has uniform and correct particle size as sieved through a standard sieve.
- Relevant information such as properties of the sample and the concentration of the analyte are available.

The samples under analysis may also be processed/prepared in such a way that it has similar particle size and homogeneity as that of the standard (control) sample.

As and when an error is noticed in the analysis through internal check, corrective measures should be taken. The error can be due to calculation or typing. If not, it requires thorough check on sample identification, standards, chemicals, pipettes, dispensers, glassware, calibration procedure and equipment. Standard may be old or wrongly prepared. Pipette may indicate wrong volume, glassware may not be properly cleaned and the equipment may be defective or the sample intake tube may be clogged in case of flame photometer or Atomic Absorption Spectrophotometer. Source of error may be detected and samples be analysed again.

Validation of the Standard Procedure

This refers to the validation of new or existing method and procedures intended to be used in many laboratories including procedures accepted by national system or ISO. This involves an inter-laboratory programme of testing the method by a member of selected renowned laboratories according to a protocol issued to all participants. Validation is not only relevant when non-standard procedures are used but also when standard procedures are used, and even more when variants of standard procedures are introduced. The results of validation tests should be recorded in a validation report from which the suitability of a method for a certain purpose can be deduced.

Inter-Laboratory sample and data exchange programme:

If an error is suspected in the procedure and uncertainty cannot readily be solved, it is not uncommon to have the sample analysed in another laboratory of the same system/organisation. The results of the other laboratory may or may not be biased, hence doubt may persist. The sample checks by another accredited laboratory may be necessary and useful to resolve the problem.

An accredited laboratory should participate at least in one inter laboratory exchange programme. Such programmes do exist locally, regionally, nationally and internationally. The laboratory exchange programme exists for method performance studies and laboratory performance studies.

In such exchange programme, some laboratories or the organizations have devised the system where periodically samples of known composition are sent to the participating laboratory without disclosing the results. The participating laboratory will analyse the sample by a given method and find out the results. It provides a possibility for assessing the accuracy of the method being used by a laboratory and also about the adoption of the method suggested by the lead laboratory. Some of Such Programmes are:

- International Plant Analytical Exchange (IPE) Programme, and
- International Soil Analytical Exchange (ISE) Program.

They come under the Wageningen Evaluating Programme for Analytical Laboratories (WEPAL) of the Wageningen Agricultural University, the Netherlands. Other programmes run by the Wageningen Agricultural University are:

- International Sediment Exchange for Tests on Organic Contaminants (SETOC).
- International Manure and Refuse Sample Exchange Programme (MARSEP).

Another International Organization operating such laboratory and method evaluation programme is Association of Official Analytical Chemists (AOAC) of USA. One of the most popular programme of AOAC is for Fertilizer Quality Control Laboratories and the analytical methods for fertilizer testing.

For quality check, each laboratory will benefit if it becomes part of some sample/method check and evaluation programme. The system of self-check within the laboratory also has to be regularly followed.

1. SOILS OF ARID AND SEMI-ARID REGIONS

The soils of arid and semi-arid regions are the products of several factors, mainly climate, parent materials and topography. The dominant rocks are limestone, sandstone and metamorphic rocks. Wind-blown sand constitutes a major part of the soil material. Gypsum is encountered in variable depths and salts accumulate because leaching is not active. Predominantly, the following types of soils are found in arid and semi-arid regions

1.1. Calcareous Soils

Most soils of the arid and semi-arid regions in the Near East are high in calcium because they were developed from limestone and sandstone of various hardness. The amount and form of $CaCO_3$ (total versus active) and its distribution down the soil profile affect soil physical and chemical characteristics. According to the research done in Lebanon by the authors, with the same amount of $CaCO_3$, soils derived from hard limestone, have less active $CaCO_3$ than the soils derived from soft limestone (marl). The $CaCO_3$ rich soils are widely spread in the Near East region due to year-round warm dry climatic conditions and insufficient annual rainfall (less than 400 mm) to dissolve the lime and leach it off the soil profile. Though, the soils have a potential for agricultural development under rainfed as well as irrigated conditions, the productivity is limited due to low fertility, low water holding capacity, shallow soil depth, prevalence of hardpan and faulty irrigation practices.

1.2. Gypsiferous Soils

Gypsum is found in soils of the arid and semi-arid regions in amounts ranging from traces to high level. In some soils, gypsum is present in sedimentary deposits from which the soil was derived and in others it is formed by precipitation of $Ca^{2+}$and SO_4^{2-} (during salinization) when the ground water is brought upward by capillary action to replace water lost by evaporation. Gypsiferous soils have different forms of gypsum in soils because of the varied sources and conditions under which it forms (Boyadgiev and Sayegh, 1992). Solubility of gypsum is low, like 2.6 g/litre of $CaSO_4.2H_2O$ in distilled water at 25°C. Continued irrigation of gypsiferous soil lead to subsidence and collapse of the irrigation and drainage systems.

Measurement of total gypsum in soils by conventional methods is unreliable as was proven by Sayegh *et al.* (1978). Figures quoted in the literature for gypsum contents are commonly much lower than the actual amount present.

1.3. Salt Affected Soils

Since ancient times man had noticed that there are soils that contain excessive amounts of salts. Plant growth on these soils is sporadic, production is low and

farmers usually abandon such lands to let them eventually become a barren desert.

The primary salinity usually spreads out in poorly drained lowlands in arid and semi-arid regions.

In arid and semi-arid regions “P/ET” (the ratio of precipitation to evapotranspiration) is 0.03 < P/ET < 0.2 and 0.2 < P/ET < 0.5, respectively (Balba, 1995). Introduction of irrigation without providing efficient drainage changes the natural water balance in the newly irrigated areas causing the ground water level to rise up with water logging, salinization or sodification. The chemical properties of salt affected soils are summarized in Table 1

Table 1. Chemical characteristics of saline, non-saline sodic and saline sodic soils

Soil	EC dS/m	ESP	pH
Saline	>4.0	<15	<8.5
Sodic (nonsaline)	<4.0	>15	>8.5
Saline Sodic	>4.0	>15	<8.5

Source: Richards, 1954

2. SOIL SAMPLING AND PREPARATION

Soils are sampled for different purposes and, so, different methods are employed to satisfy the purpose for which the sample is collected. Sampling errors are often greater than analytical errors. If the collected soil samples are not truly representative samples, results of the analyses will not reflect the properties of the soil under investigation. Therefore, collecting a representative soil sample from the field is the most important aspect of soil analysis. According to Cline (1944), the analytical values can serve as an accurate description of the soil property under investigation if:

- The gross (or bulk) sample accurately represents the whole soil from which it was taken,
- No changes occur in the gross and sub-samples prior to analysis,
- The sub-sample analyzed represents the gross sample accurately,
- The analytical data produced are truly measuring the soil parameter under investigation.

2.1. Soil Sampling Tools

Tarzi (1984) reported two important requirements of a soil sampling tool: first, that the tool allows for a uniform slice to be taken from the surface to the depth of insertion of the tool, and second, that the same volume of soil be taken from each sampling point. Bucket auger, shovels or garden trowels have proven to be useful tools in sampling arid and semi-arid soils.

In general, soil-sampling tools are divided into four major groups:

1. Various types of hand augers, such as:
   - Bucket auger: This is a cylindrical auger with specially designed cutting bits at the lower end. This type is the most suitable for medium textured soils.
   - Dutch auger: This auger is particularly effective on coherent moist and rather wet soils of high clay content. It is not effective on sandy, gravelly or stony soils or on dry soils of any texture.
   - Jarret auger: This is an open bucket auger with side cutters of robust design. It penetrates most soils and is particularly effective in gravelly soils, but will not collect samples in dry non-coherent soils unless they are wetted during boring.
   - Screw auger: The screw auger is of limited value for soil observation because of the severe disturbance of the sample during collection. It can be useful in collecting samples for fertility evaluation and rapid soil examination to check map boundaries. It is not effective on sandy or gravelly soils.

- Tube sampler: This sampler is useful for rapid sampling of topsoil in medium textured soils. It is not effective on non-coherent soils, hard clays or gravelly soils.
- Blades, shovels, spades, knives, and core samplers.

2. Tubes and cylinders.
3. Hydraulic equipment.

2.2. Sampling for Soil Fertility Tests

Chemical analysis of soil samples is a prime source of information on the relative availability of plant nutrients. When the soil test is calibrated with crop response and soil samples are properly obtained, the test results can be a strong pivotal point around which management decisions on fertilizer application and soil fertility management can be taken. However, if soil test correlations are weak or soil samples unrepresentative, then the soil test will not be very useful and it may be misleading. This leads to the following questions:

1. Does the soil nutrient level indicated by the chemical analysis actually have a relationship to the nutrient uptake and growth of plants? In other words, does the soil test correlate with fertilizer requirements and crop performance in the field?
2. How well does the soil sample represent the field in question? The analytical aspect of soil testing may correlate perfectly with crop response, but if the soil sample is unrepresentative, then the soil test result cannot have much value.

2.2.1. Time of Sampling

The correct time of sampling cannot be decisively specified. However, sampling after fertilization should be avoided. A key point is to collect samples in time to be analyzed for deciding fertilizer application rates and their application. Samples can be taken during crop growing period when soil content of nutrients is stressed. For example, samples collected in spring, as soil starts warming up, would give lower values of available-P than samples collected in autumn when soil temperature is low. The reason for the lower values for available-P in spring could be the increased soil microbiological activities, which use up part of the soil-P. It is important to take this into consideration in the evaluation.

It is usually recommended that each field be tested once every three years. In most instances this is often enough to determine whether the fertilization programme is adequate, and whether there is need for an increase or decrease in the rate of application.

2.2.2. Depth of Sampling

Samples are usually collected from soil surface layer down to a depth of 15-25 cm in cultivated fields. Some farmers plough to a depth of 30 cm, and then samples should be collected up to this depth. When fertilizers are broadcast on soil surface, still the samples must be collected all through the plough-depth of 15-25 cm. In vegetable fields, it is advisable to collect separate samples from the 0-15 and 15-30 cm layers. In fruit tree orchards, the depth of soil sampling should be extended to the depth of root zone, 0-30, 30-60 and 60-100 cm, if the root system reaches to about 100 cm of depth.

2.2.3. Methods of Sampling

A field can be sampled to estimate its fertility through soil analysis by several methods. These include, among others:

1. A composite sample, i.e., a single sample consisting of the composite of several randomly selected soil cores.
2. Multiple samples taken systematically on a grid pattern.

The multiple sampling method is the best because, in addition to providing estimates of nutrient levels, it shows variation in fertility from one part of the field to another.

Intensive soil sampling will not be practical unless the economic returns justify the costs, or where the topographic conditions are such that high variability is expected. Thus, the most commonly recommended sampling procedure is the composite sample. A good composite sample is made up of a number of soil cores taken at random from 15 – 20 sites in a 1 – 5 ha cultivated field. The purpose of this procedure is to minimize the influence of any local variability in the soil. For example, band-applied fertilizers are not uniformly applied over the soil surface. In addition, there may be some spots in the field where fertilizers were spilled or plant refuse was buried. A sample taken from such an area would be completely misleading. Consequently, most recommendations call for taking borings at 15-20 locations over the field for each composite sample.

Areas that vary in appearance, slope, drainage, soil type, and previous treatments should be sampled separately, and areas that cannot be treated or fertilized separately should be omitted. Figure 1 shows a sampling pattern in a heterogeneous land. Many growers are directing attention to these small spots in their fields and treating them as needed. Hence, it is advisable to take separate samples from these localized areas of poor crop growth.

Sampling recently fertilized bands, dead furrows, areas adjacent to roads, or where manure, compost or crop residues have been piled should be avoided. A random distribution of individual sample sites would be ideal. However, equally reliable information is obtainable with much less effort by reducing the sampling area when the fields are relatively uniform. Sampling areas are often traversed in

a zigzag pattern to provide a uniform distribution of sampling sites. Some of these methods are presented in Figure 2. In fruit tree orchards, particularly those irrigated by a drip system, soil samples should be collected from the root zone of trees, i.e., the zone moistened by irrigation, reaching to the depth of the root system. Trees, around which soil is to be sampled, are selected in a random or systematic pattern. A reasonable number of sites (trees) would range from 5-20% of total number of trees.

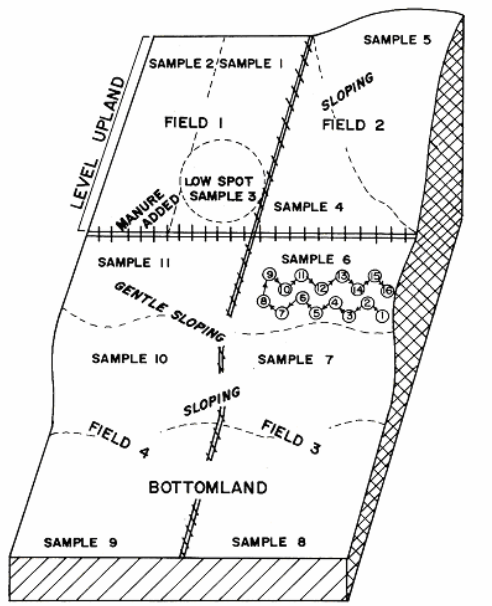

Figure 1. Sampling pattern for fertility test in a non-uniform land

(Sample numbers refer to composite samples) (Source: Tarzi, 1984)

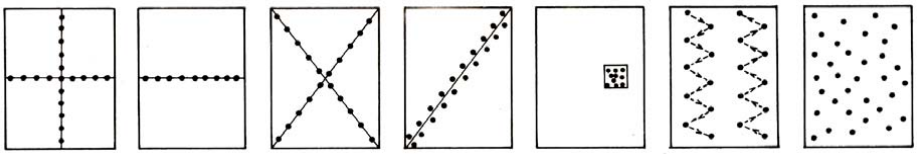

Figure 2. Sampling-sites selection methods for fertility test

2.3. Soil Sampling for Soil Survey and Classification Studies

Soil survey is a type of pedological study the purpose of which is to describe soil characteristics for areas of a few to hundreds or thousands of hectares, and delineate these areas on a map. Normally, these surveys are government projects carried out to determine and develop land use and management.

In soils having distinguishable genetic horizons, pits are dug to about two meters depth or to bed rock if it is shallower than 2 m. Soil profiles are studied and samples are taken from each horizon. Where surface soil did not develop from the underlying parent materials, as in depositional soils, samples are collected from a sequence of depth intervals, e.g. 20-30 cm intervals.

Soil surveyors commence from a convenient point or landmark, and then select fields or sites for boring or digging of pits. The methodology will vary in details depending upon the type of terrain, geology, landforms and spatial variability of the land. More important are the survey objectives, the mapping scale, and the complexity of the soil pattern to be surveyed. Arial photos taken for the terrain to be surveyed, and now images taken by remote sensing from satellites, are first studied to collect some basic information about relief and other physical feature of the terrain to be surveyed. The dependability of these images serves in approaching and executing soil survey projects.

In areas with a relatively simple soil pattern, the average observation density will be one pit per 15-20 hectares. In areas with complex soil patterns, the density will be one per 10-15 hectares. The observation density will be lower in areas of poor soils such as shallow soils, rocky soils, undulating and ridges. Soil surveyors correlate soil series and mapping units with landform units and land surface features.

2.4. Preparation of Soil Samples

Following the sampling process, soil cores are placed in a clean container and clods are crushed. After mixing well the gross soil sample, about one kg is transferred into a clean plastic or canvas lined with plastic bag. This is the composite sample to be sent for analysis. Bags should be properly labelled. Information such as sample number, depth, and date of sampling should be written on the bag from outside, and on a sample card placed inside the bag. Bags should be closed tightly, placed in wooden or cardboard box, and then shipped or taken to the laboratory.

It is essential that a Field Data Sheet be filled and sent with the samples to the laboratory (Figure 3). Information recorded on the data sheet must be accurate. Questions for which reliable answers cannot be provided should be left unanswered. In the laboratory, the collected sample is spread thinly on a plastic sheet or tray for air-drying. Air-drying is the most accepted procedure of sample preservation and may reduce the rate of possible reactions in the disturbed soil sample. A soil sample should not be allowed to stay moist for extended periods

of time. Soil aggregates should be broken carefully to accelerate the drying process. It is generally assumed that chemical and biochemical reactions in air-dry soils are reduced to a minimum, although these reactions are still possible sources of error.

FIELD DATA SHEET

Sample No. _____

Collector _____ Address_____ Date _____

Area _____ Location_____ Owner _____

Farm Size _____ Vegetative Cover_____

Source of Water _____ Water Quality _____

Sample Depth _____ Previous Crop _____

Site Selection Method:
- ☐ Random
- ☐ Zig Zag
- ☐ Two Way Diagonal
- ☐ Two Way Cross-Strip
- ☐ Test Plot

Sample Type:
- ☐ Individual
- ☐ Composite
- ☐ No. of cores

Purpose of Analysis:
- ☐ Capability Assessment
- ☐ Fertility Evaluation
- ☐ Salinity Appraisal
- ☐ Soil Classification

Slope:
- ☐ 1-2%
- ☐ 2-5%
- ☐ 5-10%
- ☐ 10-25%
- ☐ > 25%

Irrigation Method:
- ☐ Flood
- ☐ Furrow
- ☐ Sprinkler
- ☐ Center Pivot
- ☐ Drip
- ☐ Rainfed

Years of Irrigation:
- ☐ Never Irrigated
- ☐ 1-5
- ☐ 5-15
- ☐ > 15

Years of Cultivation:
- ☐ Never Cultivated
- ☐ 1-5 years
- ☐ 5-15 years
- ☐ >15 years

Drainage:
- ☐ Good
- ☐ Moderate
- ☐ Poor

Manure/Fertilizer Application History:

Manure (type) _____ Rate (kg/ha)_____

Fertilizers (mineral) _____ Rate (kg/ha)_____

Note: Questions for which accurate answers cannot be provided should be left unanswered.

Figure 3. Field data sheet

To accelerate the drying process, samples may be placed in forced draft of moving air, but not in heated air. The temperature must not exceed 35°C because drying at elevated temperatures may cause drastic changes in the physical and chemical characteristics of the soil sample (Hesse, 1972). Drying may also result in increased cementation, which may particularly affect particle size distribution analysis. Other possible results from drying at higher temperatures are chemical changes in the oxidation status of elements, variation in the content of available nutrients (Sayegh, 1986) and microbiological reactions. The degree to which such changes occur varies with temperature and time of drying.

For some quick soil analysis, like NO_3-N and NH_4-N, the measurements are done on moist soil samples as collected from the field. A separate sample is taken to determine soil moisture which is then used to convert results to oven-dry basis.

2.5. Grinding and Sieving of Soil Samples

Thorough mixing requires that the sample be crushed and ground to particles of uniform size. After drying the sample, clods and large aggregates are crushed and mixed. Then the crushed material is further ground to pass 2 mm sieve. Care should be taken not to break the individual soil particles during the grinding process. The purpose of grinding is to reduce heterogeneity and to provide maximum surface area for physical and chemical reactions. Various devices are used for crushing and grinding soils. The choice of equipment depends on four factors:

1. The amount of sample to be crushed or ground.
2. The degree of fineness to be attained.
3. The contamination that can be tolerated.
4. The analysis in question.

Soil aggregates can be crushed by using jaw crushers, hardened steel mortars or rocking boards (Tan, 1996). Jaw crushers are used for crushing large aggregates, steel mortars for smaller aggregates, and rocking boards for small aggregates. The types of grinders used are plate grinders (friction mills), ball mills, rod mills, agate mortars, and boron carbide mortars. For large amounts of samples, plate grinders or ball mills or rod mills are used. The sample is mixed with stainless steel rods or balls, in a container and the container is rolled over a period of time. When properly operated, rod and ball mills are efficient grinders (Coghill and Devaney, 1937). For least contamination and for small amounts of samples, an agate or boron carbide mortar can be used.

After grinding, the soil is sieved through a 2 mm sieve and stored in air-tight glass or clean plastic containers as soon as possible to avoid adsorption of gases in the laboratory. This will serve as stock samples for analysis. Then,

samples should be stored in a cool and well-ventilated room. Analysis of samples that are passed through sieves of unspecified sizes may produce results that would not be comparable to internationally accepted data. Therefore, the sieve size should be reported with the results of analysis.

2.6. Reduction of Sample Size

When a very large sample is collected, it is necessary to reduce the size of the sample for ease of storage and handling. The bulk sample must be reduced in size, and the sub-sample taken for analysis should represent the soil characteristic of the field under investigation. In order to achieve this goal, a random and unbiased method of sub-sampling is essential. Sample splitting can be performed with a mechanical sample splitter, such as a riffle sampler, by which the sample is divided in half by a series of chutes (Krumbein and Pettijohn, 1938; Willard and Dhiel, 1943; Hesse, 1972). This process can be repeated as many times as necessary.

Another way for reduction of sample size is by *quartering*. The sample is spread uniformly over a plastic sheet and divided into four equal portions (Figure 4). Portions 2 and 3 are collected and thoroughly mixed, whereas the remainder is discarded. This process of quartering can be repeated as many times as necessary until the proper size of sample is attained.

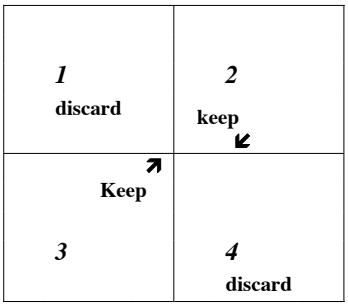

Figure 4. Reduction of sample size by quartering

3. SOIL MOISTURE

Water is held in soil by adhesive and cohesive forces. Adhesion is the force of attraction between the solid soil particles and water molecules. Cohesion is the mutual force of attraction between water molecules. Another force that affects water retention and movement in soil is the capillary force, which is a function of the size of micropores or capillaries.

The pF is the term mostly used to express soil moisture, although other terms are also used, like atmosphere or bar. Water can exist in soil under a tension varying from pF = 0 (no tension) to pF = 7.0 (high tension). The point at which water is held in soil after excess water has drained out by gravity is called field capacity (pF = 2.54). The point at which water is held in soil at a force that plants cannot extract at a sufficient rate to maintain turgor, is known as wilting point (pF = 4.2). At this point the plants start to wilt. The amount of water between field capacity and wilting point is called available water. Water in air dry soil is held with a tension of pF 6.0.

Apparatus

- Moisture determination cans
- Analytical balance
- Drying oven
- Desiccator

Procedure

1. Weigh accurately a metal can with lid (W_1).
2. Place about 50 g of soil in the can and weigh accurately along with the lid (W_2).
3. Place the can with the lid under it in a drying oven at 105°C for 24 – 48 hours, or until constant weight is reached.
4. Remove the can from the oven, cover it tightly with the lid, and place in a desiccator to cool.
5. After cooling, weigh the can accurately with the oven-dry soil in it. Record the weight (W_3).
6. Compute percent moisture content on oven-dry basis.

Calculation

$$\text{Weight of water} = W_2 - W_3$$

$$\text{Weight of oven dry soil} = W_3 - W_1$$

$$\text{Moisture \% (oven - dry basis)} = \frac{W_2 - W_3}{W_3 - W_1} \times 100$$

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

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

Normally, soil moisture is expressed on oven-dry basis. However, for certain purposes, moisture content is expressed on wet-soil basis. To do so, the weight of the wet-soil sample ($W_2 - W_1$) is used instead of the oven-dry weight ($W_3 - W_1$):

$$\text{Weight of water} = W_2 - W_3$$

$$\text{Weight of wet - soil} = W_2 - W_1$$

$$\text{Moisture \% (wet} - \text{soil basis)} = \frac{W_2 - W_3}{W_2 - W_1} \times 100$$

4. SOIL TEXTURE – PARTICLE SIZE DISTRIBUTION

4.1. Introduction

Soil texture, or particle size distribution, is a rather stable soil characteristic which influences the physical and chemical properties of the soil. There is a direct relation between particle size and the total surface area of particles in a given weight of soil. As particle size decreases, total surface area, better known as specific surface area, increases. Since most of the physical and chemical properties of soil are related to surface activity, determination of particle size distribution is a standard procedure for characterizing and classifying soils.

As soil particles are freely settling down the water column, they are sorted according to particle size. Coarse particles, like sand, move down faster than fine particles. Because of their differential settling rate in water, the size fractions are sorted into different size ranges. The Bouyoucos Hydrometer is calibrated to read the amount of solid particles remaining in suspension, hence the method is known as Bouyoucos Method.

Two basic conditions are required in this method:

- Dispersion of the soil sample into a state of single grain particles
- During sedimentation, particles should be moving down freely

Determination of the particle size distribution of gypsiferous-calcareous soils is a tedious and time-consuming process. Gypsum, which inhibits soil dispersion, is usually removed from soil samples before analysis, although gypsum has marked effects on the physical properties of soils and it is most desirable to determine the particle size distribution without removing the gypsum fraction. Hesse (1974) and Matar and Douleimy (1978) developed methods for the preparation of a stable suspension of gypsiferous soils without removing the gypsum fraction. Vielliefom (1979) gave a substantially improved method based on that of Hesse. So far, no method for the determination of the particle size distribution of gypsiferous-calcareous soils is entirely satisfactory.

The estimation of texture under field conditions is misleading because of the presence of gypsum crystals in various sand-sized fractions. The forms and degree of crystallization of gypsum particles influence the feel of the soil and as a result field estimates of texture are generally coarser than indicated by laboratory determinations.

Based on the experience gained from the analysis of a large number of gypsiferous soil samples, the following can be concluded:

1. The sum of the various size-fractions of gypsiferous horizons may be less than 100 percent due to dehydration of $CaSO_4.2H_2O$ during oven drying at 105°C.
2. The distribution of gypsum within the various size-fractions depends on the total amount of gypsum (Vieillefon, 1979). The difference between the weight of such fractions obtained after treatment at 50°C and 105°C shows the following:
    - The fraction less than 20 μm in diameter is greater when the total content of gypsum is about 10 percent, and decreases with the increase of gypsum content to about 25 percent. This fraction does not change as gypsum content increases from 25 to 45 percent, but it increases again as gypsum content goes above 45 percent.
    - The amount of the fractions greater than 20 μm in diameter increases as the total amount of gypsum increases. For most samples with gypsum content between 10 and 25 percent, the relationship is not significant.
3. Gypsum is found in all size fractions, but it is mostly present in the coarse and fine sand fractions (0.02-2.0 mm) followed by the silt fraction.

4.2. Dispersion

Individual soil particles must be separated from each other, and kept separated during the determination in order to correctly measure particle size distribution. Since aggregates of solid particles are usually held together by some kind of binding agent, it is first necessary to remove these substances, or at least render them ineffective. Once the soil aggregates are separated into individual particles, they are described as dispersed particles.

Dispersion is achieved by chemical and mechanical means. Sodium-hexametaphosphate is an effective chemical dispersing agent for two reasons:

1. The sodium monovalent cation replaces the usual polyvalent cations adsorbed on soils, thereby breaking interparticle linkages. The polyvalent cations are also reduced in activity as a result of reaction with the phosphorus and consequent precipitation.
2. The adsorbed sodium cations raise the electronegativity of colloids until these particles repel each other and remain dispersed.

After the binding agents are removed, aggregates breakdown is further facilitated by mechanical stirring. The mixture of dispersed soil particles in water is called a soil suspension.

4.3. Sedimentation

In sedimentation techniques, the settling rates of dispersed particles in water are measured. Large particles are known to settle out of suspension more rapidly than do small particles. This is because larger particles have less specific surface area and hence less buoyancy than small particles. Stocke's law is used to express this relationship:

$$V = \frac{2}{9} x \frac{r^2 g(d_1 - d_2)}{n}$$

The formula shows that settling velocity, **V**, is directly proportional to the square of the particle's effective radius, **r**; the acceleration of gravity, **g**; and the difference between the densities of the particle, $\mathbf{d_1}$, and that of the liquid, $\mathbf{d_2}$; but inversely proportional to the viscosity of the liquid, **n**. Density of water and its viscosity are both affected by temperature, and thus, particles settle faster with increased temperature. This is why it is necessary to apply correction for temperature.

In practice, the amount of material remaining in suspension at any time is measured with a hydrometer, which indicates the density of the suspension at the hydrometer's centre of buoyancy. Bouyoucos determined that after 40 seconds all sand-sized particles (0.02 mm and larger) settle out of the suspension and do not influence the hydrometer reading. After two hours, particles larger than clay (0.002 mm) settle out of the suspension and do not affect the hydrometer reading any more.

4.4. Bouyoucos Method

Apparatus

- Electric mixer (stirrer), with baffled stirring cup
- Settling cylinder
- Graduated cylinder, 1 litre, with 1 000 ml mark 36 ±2 cm from bottom
- Bouyoucos Hydrometer calibrated at 200°C
- Thermometer C°

Reagent

- Sodium hexametaphosphate, $Na_6O_{18}P_6$ solution (examples of commercial names: Calgon, Graham's salt, glassy sodium): Dissolve 50 g of Calgon in water and dilute the solution to a volume of 1 litre

Procedure

1. Weigh 50 g oven dried fine textured soil (100 g of coarse textured soil) into a baffled stirring cup. Fill the cup to its half with distilled water and add 10 ml of sodium hexametaphosphate solution.
2. Place the cup on stirrer and stir until soil aggregates are broken down. This usually requires 3-4 minutes for coarse textured soils and 7-8 minutes for fine textured clay.
3. Transfer quantitatively the suspension to the settling cylinder by washing the cup with distilled water. Fill the cylinder to the lower mark with distilled water after placing the hydrometer in the liquid. If 100 g of coarse textured sample was used, fill to the upper mark on the settling cylinder.
4. Remove hydrometer and shake the suspension vigorously in a back and forth manner. Avoid creating circular currents in the liquid, as they will influence the settling rate.
5. Place the cylinder on a table and record the time. After 20 seconds, carefully insert the hydrometer and read the hydrometer at the end of 40 seconds.
6. Repeat step 4 and 5 to obtain hydrometer readings within 0.5 g differences from each other. The hydrometer is calibrated to read grams of soil material in suspension.
7. Record the readings on the Data Sheet for Hydrometer Readings (a sample is shown in Figure 5).
8. Measure the temperature of the suspension. For each degree above 20°C add 0.36 to the hydrometer reading, and for each degree below 20°C, subtract 0.36 from the hydrometer reading. This is the corrected hydrometer reading.
9. Re-shake the suspension and place the cylinder on a table where it will not be disturbed. Take a hydrometer reading exactly two hours later. Correct for temperature as described above.
10. From the percentage of sand, silt and clay as calculated on the Data Sheet, use the diagram for textural triangle (Figure 6) to determine the textural class of the soil.

(1)	Soil sample identification number	_____
(2)	Soil weight (g)	_____
(3)	Forty second hydrometer reading (g)	_____
(4)	Temperature of suspension (C°)	_____
(5)	Corrected 40-second hydrometer reading (g)	_____
(6)	Two hours hydrometer reading (g)	_____
(7)	Temperature of suspension (C°)	_____
(8)	Corrected 2-hour hydrometer reading (g)	_____
(9)	Grams of sand (the sand settles to the bottom of the cylinder within 40 seconds, therefore, the 40-second corrected hydrometer reading actually gives the grams of silt and clay in suspension. The weight of sand in the sample is obtained by subtracting line 5 from line 2)	_____
(10)	Grams of clay (the corrected hydrometer reading at the end of two hours represents grams of clay in the suspension since all sand and silt has already settled by this time).	_____
(11)	Percent sand (line 9 ÷ line 2) × 100	_____
(12)	Percent clay (line 10 ÷ line 2) × 100	_____
(13)	Percent silt (find the silt by difference. Subtract the sum of the percent sand and clay from 100).	_____
(14)	Soil class (as per Figure 6)	_____

Figure 5. Data sheet for recording of hydrometer readings

Some experienced field men take a sample of soil in their hand, feel it with their fingers when dry, and then inspect its stickiness after wetting, and then they come up with a skilled guess about the textural class of the soil (Figure 7).

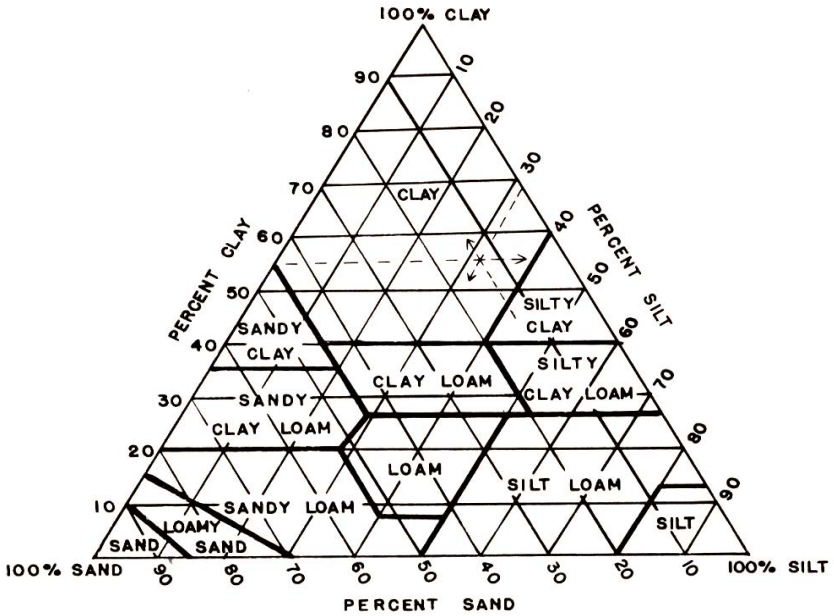

Figure 6. Texture triangle showing the percentages of sand, silt and clay in the textural classes

(the intersection of the dotted lines shows that a soil with 55 percent clay, 32 percent silt and 13 percent sand has a clay texture).

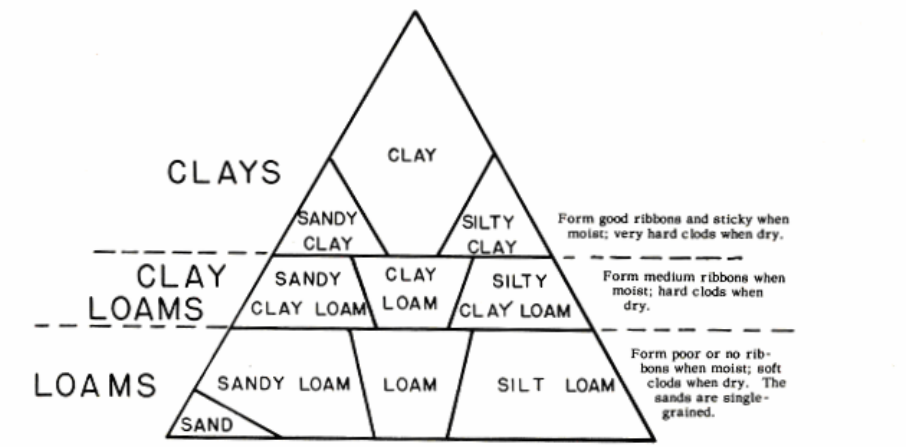

Figure 7. Modified textural triangle for determining soil texture by the feel method (Source: Foth *et al.*, 1977)

4.5. Gypsum Removal from Soil

For certain gypsiferous soils, it is recommended that gypsum be removed from the soil sample prior to its analysis for particle size distribution. The following are the methods that could be used for this purpose. Method 4.5.3 is preferred because gypsum is not removed from the sample and the results are closer to the field conditions.

4.5.1. Gypsum Removal by Ammonium Oxalate (Coutinet, 1965)

1. Weigh 40 g of soil in an Erlenmeyer flask, and add to it about 40 ml of distilled water.
2. Bring to boiling while stirring. Then add 2–3 ml of hydrogen peroxide (H_2O_2) to destroy the organic matter. Repeat the addition of H_2O_2 until effervescence stops.
3. Transfer the content into a 600 ml Erlenmeyer flask, by repeated washing of the soil with distilled water.
4. Add more distilled water to bring the total volume to about 300 ml.
5. If the gypsum content is not more than 25 percent (based on pre-estimation to know the range), add 5 g of ammonium oxalate and boil the mixture for one hour. Discard the supernatant.
6. Repeat steps 4 and 5 until no more calcium sulphate crystals are seen in solution.
7. Add 20 ml of sodium-hexametaphosphate solution (40 g/l) and boil the mixture for 3 hours.
8. Wash the content and quantitatively decant into the cylinder, then proceed to determine the particle-size fractions.
9. If gypsum content is more than 25 percent, follow the same procedure as above, but use sodium chloride solution (131.6 g/l) instead of ammonium oxalate.

4.5.2. Gypsum Removal by Hydrochloric Acid (Loveday, 1974)

This procedure is used for soils containing visible gypsum crystals, and having an electrical conductivity ($EC_{1:5}$) >3 mS/cm.

1. Weigh 25 g of air-dry soil and transfer into an 800 ml Erlenmeyer flask.
2. Add 25 ml of 2M HCl to the flask and gently swirl to destroy the $CaCO_3$ content of the soil. Allow to stand for 2-3 minutes.
3. Add 5 drops of H_2O_2 and gently swirl the flask to destroy organic matter. Add more drops until effervescence stops.

4. Add 500 ml distilled water and place on a magnetic stirrer. Stir for one hour, allow to settle and decant the clear supernatant.
5. Repeat step 4 until the crystals of gypsum do not show anymore on the sides of the beaker.
6. Add 5 ml of 1M NaOH and 10 ml of 10% sodium-hexametaphosphate, swirl gently and leave for 20 minutes to allow the dispersing of the soil sample.
7. Wash the content and quantitatively decant into the cylinder, then proceed to determine the particle-size fractions.

4.5.3. Pre-treatment of Soil with $BaCl_2$ to Coat Gypsum with $BaSO_4$ (Hesse, 1974)

1. Transfer 10 g of soil into a 100 ml centrifuge tube, and then add 40 ml of a solution containing 50 g/l barium chloride ($BaCl_2$) and 20 ml of 45 ml/l tri-ethanolamine, and shake gently for one hour.
2. Centrifuge and decant the supernatant.
3. Add 40 ml water in the tube, then shake and decant. Repeat washing the soil with water until no more barium ions can be detected in the supernatant. The presence of Ba can be confirmed if after adding a few drops of potassium chromate solution a yellow precipitate forms.
4. Add 15 ml of a solution containing 40 g/l sodium hexametaphosphate, 10 g/l anhydrous sodium carbonate, and 10 percent sodium hydroxide to the treated soil, and disperse by shaking for 30 minutes.
5. Transfer the tube content by several washings with distilled water into the graduated cylinder for particle-size determination, and proceed as in procedure in section 4.4.

4.5.4. Pre-treatment of Soil with $BaCl_2$ Solution followed by Ethanol (Mater and Douleimy, 1978)

1. Place 10 g of soil in a small funnel fitted with a filter paper, and slowly leach with 0.1M $BaCl_2$ solution.
2. Leach the excess Ba ions with pure ethanol until no more Ba is detected in the filtrate. The presence of Ba in the solution can be determined as indicated in 4.5.3
3. Transfer the soil into the suspension cylinder and stir the suspension for 12 minutes after adding distilled water and 10 ml of sodium-hexametaphosphate (40 g/l).
4. Proceed to determine the particle-size fractions.

4.5.5. Pre-treatment with $BaCl_2$ Solution (Modified Method by Vieillefon, 1979)

1. Shake 10 g soil with 10 ml $BaCl_2$ (50 g/l) and 20 ml triethanolamine [$(HOCH_2CH_2)_3N$], in a centrifuge tube.
2. Shake for 1 hour and then centrifuge the suspension.
3. Discard the supernatant liquid.
4. Add 40 ml distilled water, centrifuge, and discard the supernatant liquid.
5. Add 15 ml of dispersing solution [4% sodium hexametaphosphate + 1% of sodium carbonate (Na_2CO_3)], adjust pH to 8.2 and shake.
6. Determine the various particle-size fractions.

5. SOIL DENSITY AND TOTAL PORE SPACE

5.1. Introduction

Soil bulk density (BD) is defined as the mass of oven-dried solids divided by the bulk volume of the solids plus pore space at a specified soil water content, usually the moisture content at sampling.

Soil particle density (PD) is defined as the mass of oven-dried solids divided by the volume of the solid particles alone. Actually, it is the density of the soil particles, irrespective of the volume of voids between particles. The magnitude of PD depends on the type of minerals in the particles, and the content of organic matter in the soil. The particle density of most mineral soils is about 2.65 g/cm^3. It varies little from soil to soil and, therefore, is of little practical significance. It is used with bulk density to calculate soil porosity.

Bulk density is an extremely useful parameter, as it indicates soil structure and void space. It is required to calculate porosity when particle density is known, to convert weights to volumes, and to estimate weights of soil volumes too large to weigh. It is also required to convert weight-based determinations to a volume-based figure, which are often, more interesting. For example, the volumetric content of water in a soil layer is obtained by multiplying the gravimetric water content by the product of the bulk density and the volume of the layer.

A medium textured mineral soil that is in good structural condition for plant growth contains about 50% total pore space on volume basis. This pore space is important for gas exchange (O_2 and CO_2) between the soil and the atmosphere, and water storage and movement. The total pore space consists of the pore spaces between adjacent sand, silt and clay particles and those between aggregates. Therefore, texture and structure are the main factors governing the amount of pore space in soil. Organic matter affects pore space indirectly by improving structure.

Bulk density is an indirect measure of the total pore space in the soil and is also affected primarily by texture and structure. If the aggregation of a particular soil is increased, the total pore space will be increased, and the weight per unit volume or bulk density of the soil will decrease. The bulk density of fine texture mineral soils ranges from about 1.0 to 1.3 g/cm^3, and that of sandy soils ranges between 1.3 and 1.7 g/cm^3. The bulk density of organic soils is usually much less than that of mineral soils and may be as low as 0.4 g/cm^3. Bulk density and total pore space are readily altered by tillage operations.

5.2. Measurement of Bulk Density

Two methods are commonly used to determine soil bulk density: one uses samples of disturbed soil, and the other uses samples of undisturbed soil. The second method uses consolidated soil masses, like clods and cores.

5.2.1. Bulk Density of a Disturbed Soil Sample

This method is used when it is not possible to take a consolidated sample of soil, as in sandy soils and soils of greenhouses and nurseries because they are loose and very friable.

Procedure

1. Fill a pre-weighed 100 ml graduated cylinder with air-dry soil.
2. Compact the soil in the cylinder by tapping the cylinder firmly 15 times on the palm of the hand.
3. Record the volume of the packed soil in the cylinder.
4. Record the weight of the cylinder and the soil.
5. Calculate the weight of the soil.
6. On a separate sample, determine the moisture content of the soil sample and calculate the oven-dry weight of the soil in the cylinder.
7. Calculate bulk density.

Calculation

$$\text{BD } (g/cm^3) = \frac{\text{Weight of oven-dry soil (g)}}{\text{Volume of soil sample } (cm^3)}$$

Note: Bulk density is commonly calculated on oven-dry basis, but for certain uses it is calculated on a wet-soil basis.

5.2.2. Bulk Density of an Undisturbed Soil Sample

Two methods are used to determine the bulk density of an undisturbed soil sample: the soil clod or ped method, and the core method.

5.2.3. The Clod or Ped Method

Reagent

- A resin, such as Dow Saran F 310 (general purpose non-crystalline co-plolymer), is dissolved in acetone at a saran:solvent ratio of 1:7. Acetone is flammable, therefore, this mixture should be prepared in a fume hood and it should be kept in a tightly closed container to prevent volatilization. Melted wax, by heating on medium flame, could be used as a replacement to the dissolved saran resin.

Procedure

1. Carefully collect soil clods from a soil profile. If roots are present, cut them carefully with scissors.
2. Tie and hold the clod with a fine copper wire and weigh it.
3. Dip the clod in the saran solution, hang it to dry for 30 minutes. Additional saran coatings may be applied to make the clod more waterproof.
4. Weigh the coated clod and wire in air (W_a).
5. To determine the volume of the clod, weigh it while suspended in water with a balance that can accept the clod hanging on the balance beam by the thin copper wire (W_w). The drop in weight ($W_a - W_w$) is equal to the weight or volume of the water displaced, which is the volume of the clod.
6. If such a balance is not available, immerse the clod completely in a graduated cylinder half full with water, and detect the change in volume of water in the cylinder (V).
7. Break the clod and take a sample for the determination of soil moisture content. This is needed to calculate the oven-dry weight of the soil (W_{od}).

Calculation

$$BD = \frac{W_{od}}{(W_a - W_w)}$$

W_{od} is the mass of solid particles in the clod in grams.

($W_a - W_w$) is the weight of the water displaced by the clod in grams, or volume of the clod in cm^3.

If the volume of the clod is measured as indicated in step 6:

$BD = W_{od}/ V$

V is the change in volume of water in the graduated cylinder in cm^3.

Note: The clod method may yield higher BD values than other methods.

5.2.4. The Core Method

Procedure

1. Carefully drive a thin-walled steel tubing or pipe (of known weight and volume) into the soil with a block of wood and a hammer. Be careful to avoid compaction of the soil during collection of the cores. After careful removal of the soil core, examine it and trim the ends carefully.
2. Weigh the soil and tubing. Calculate the weight of the soil sample alone by subtracting the weight of the steel tubing.
3. Take a portion of this soil for the determination of soil moisture.
4. Knowing the moisture content of the soil core, calculate the oven-dry weight of the soil sample.
5. Calculate the bulk density in g/cm^3 by dividing the weight of soil core, on oven dry basis, by the volume of the soil core, which is the volume of the steel tube.

$$\text{BD (g/cm}^3\text{)} = \frac{\text{Wt. of soil core (dry basis) (g)}}{\text{Vol. of soil core (cm}^3\text{)}}$$

Values of BD of undisturbed cores are of practical significance as it indicates soil aggregation and structure under field conditions.

5.3. Measurement of Particle Density

Two methods for the determination of particle density (PD) are discussed. In the first method a graduated cylinder is used, in the second method a volumetric flask is employed. Both analyses are very simple and rapid. The particle density of most soils varies from 2.60 to 2.75 g/cm^3. An average particle density value of 2.67 is commonly used as the specific gravity of soils.

5.3.1. The Graduated Cylinder Method

Procedure

1. Weigh 40 g of soil in a 100 ml graduated cylinder.
2. Add 50 ml of water to the soil in the cylinder. Be sure that no soil material is on the inner walls of the cylinder.
3. Stir thoroughly with a stirring rod to displace the air, and rinse the stirring rod and the inner walls of the cylinder with 10 ml water.
4. Allow the mixture to stand for 5 minutes and record the volume of the soil plus 60 ml water.

5. Determine separately the moisture content of the soil sample by the gravimetric method. The amount of moisture should be added to the amount of added water to obtain the total amount of water used.

Calculation

$$\text{Volume of total solids} = \text{Volume of } (\text{soil} + \text{water}) - \text{Volume of added water}$$

Volume of (soil + water) = as shown on graduated cylinder

Volume of added water = 60 ml + soil moisture (ml)

$$\text{Particle Density (PD), g/cm}^3 = \frac{\text{Oven - dry wt of soil (g)}}{\text{Volume of total solids (cm}^3)}$$

5.3.2. The Volumetric Flask Method

Procedure

1. Fill a pre-weighed 100 ml volumetric flask to the mark with boiled distilled water cooled to room temperature.
2. Weigh the flask plus water (W_1), and then discard the water and dry the flask thoroughly.
3. Weigh accurately 50 g of soil and transfer quantitatively to the volumetric flask (W_s).
4. Pipette 50 ml of water into the volumetric flask, washing down any soil particles adhering to the neck.
5. Heat the flask gently on a hot plate until the water starts to boil in order to drive out air from the soil.
6. Cool the content and bring up to the 100 ml mark with boiled distilled water cooled to room temperature.
7. Weigh the volumetric flask with its content (W_2).
8. Determine on a separate sample the moisture content of the soil by the gravimetric method to find the oven-dry weight of the soil in the flask.
9. Calculate first the volume of soil particles and then particle density (PD).

Calculation

$$\text{Volume of soil particles (cm}^3) = W_s + (W_1 - W_2)$$

$$\text{Particle density (PD), g/cm}^3 = \frac{W_s}{W_s + (W_1 - W_2)}$$

5.4. Calculation of Percent Pore Space

The pore space (voids) is the portion of bulk soil volume not occupied by solid particles. It is filled with air and water. Depending on pore size, pore spaces are given the name macropores (large) or micropores (small). There is no sharp line of demarcation between the two pore sizes.

Calculation

$$\%\,\text{Pore Space (PS)} = \frac{PD - BD}{PD} X100$$

Example

A soil sample weighs 110 g and contains 15% moisture. The volume of the soil sample is 75 ml. The sample displaced 36.8 ml water. Calculate BD, PD and %PS

- Oven-dry wt = 110 x 100/115 = 95.65 g
- BD = 95.65 ÷ 75 = 1.3 g/cm^3
- PD = 95.65 ÷ 36.8 = 2.6 g/cm^3
- %PS = 100(2.6-1.3) / 2.6 = 50

6. ANALYSIS OF SATURATION PASTE EXTRACT

6.1. Introduction

A good method for estimation of soil salinity is the measurement of the electrical conductivity of the saturation extract because it is related to the field conditions. Over considerable textural range of soils, the soil moisture of the saturation paste is approximately equal to two times soil moisture at field capacity and four times of the wilting point. For this reason the conductivity of the saturation extract (ECe) can be used for estimating the soil salinity in the field.

6.2. Preparation of Saturation Paste

Apparatus

- Balance
- Enamelled cup or 600 ml evaporating dish
- Spatula
- Graduated cylinder or burette - 100 ml

Procedure

1. Weigh 300 g of air-dry* soil and transfer into an enamelled cup.
2. Using a graduated cylinder, or a burette, slowly add distilled water to the sample while stirring the soil with a spatula until a condition of saturation is reached. Record the amount of water used to reach the saturation point.
3. At saturation point, the soil paste, glistens as it reflects light, flows slightly when the container is tipped, slides freely off the spatula, and consolidates easily by tapping the container after a trench is formed in the paste with the flat side of the spatula.
4. After the paste is prepared, cover the container with aluminium foil and allow it to stand overnight to permit the soil to imbibe water.
5. The following day, recheck the criteria for saturation as described above. If the sample hardened, add more water and mix it again. Alternatively, if more water has been added to the paste, add an additional weighed quantity of air dry soil and mix. Recheck again the criteria for saturation. Record the total amount of water used to prepare the saturation paste.

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* Soil samples should not be oven-dried before being used to make a paste because heating to 105°C partially converts gypsum, $CaSO_4 2H_2O$ to $CaSO_4 ½H_2O$. This partially hydrated gypsum $CaSO_4.½H_2O$ is more soluble in water than the fully hydrated gypsum, $CaSO_4.2H_2O$.

6.2.1. Calculation of Saturation Percentage

Saturation percentage (SP) is calculated by dividing the total amount of water added (ml) by the oven-dry weight of the soil (g) used and multiplying by 100. Soil moisture, as determined on a separate sample, is taken into consideration by adding it to the amount of water used in preparing the saturation paste.

Example

The weight of a soil sample (air-dry) used is 300 g, and 121 ml of distilled water was required to prepare the saturation paste. Moisture content of the air-dry soil is 8% on oven-dry basis. What is the saturation percentage?

Calculation

Let **X** be the weight of oven-dry soil.

$$X + (8\%X) = 300 \text{ g}$$

$$X + 0.08X = 300 \text{ g}$$

$$1.08X = 300 \text{ g}$$

$$X = \frac{300}{1.08} = 277.78 \text{ g of oven - dry soil}$$

Amount of water in the soil sample is: 300 - 277.78 = 22.22 ml
Total amount of water in the soil saturation paste is: 121 + 22.22 = 143.22 ml
Saturation percentage is:

$$SP = \frac{143.22}{277.78} X100 = 51.6$$

6.2.2. Determination of Soil pH

Apparatus

- pH meter with glass electrode
- Glass beakers - 25 ml

Reagent

- Standard pH buffer solutions. Since soils of arid and semi-arid regions are alkaline in reaction, it is recommended to use, beside the pH 7 standard buffer solution, another standard solution in the pH range of 8.8 – 9.2 to calibrate the pH meter.

Procedure

1. Standardize the pH meter using the standard pH buffers, with ample rinsing of the electrode with distilled water each time it is dipped into a

buffer solution. Make sure to make adjustment for temperature correction according to instruction usually provided with the buffer.

2. Transfer a portion of the already prepared saturated paste to fill about 3/4 of a 25 ml tall beaker.
3. Rinse the electrode carefully with distilled water and immerse into the paste.
4. Raise and lower the beaker repeatedly to have better contact between the electrode and the paste. Record the pH reading.

Note: pH can also be measured in the filtrate of 1:2 soil:distilled water or soil:$CaCl_2$ (0.01M) suspension. In case of saturation paste, it can also be measured in the filtrate. KCl can also be used instead of $CaCl_2$.

6.3. Preparation of Saturation Extract

Determination of electrical conductivity in saturation extract is recommended for soil salinity appraisal because saturation percentage (SP) is directly related to field moisture range. For example, permanent wilting point (PWP) is about one fourth of SP, and field capacity (FC) is about one half of SP. The extract is also used for the determination of some of the soluble constituents (Na, K, Ca, Mg, Cl, SO_4, NO_3, HCO_3, and CO_3) as an assessment of their availability.

For correlation of soluble salt concentration with plant growth, the electrical conductivity should be determined in extracts obtained when soil water tension is in the range of 0.33 – 2.0 atmospheres, similar to that at which plants grow.

Apparatus

- Extraction unit fitted with Buchner funnel and receiving bottles.
- Suction system and flasks.

Procedure

1. Transfer the saturated paste into a Buchner funnel fitted with Whatman No. 41 filter paper and connected to a suction system.
2. Apply suction and collect the filtrate in 50 ml receiving bottles. Stop the filtration when air starts to pass through the soil cake.
3. If the filtrate is turbid, pour it on the soil cake in the Buchner funnel and filter again.
4. Save the extract for the determination of soluble cations, anions and electrical conductivity.

5. To inhibit the precipitation of calcium during storage, add to each 25 ml of the extract one drop of 1 g/l solution of sodium hexametaphosphate, and store in glass bottles at 4°C.

6.3.1. Determination of Soil Salinity (Electric Conductivity)

Electrical conductivity (EC) of a soil solution or extract indicates the concentration of total soluble salts in solution, thus reflecting the degree of soil salinity.

The unit of measurement is called millimhos per centimeter (mmhos/cm), or millisiemen per centimeter (mS/cm). The EC is reported to a standard temperature of 25°C by adjustment factors according to Appendix F.

Salinity affects plants at all stages of development and for some crops sensitivity varies from one growth stage to another. For example barley, wheat, and maize are more sensitive to salinity during early seedling growth than during germination or at advanced stages of growth and grain development (Maas and Hoffman, 1977).

Soil salinity is extremely important during germination and emergence of seedlings. Failure in germination and emergence leads to poor stand and significant reduction in yield (Maas and Hoffman, 1977). Maas and Hoffman further stated that rootstock differences are an important factor in the salt tolerance of fruit trees and grapevine. They also stated that fruit trees are not only sensitive to salinity per se, but are particularly susceptible to the toxic effects of sodium and chloride ions.

Apparatus

- Electrical conductivity meter

Reagents

1. Standard potassium chloride (KCl) solutions; 0.01 and 0.1 M:
   A. For the 0.1 M solution (12.9 mS/cm at 25°C), dissolve 7.456 g of KCl in distilled water, and then fill the 1 litre volumetric flask to the mark.
   B. For the 0.01 M solution (1.412 mS/cm at 25°C), transfer 100 ml of solution **A** into a 1 litre volumetric flask, mix well and bring to volume. Or, dissolve 0.7456 g KCl in 1 litre distilled water as in **A**.

Procedure

1. Wash the conductivity electrode with distilled water and rinse with solution **B**.
2. Pour some of solution **B** into a 25 ml beaker and dip the electrode in the solution, and adjust the conductivity meter to read 1.412 mS/cm, corrected to 25^{o}C.
3. Wash the electrode, and dip it in the saturated paste extract.

4. Record the digital display corrected to 25°C. The reading in mS/cm of electrical conductivity is a measure of the soluble salts content in the extract, and an indication of salinity status of the soil.

6.3.2. Determination of Soluble Sodium and Potassium

Apparatus

- Flame photometer

Reagents

1. Standard K and Na solutions: Prepare a series of K and Na standard solutions in the range of 0 – 2 meq/l of K, and 0 – 4 meq/l of Na. For better results, add 212.5 mg LiCl in each standard to yield a final concentration of about 5 meq/l of LiCl. For the preparation of 2 meq K/l, dissolve 149.2 mg KCl in a litre of distilled water and for the preparation of 4 meq Na/l, dissolve 234 mg NaCl in a litre of distilled water.

Procedure

1. Switch on the flame photometer and let it warm-up for 15 minutes.
2. Calibrate the instrument with blank and standard solutions.
3. Fill the capsules with the soil extracts. Insert the suction tubing in the capsule and record the reading. Dip the tubing in distilled water to wash the system, and then read the sample.
4. The readings for samples express the concentration of K or Na as meq/l of the saturation extract.

Calculation

$$\text{meq of soluble Na or K/100 g soil} = \frac{\text{meq/litre X SP}}{1000}$$

6.3.3. Determination of Soluble Calcium and Magnesium

Water-soluble calcium and magnesium are measured in the soil saturation extract. Exchangeable Ca and Mg are determined in ammonium acetate extraction solution.

Concentration of Ca and of Mg can be determined by atomic absorption spectrophotometric techniques. Usually titration methods are used because these cations are present in high concentrations in arid and semi-arid soils. To use an atomic absorption spectrometer, a number of dilutions are required.

Apparatus

- Microburette - 10 ml

Reagents

1. Ammonium chloride - Ammonium hydroxide buffer solution: Dissolve 67.5 g of ammonium chloride in 570 ml of concentrated ammonium hydroxide and dilute to 1 litre.
2. Sodium hydroxide (NaOH) 4 M: Dissolve 160 g of sodium hydroxide in 1 litre distilled water.
3. Calcium chloride ($CaCl_2$) standard 0.01 N: Dissolve 0.5 g of pure calcium carbonate crystals in 10 ml of approximately 3 M hydrochloric acid and dilute to 1 litre.
4. Eriochrome black T indicator: Dissolve 0.5 g of Eriochrome black T and 4.5 g of hydroxylamine hydrochloride in 100 ml of 95% ethanol.
5. Calred indicator, 2-Hydroxy-1-(2-Hydroxy-4 Sulfo-1-Naphthyle 20)-3-Naphtholic acid-original salt.
6. Ethylenediaminetetraacetic acid (EDTA) 0.01 N: Dissolve 2.0 g of EDTA in water and make up to 1 litre. Standardize the solution against 0.005 M standard $CaCl_2$ solution

Procedure

a. Determination of calcium

1. Pipette an aliquot (2 to 5 ml) of soil extract in 50 ml white porcelain dish.
2. Dilute with distilled water to a volume of approximately 25 ml.
3. Add 2 ml of 4 M NaOH and 2-3 mg of calred indicator.
4. Titrate the contents slowly with 0.01 N EDTA until a sky-blue end point is obtained.
5. If the sample is over titrated with EDTA, it can be back titrated with the standard 0.01 N calcium chloride solution.
6. Prepare a blank using 2 – 5 ml distilled water, and follow steps 2 to 4.
7. Express the Ca in meq/litre of the saturation extract.

Calculation

$$\text{meq of Ca/litre} =$$

$$1000 \text{ X} \frac{(\text{ml EDTA used for soil extract} - \text{ml EDTA for blank}) \text{ X N of EDTA soln.}}{\text{ml of sample taken (aliquot)}}$$

b. Determination of Calcium and Magnesium

1. Pipette an aliquot (2 - 5 ml) into 50 ml porcelain evaporating dish.
2. Dilute with distilled water to a volume of about 25 ml and add 5 ml of ammonium chloride - ammonium hydroxide buffer solution and 3 to 4 drops of Eriochrome black T indicator.
3. Titrate the contents with 0.01 N EDTA until a sky-blue end point is obtained.
4. Prepare a blank using 2–5 ml distilled water, and follow steps 2 and 3.
5. Express the amount of Ca + Mg in the sample in meq/l.

Calculation

$$(\text{Ca} + \text{Mg}) \text{ meq/litre} =$$

$$1000 \text{ X} \frac{(\text{ml EDTA used for soil extract} - \text{ml EDTA for blank}) \text{ X N of EDTA soln.}}{\text{ml of sample taken (aliquot)}}$$

Determination of Magnesium

Concentration of Mg, as meq/l, is calculated by subtracting meq/l of Ca from meq/l of (Ca + Mg). The difference is the concentration of Mg as meq/l.

6.3.4. Determination of Carbonate and Bicarbonate

Carbonate and bicarbonate ions are species of the same acid, carbonic acid. Their proportionate content is a function of pH. The CO_3^{2-} starts to form as pH rises above 8.4.

Apparatus

- Magnetic stirrer
- Microburette - 10 ml
- White Porcelain crucibles

Reagents

1. Sulphuric acid (H_2SO_4) standard solution, 0.01 M. Dilute 0.56 ml of conc. sulphuric acid in 1 litre distilled water and standardize using a primary standard to determine exact molarity.
2. Phenophthalein indicator: Dissolve 0.25 g of phenolphthalein in 100 ml of 60% alcohol.
3. Methyl orange indicator: Dissolve 0.1 g of methyl orange in 100 ml of water.

Procedure

1. Pipette 5 ml of extract into 50 ml Erlenmeyer flask and dilute with boiled distilled water to a volume of approximately 25 ml.
2. Add 3 or 4 drops of phenolphthalein indicator. The appearance of a pink colour indicates the presence of carbonates in the sample.
3. Place the flask on a magnetic stirrer and titrate the content in the flask with 0.01 M H_2SO_4 by adding one drop every 2-3 seconds until the pink colour disappears.
4. Record the volume of H_2SO_4 titrant used (V_{ph}).
5. To the colourless solution add 2 or 3 drops of methyl orange indicator.
6. Continue the titration, without refilling the burette, to the pink end point.
7. Record the total volume of H_2SO_4 used (V_t).

Save the solution for chloride determination. Make a blank correction for the methyl orange titration. Express the amount of CO_3^{2-} and HCO_3^- in the sample as meq/l.

Calculation

a. For CO_3^{2-} concentration, the phenolphthalein end point is considered:

$$\text{meq/litre of } CO_3^{2-} = \frac{1000 \text{ ml}}{5 \text{ ml aliquot}} X\, 2 \left(V_{ph} \text{ X M of } H_2SO_4\right)$$

For HCO_3^- concentration, the methyl orange endpoint is considered:

$$\text{meq/litre of } HCO_3^- = \frac{1000 \text{ ml}}{5 \text{ ml aliquot}} X \text{ M of } H_2SO_4 \left(V_t - 2V_{ph}\right)$$

6.3.5. Determination of Chloride

Chloride is usually determined in soil saturation extract to assess the concentration of soluble salts. Estimation by silver nitrate tiration method is described.

Apparatus

- 10 ml microburette

Reagents

1. Potassium Chromate (K_2CrO_4) indicator 5%: Dissolve 5 g of K_2CrO_4 into 90 ml water. Add a saturated $AgNO_3$ solution until some brownish red $AgCrO_4$ precipitate forms. Place the solution in dark for 24 hours, filter and make the volume to 100 ml.
2. Silver nitrate ($AgNO_3$) standard, 0.005 M: Dissolve 0.8495 g of $AgNO_3$ in distilled water and dilute to 1 litre.

Procedure

1. Add 5 drops of K_2CrO_4 indicator to the solution saved after the titration of the carbonate and bicarbonate, or start with another 5 ml aliquot of the extract.
2. Titrate the contents under bright light with the standard $AgNO_3$ to a brownish-reddish end point.
3. Prepare a blank in order to (a) correct for the amount of Ag^{2+} used to form the silver chromate (Ag_2CrO_4) red precipitate, and (b) to use as a reference for the end point. The volume of solution at the end of titration of the blank should be almost equal to that of the unknown.

Calculation

$$\text{meq of Cl/litre} = \frac{1000\text{ ml}}{5\text{ ml aliquot}} \text{X ml of } AgNO_3 \text{ used X } 0.005\text{ M of } AgNO_3$$

7. CALCIUM CARBONATE

Calcium carbonate, a major component of calcareous soils, ranges from a few percent in slightly calcareous soils to more than 80 percent in some extremely calcareous soils. The amount and form of calcium carbonate (total versus active) and its distribution down the soil profile, affect soil physical and chemical characteristics. It was found that when total $CaCO_3$ was above 20%, active $CaCO_3$ was more than 10%. Carter (1981) gave 11 to 30% total carbonate and 7 to 9% active $CaCO_3$ as the critical levels that adversely affected crop growth.

The authors showed that soil retention of P, Mn, Zn and Cu was directly related to carbonate content and to the distribution of total and active calcium carbonate between the clay and silt fractions. When total $CaCO_3$ was less than 20%, the retention of those elements was affected mainly by the total amount of carbonates, but, when it was above 20%, nature of the carbonates was more important in governing retention. The active $CaCO_3$ was more than 10% when the total $CaCO_3$ was above 25% in the studied soils. Therefore, one could give the limit of about 10% active $CaCO_3$, which will contribute significantly to the retention of certain essential elements in calcareous soils.

***Physical effects*:** The active-$CaCO_3$ portion and the distribution of $CaCO_3$ in the different particle size fraction affects the properties (soil-water relationships) of calcareous soil (Deb and Chadha, 1970; Thabet, 1975). Calcareous soils with 15% calcium carbonate content have higher water diffusivity and faster water movement than non-calcareous soils of similar texture. Evidently, $CaCO_3$ assists in the formation of stable soil aggregates. But, increased $CaCO_3$ content (25% or more) tends to precipitate within the capillary tubes causing an increase in the proportion of micropores, thus reducing the percolation of water.

Effect on plants: Continuous horizons of carbonate accumulation in soil profile may prevent root penetration and thus may retard the degree of plant development and reduce the yield. Sys (1975) classified the sensitivity of crops to $CaCO_3$ into three groups as follows:

1. Tolerant crops: wheat, alfalfa, figs, olives and dates
2. Moderately tolerant crops: barley, clover, cotton, maize, millets, rice, grapes, sugarcane, sugar beet, watermelons, lettuce, tomatoes, beans, artichokes, tobacco and onions.
3. Sensitive crops: citrus, banana and potatoes.

7.1. Determination of Total Calcium Carbonate

Apparatus

- 25 ml and 100 ml Erlenmeyer flasks
- Burette, 25 ml

Reagents

1. Hydrochloric acid (HCl) Standard 1 M: Add 81 ml HCl to about 500 ml water in a 1 litre volumetric flask, cool and make to volume with distilled water. Standardize it against a primary standard.
2. Sodium hydroxide (NaOH) Standard 0.5 M: Dissolve 20 g NaOH in 800 ml distilled water in a 1 litre volumetric flask, cool and dilute to 1 litre. Standardize it against a primary standard.
3. Phenolphthalein indicator 1% in 60% ethanol: Weigh 1 g phenolphthalein crystals in 100 ml volumetric flask add 60 ml of ethyl alcohol and dilute to volume with distilled water. Shake the flask until the crystals dissolve completely.

Procedure

1. Weigh 5 g of soil and transfer into a 250 ml Erlenmeyer flask.
2. Add 100 ml of 1.0 M HCl.
3. Cover the flask with aluminium foil and keep it overnight or heat it to boiling for 5 minutes and let it cool to room temperature.
4. Filter, and pipette 10 ml of the filtrate into a 100 ml Erlenmeyer flask.
5. Add 2 or 3 drops of phenolphthalein to the content and titrate with 0.5 M sodium hydroxide.

Calculation

$$\%\ CaCO_3 = \left[\left(mlHCl \times 1M\right) - \left(mlNaOH \times 0.5M\right)\right] \times \frac{Vol.\ HCl\ (100ml)}{Vol.\ filtrate\ aliquote\ (10ml)} \times \frac{100}{1000 \times 2} \times \frac{100\ g}{Wt.\ of\ soil\ g}$$

$$\%CaCO_3 = \left[\left(10 \times 1\right) - \left(mlNaOH \times 0.5\right)\right] \times 10$$

7.2. Determination of Active Calcium Carbonate (modified Drouineau method)

Reagents

1. Ammonium Oxalate $(NH_4)_2C_2O_4$ 0.2N: Dissolve 12.61 g $(NH_4)_2C_2O_4$ in 1 litre of distilled water.
2. Sulphuric Acid Concentrated (analytical grade).
3. Potassium Permanganate ($KMnO_4$) 0.1N: Dissolve 3.16 g $KMnO_4$ in 1 litre of distilled water. Keep the solution at a gentle boil for about 1 hour, cover and let stand overnight. Filter and store in amber glass bottle.

The potassium permanganate can be standardized by titrating with the primary standard sodium oxalate, $Na_2C_2O_4$, which is dissolved in sulphuric acid to form oxalic acid:

$$5H_2C_2O_4 + 2MnO_4^- + 6H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

The solution must be heated to 80 – 90°C for rapid reaction. The reaction is catalyzed by Mn^{+2} produced and it goes very slowly at first until some Mn^{+2} is formed. The first persistent pink colour (30 sec.) should be taken as the end point. Determine a blank by titrating an equal volume of 1 M H_2SO_4.

Procedure

1. Weigh accurately 2.5 g of soil (sieved through a 2 mm sieve) into a 500 ml Erlenmeyer flask.
2. Add 250 ml of the ammonium oxalate solution and shake for two hours.
3. Filter the suspension and collect the filtrate (discard the first few ml).
4. Pipette 10 ml of the filtrate into an Erlenmeyer flask.
5. Add to it 100 ml of distilled water and 5 ml of concentrated sulphuric acid and heat to a temperature of 60 - 70°C.
6. Titrate with $KMnO_4$ (0.02 M) to a pink endpoint, and note down the volume used (V_{sample}).
7. Prepare a blank in the same manner using 10 ml of the ammonium oxalate solution, and record the volume of the titrant used (V_{blank}).
8. Calculate percent of active calcium carbonate content of the soil.

Calculation

$$\% \text{ Active } CaCO_3 = N_{KMnO_4} (V_{blank} - V_{sample}) \text{ X } \frac{(NH_4)_2C_2O_4 \text{ (ml)}}{\text{filtrate aliquote (ml)}} \text{ X } \frac{100 \text{ g}}{2.5 \text{ g}} \text{ X } \frac{5}{1000}$$

Since 0.1 meq MnO_4^{2-} reacts with 5mg $CaCO_3$

Therefore,

$$\% \text{ Active } CaCO_3 = N_{KMnO_4} (V_{blank} - V_{sample}) X \frac{250 \text{ ml}}{10 \text{ ml}} X \frac{100 \text{ g}}{2.5 \text{ g}} X \frac{5}{1000}$$

$$\% \text{ Active } CaCO_3 = N_{KMnO_4} (V_{blank} - V_{sample}) X 5$$

Note: The maximum concentration of active calcium carbonate that can be dissolved by the above method is 20%. If active $CaCO_3$ content obtained is greater than 17%, then the analysis should be repeated with a smaller amount of soil or larger volume of oxalate extractant.

8. CATION EXCHANGE CAPACITY (CEC)

Presence of high concentrations of calcium, especially in the form of gypsum interferes with the determination of cation exchange capacity, which is an important parameter for soil fertility and mineralogical characterization.
The exchangeable cations and cation exchange capacity (negative charges on the surface of soil particles) are expressed in terms of milliequivalents of negative charge per 100 g of oven-dried soil (1 meq/100 g soil = 1 cmol/kg in SI system). The unit meq/100 g has been used in this manual because most of the soil testing laboratories in the Near East still use and are familiar with meq/100g for CEC and exchangeable cations measurements.

The definitions of equivalent and equivalent weight are as follows:

- **Atomic weight**: Weight in grams of 6×10^{23} atoms of the substance. *One mole* of substance is 6×10^{23} atoms, molecules, ions, compounds and so on; therefore, units of atomic weight are grams per mole (g/mole).

$$\text{Atomic Weight} = \text{grams per } 6 \times 10^{23} \text{ ions or molecules}$$

- **Equivalent weight**: Quantity (mass) of a substance (e.g. cation, anion, compound, etc.) that will react with or displace one gram of hydrogen (H^+), which equals Avogadro's number of charges (+ or -). This is equal to the weight in grams of 6×10^{23} charges, therefore, units of equivalent weight are grams per equivalent (g/eq).

$$\text{Equivalent Weight} = \text{grams per } 6 \times 10^{23} \text{ charges } (+ \text{ or } -)$$

The use of equivalents to express concentrations or quantities of nutrients in soil is very convenient and widely used in soil testing laboratories (one Ca^{2+} cation replaces two K^+ cations, but one equivalent of Ca^{2+} replaces one equivalent of K^+ or one equivalent of any other cation). Thus, for clarity, it will be followed in this manual also.

$$\text{Equivalent weight of X} = \frac{\text{Atomic weight of X}}{\text{Valence of X}}$$

Examples:

$$\text{Equivalent wt. of } K^+ = \frac{39.1 \text{ g/mole}}{1 \text{ eq/mole}} = 39.1 \text{ g/eq}$$

$$\text{Equivalent wt. of } Ca^{2+} = \frac{40 \text{ g/mole}}{2 \text{ eq/mole}} = 20 \text{ g/eq}$$

$$\text{Equivalent wt. of } Al^{3+} = \frac{27 \text{ g/mole}}{3 \text{ eq/mole}} = 9 \text{ g/eq}$$

8.1. Determination of Cation Exchange Capacity (CEC)

Apparatus

- Centrifuge
- 50 ml round bottom centrifuge tubes
- Mechanical shaker
- Flame photometer

Reagents

1. Sodium acetate (NaOAc) 1.0 M: Dissolve 136.08 g of sodium acetate trihydrate in distilled water and bring volume to 1 litre. Adjust the pH to 8.2.
2. Ethanol 95%
3. Ammonium acetate (NH_4OAc) 1.0 M: Dissolve 77.09 g of ammonium acetate in distilled water and dilute to 1 litre. Adjust pH to 7.0. Or, add 57 ml of conc. acetic acid (analytical grade) to 700-800 ml distilled water in 1 litre beaker. Then, with constant stirring, add 68 ml of conc. ammonium hydroxide. Add more distilled water to bring the volume close to 1 litre, and adjust pH to 7.0 by the addition of more ammonium hydroxide or acetic acid.
4. Na standard solution: Refer 6.3.2.

Procedure

1. Weigh accurately about 5 g soil and transfer the sample to a 50 ml centrifuge tube.
2. Add 30 ml of 1.0 M sodium acetate solution to the tube, stopper and shake in a mechanical shaker for 5 minutes.
3. Centrifuge at 2000 rpm for 5 minutes or until the supernatant liquid is clear.
4. Decant the liquid completely and repeat the extraction three more times. Discard the decants.
5. Repeat steps 2 – 4 with ethanol or isopropyl alcohol until the EC of the decant reads less than 40 mS/cm (usually it takes 4 to 5 washings).
6. To displace the adsorbed Na, repeat steps 2 – 4 using the ammonium acetate solution. Collect the decants in 100 ml volumetric flask fitted with a funnel and filter paper. Make up to volume with ammonium acetate solution.

7. To determine sodium concentration by flame photometry (see section 6.3.2), prepare a series of Na standard solutions in the range of 0 – 4 meq/l of Na. For better results, add LiCl in each standard to yield a final concentration of about 5 meq/l of LiCl.

Calculation

$$\text{meq of Na/100 g soil} = \text{Emission Reading (R meq/l)} \times \frac{100 \text{ ml}}{1000 \text{ ml}} \times \frac{100 \text{ g}}{\text{Wt. of soil (g)}}$$

$$= \frac{R \times 10}{\text{Wt. of soil (g)}}$$

Where, R is the meq/l of Na as determined by the flame photometer.

The displaced Na is actually a measure of the Cation Exchange Capacity (CEC) of the soil. So, the meq/100 g of Na is actually meq/100 g exchangeable cations (Ca, Mg, Na and K).

8.2. Determination of CEC in Gypsiferous and Calcareous Soils

Apparatus

- Centrifuge
- 50 ml round bottom centrifuge tubes
- Mechanical shaker
- Flame photometer

Reagents

1. Sodium oxalate ($Na_2C_2O_4$) saturated solution: Add 10 g sodium oxalate crystals to 100 ml distilled water. Allow to stand with occasional shaking for 8 hrs or longer. Let it settle until clear or filter.
2. Ethanol 95% or isopropyl alcohol
3. Ammonium acetate (NH_4OAc) 1.0 M solution: Add 57 ml of conc. acetic acid (reagent grade) to 700-800 ml distilled water in a 1 litre beaker. Then, with constant stirring, add 68 ml of conc. ammonium hydroxide. Bring the volume close to 1 litre, and adjust pH to 7.0 by the addition of more ammonium hydroxide or acetic acid. Or, dissolve 77.09 g of ammonium acetate in distilled water and dilute to 1 litre. Adjust pH to 7.0.
4. Na standard solution: Refer 6.3.2.

Procedure

1. Weigh accurately 4 g of soil and transfer to a 50 ml centrifuge tube.
2. Add 30 ml of saturated sodium oxalate solution to the tube, stopper and shake for two hours.
3. Centrifuge at 2000 rpm for 5 minutes or until the supernatant liquid is clear.
4. Decant the liquid completely and repeat the extraction three more times. Discard the decants.
5. Repeat steps 2 – 4 with ethanol 95% or isopropyl alcohol until the EC of the decant reads less than 40 mS/cm (takes 4 to 5 washings).
6. To displace adsorbed sodium, repeat steps 2 – 4 using ammonium acetate solution. Collect the decants in a 100 ml volumetric flask fitted with a funnel and filter paper. Make up to volume with ammonium acetate solution.
7. Determine sodium concentration as in section 6.3.2.

Calculation

$$\text{meq of Na/100 g soil} = \text{Emission Reading (R meq/l)} \times \frac{100 \text{ ml}}{1000 \text{ ml}} \times \frac{100 \text{ g}}{\text{Wt. of soil (g)}}$$

$$= \frac{\text{R X 10}}{\text{Wt. of soil (g)}}$$

Where R is the meq/l of Na as determined by the flame photometer.

As was explained above (section 8.1), meq/100 g of Na displaced by NH_4, is actually the meq/100 g of exchangeable cations (Ca, Mg, Na and K) or the CEC of the soil.

8.3. Exchangeable Sodium Percentage

Exchangeable Sodium Percentage (ESP) is the relative amount of exchangeable Na to the sum of exchangeable cations, or CEC.

As more and more of the cation exchange capacity of soil becomes satisfied with Na on the expense of Ca, Mg and K, the clay fraction become dispersed and deflocculated causing the destruction of soil structure.

Some critical values were internationally given to ESP for the classification of sodium-affected soils and its effect on soil structure and plant growth. However, it is a common observation in the sandy soils of the Persian Gulf Countries, and in the Fezzan province of Libya, that ESP may be as high as 50 percent or more, but soil structure is not impaired and so is plant growth and yield. The reason, probably, is the single grain structure of the predominantly

sandy soils. In contrast, soil structure of clayey soils in Sudan would be seriously impaired at ESP values of only 8 percent due to de-flocculation of the clay fraction. Accordingly, ESP values that are critical in clayey soils are tolerated in sandy soils.

Calculation

$$ESP = \frac{\text{Exchangeable Na (meq/100 g)}}{\text{CEC (meq/100 g)}} \text{ X } 100$$

9. SOIL GYPSUM

Precise determination of gypsum in soils is difficult, because of inherent errors involved in the extraction of this mineral with water. The factors, other than the solubility of gypsum, that may influence the amount of Calcium and Sulphate extracted from gypsiferous soils are (1) the solution of calcium and sulphate from sources other than gypsum, (2) exchange reactions in which soluble calcium replaces other cations, such as sodium and magnesium.

Conventional standard methods for the determination of gypsum in soils do not extract the total amount. Results are, therefore, lower than the real amounts present. Sayegh *et al.* (1978) improved gypsum determination by grinding the soil sample to 270 mesh (0.053 mm) instead of 100 (2.0 mm), and by using a larger volume of water. Figure 8 shows the higher values obtained for gypsum content with increasing water to soil ratio, and also with increased mesh size. Determination of soil gypsum by precipitation with acetone is described here.

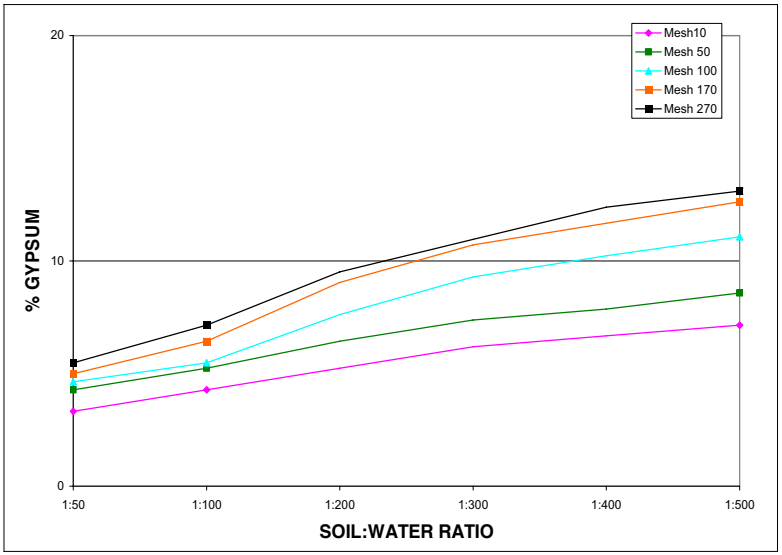

Figure 8. Effect of soil:water ratio and particle size on total gypsum extraction

Apparatus

- Centrifuge
- Centrifuge tubes – 50 ml
- Mechanical shaker

Reagent

- Acetone (analytical grade).

Procedure

1. Place 1 g of air-dried soil, ground to pass through a 270 mesh (0.053 mm) sieve, in an Erlenmeyer flask.
2. Add 500 ml of distilled water, stopper the flask, and shake for 20 minutes on a mechanical shaker.
3. Filter the content through Whatman No. 41 filter paper.
4. Transfer 20 ml aliquot of the filtered extract into a 50 ml centrifuge tube.
5. Add 20 ml of acetone, mix and allow to stand for 15 minutes or until the precipitate flocculates.
6. Centrifuge the content at 2000 rpm for 3 minutes, carefully decant the supernatant, then invert the tube on a clean filter paper and let it drain for 5 minutes.
7. Wash the sides of the tube with 10 ml acetone and disperse the precipitate.
8. Repeat step 6.
9. Add 40 ml of distilled water to the tube, stopper and shake until the precipitate is completely dissolved.
10. Measure the EC of the solution and correct conductivity reading to 25°C.
11. Determine the gypsum concentration in solution from Table 2, which shows a direct relationship between the EC of the extract and its gypsum content.

Table 2. Electrical conductivity values for different $CaSO_4$ concentrations in water

$CaSO_4$ concentration (meq/l)	EC at 25°C (mS/cm)
1	0.121
2	0.226
5	0.500
10	0.900
20	1.584
30.5	2.205

Source: Richards, 1954.

Calculation

Gypsum content per 100 g soil is calculated as follows:

$$\text{meq of } CaSO_4 \text{ in aliquot} = \text{meq/l of } CaSO_4 \text{ from EC reading X } \frac{\text{ml of water used}}{1000 \text{ ml}}$$

$$\text{meq of gypsum/100 g soil} = \frac{100 \text{ X meq of } CaSO_4 \text{ in aliquot}}{\text{Soil : water ratio X ml of water extract used}}$$

$$= \frac{100 \text{ X meq of } CaSO_4 \text{ in aliquot X } 500}{20}$$

10. SOIL ORGANIC MATTER

10.1. Walkley – Black Wet Combustion Method

Soil organic matter is defined as the organic fraction of soil including plant, animal and microbial residues at all stages of decomposition including fresh and humus fractions. Organic matter can be estimated in soils by determination of the change in weight of a soil sample resulting from destruction of organic compounds by H_2O_2 treatment or by ignition at high temperature. The H_2O_2 method does not quantitatively remove all organic matters, while the ignition method gives an overestimate because inorganic fractions may also be lost during ignition. The wet combustion analysis of soils by chromic acid digestion has been accepted as a standard method for determining total C, as it gives acceptable results. The organic matter content of a soil may be estimated by multiplying the organic carbon concentration by a constant factor based on the percentage of Carbon (C) in organic matter. Published organic C to total organic matter conversion factors for surface soils vary from 1.724 to 2.0. In the soils of arid and semi-arid regions, a value of 1.724 is an acceptable factor and is commonly used, although whenever possible the appropriate factor must be determined experimentally for each type of soil. In the following procedure the factor 1.724 is used for calculation.

Apparatus

- Erlenmeyer flasks, 500 ml
- Magnetic stirrer
- Burettes, 10 ml
- Thermometer, 200°C

Reagents

1. Potassium dichromate ($K_2Cr_2O_7$) solution, 0.1667 M: Dissolve 49.04 g of potassium dichromate in water and dilute to 1 litre.
2. Sulphuric acid concentrated, containing silver sulphate: Dissolve 25 g silver sulphate in a litre of sulphuric acid (96%, reagent grade).
3. Ferroin indicator (ortho-phenanthroline ferrous sulphate, 0.025 M): Dissolve 14.85 g *o*-phenanthroline monohydrate and 6.95 g ferrous sulphate in water and dilute to 1 litre.
4. Ferrous sulphate ($FeSO_4.7H_2O$), 0.5 M: Dissolve 140 g of $FeSO_4.7H_2O$ in water, add 15 ml of concentrated sulphuric acid, cool to room temperature, and dilute to 1 litre. Standardize this solution daily against 10 ml of 0.1667 M potassium dichromate, as given in the procedure below.

Procedure

1. Grind the soil to pass through 0.5 mm screen, avoiding contact with iron or steel.
2. Transfer a weighed sample, not exceeding 5 g and containing from 10 to 25 mg of organic carbon (always a few trial samples are to be done in an unknown situation) to a 500 ml wide mouth Erlenmeyer flask (1.0 g for clay soil and 2-3 g for sandy soil).
3. Add 10 ml of 0.1667 M potassium dichromate. Swirl to disperse the soil, then add 20 ml of conc. H_2SO_4.
4. Swirl the flask, insert a thermometer, and heat gently to a temperature of 150°C. Keep contents of flask in motion in order to prevent local overheating, which results in error caused by thermal decomposition of dichromate.
5. Place the flask on an asbestos pad, and allow to cool to room temperature slowly.
6. Add 200 ml of water and 4 to 5 drops of Ferroin indicator.
7. Titrate with 0.5 M ferrous sulphate until colour changes from green to red.
8. Since some soils adsorb the *o*-phenanthroline indicator, the titration may be improved by a prior filtration, using a rapid filter paper in a Buchner funnel. In that case, filter after the addition of water and add the indicator to the filtrate.
9. Make a blank determination in the same manner, but without soil, to standardize the reagents.
10. If more than 80% of the dichromate solution is reduced, then the analysis should be repeated with a smaller amount of soil or larger volume of dichromate.

Calculation

$$\text{Organic C \%} = \frac{(\text{meq of } K_2Cr_2O_7 - \text{meq of } FeSO_4) \text{ X } 0.336}{\text{Oven - dry soil (g)}}$$

$$\text{Organic matter \%} = \text{Organic C \% X } 1.724$$

Remarks: The Walkley - Black method for the determination of organic carbon in soils has been found to give approximately 89% recovery of carbon as compared to the dry combustion method. The conversion factor 0.336 was obtained by dividing 0.003, the milliequivalent weight of carbon, by 89 and multiplying by 100 to convert to percent. Chloride interference is eliminated by the addition of the silver sulphate to the digesting acid as indicated. The presence of nitrates and carbonates up to 5 percent and 50 percent, respectively, do not interfere.

However, in a study by Sayegh and Salib (1969) on calcareous Lebanese soils collected from the Beka'a Valley, it was found that recovery of organic

carbon when measured by the wet combustion method was 78% of the dry combustion method.

11. SOIL NITROGEN

11.1. Total Nitrogen (Kjeldahl method)

Apparatus

- Kjeldahl digestion unit
- Ammonium-N distillation unit

Reagents

1. Sulphuric - salicylic acid: Dissolve 1 g of salicylic acid in 30 ml of concentrated sulphuric acid.
2. Sodium thiosulphate ($Na_2S_2O_3.5H_2O$): Twenty-mesh dried powdered crystals.
3. Sulphate mixture: Mix 10 parts of potassium sulphate, 1 part of ferrous sulphate and 1/2 part of copper sulphate, grind the mixture and pass through a 40-mesh screen.
4. Sodium hydroxide (NaOH) 45% solution: Dissolve 450 g NaOH in 1 litre of distilled water.
5. Mossy Zinc pieces.
6. Boric acid 4% solution: Dissolve 40 g of boric acid in 1 litre of distilled water.
7. Sulphuric acid (H_2SO_4) standard solution, 0.05 M: Dissolve 2.8 ml H_2SO_4 in 1 litre of distilled water and standardize using a primary standard.
8. Bromocresol green - red methyl mixed indicator: Mix both indicators at a ratio of 1:1 in powder form.

Procedure

1. Weigh 10 g of soil (which has been passed through a 20 mesh sieve) and transfer into an 800 ml Kjeldahl flask.
2. Add 50 ml of sulphuric-salicylic acid mixture to the flask and swirl to bring the sample quickly into intimate contact.
3. Allow it to stand overnight. Add 5 g of sodium thiosulphate and heat gently for about 5 minutes, taking care to avoid frothing.
4. Cool the flask, add 10 g of the sulphate mixture and digest on the Kjeldahl apparatus gradually raising the temperature until the digest becomes clear. Digest further at full heat.

5. Cool, add 300 ml of distilled water and mix. Slowly add 100 ml of concentrated sodium hydroxide by letting it run down the neck and settle in the bottom of the flask.
6. Add a large piece of mossy zinc and a spoon of glass beads, connect the flask to the distillation unit, shake by swirling, turn on heat, and distil 150 ml into an Erlenmeyer flask containing 50 ml of 4 percent boric acid solution.
7. Add 10 drops of bromocresol green-methyl red indicator and titrate with the 0.05 M standard sulphuric acid solution to the first faint pink.
8. Titrate a blank prepared in the same manner but without adding a soil sample.

Calculation

$$\text{Kjeldahl N}\,(\%) = (T - B)\ X\ M\ X\ \frac{2.8}{S}$$

T = ml of standard acid with sample titration

B = ml of standard acid with blank titration

M = molarity of sulphuric acid

S = weight of soil sample in g

11.2. Determination of Mineral Nitrogen

Inorganic N in soil is present predominantly as nitrates NO_3^- and ammonium ions NH_4^+. Nitrite is seldom present in detectable amounts, and its determination is normally unwarranted except in neutral to alkaline soils following the application of NH_4 or NH_4-forming fertilizers (Keeney and Nelson, 1982).

Nitrate is highly soluble in water, and a number of solutions including water have been used as extractants. These include, saturated 0.35% $CaSO_4.2H_2O$ solution, 0.03 M NH_4F, 0.015 M H_2SO_4, 0.01 M $CaCl_2$, 0.5 M $NaHCO_3$ pH 8.5, 0.01 M $CuSO_4$, 0.01 M $CuSO_4$ containing Ag_2SO_4 and 2.0 M KCl.

Exchangeable NH_4 is defined as NH_4 that can be extracted at room temperature with a neutral K salt solution. Various extractants at different molarities have been used, such as 0.05 M K_2SO_4, 0.1 M KCl, 1.0 M KCl, and 2.0 M KCl.

The methods for the determination of $NO3^-$ and $NH4^+$-N are even more diverse than the methods of extraction (Keeney and Nelson, 1982). These range from specific ion electrode to manual colorimetric techniques, micro-diffusion, steam distillation, and flow injection analysis. Steam distillation is still a preferred method when using N^{15}; however, for routine analysis automated colorimetric techniques and phenoldisulfonic acid colorimetric methods are commonly used.

11.2.1. Determination of Nitrate by the Phenoldisulfonic Acid Method

One of the major difficulties in estimating NO_3 in soils by colorimetric methods is obtaining a clear colourless extract with low contents of organic and inorganic substances, which interfere with the colorimetric method. In arid and salt affected soils, chloride (Cl) is the major anion, which interferes with colour development of the phenoldisulfonic acid method. Therefore, if the chloride concentration is more than 15 µg/g, it should be removed before analysis by the use of Ag_2SO_4 to precipitate chloride as AgCl. The Ag_2SO_4 is added to the extract or to the reagent used for extraction, and the AgCl is removed by filtration or centrifugation after precipitation of the excess Ag_2SO_4 by an alkaline reagent such as $Ca(OH)_2$ or $MgCO_3$. It is necessary to remove the excess silver ions before analysis of the extract because they interfere with the phenoldisulfonic acid method of determining NO_3.

Apparatus

- Reciprocating shaker
- Heavy-duty hot plate
- Spectrophotometer
- Dispenser

Reagents

1. Phenoldisulfonic acid (phenol 2,4-disulfonic acid): Transfer 70 ml of pure liquid phenol (carbolic acid) to an 800 ml Kjeldahl flask. Add 450 ml concentrated H_2SO_4 while shaking. Add 225 ml fuming H_2SO_4 (13-15% SO_3). Mix well. Place the Kjeldahl flask (loosely stoppered) in boiling water in a beaker and heat for 2 hours. Store the resulting phenoldisulfonic acid $[C_6H_3OH(HSO_3)_2]$ solution in a glass-stoppered bottle.
2. Dilute ammonium hydroxide solution (NH_4OH), about 7.5 M: Mix one part NH_4OH (sp. gr. 0.90) with one part H_2O.
3. Copper sulphate ($CuSO_4$) solution, 0.5 M:. Dissolve 125 g $CuSO_4.5H_2O$ per 1 litre of distilled water.
4. Silver sulphate (Ag_2SO_4) solution (0.6%): Dissolve 6.0 g Ag_2SO_4 per 1 litre of distilled water. Heat or shake well until all the salt is dissolved.
5. Nitrate-extracting solution: Mix 200 ml of a 0.5 M copper sulphate solution and 1 litre of a 0.6% silver sulphate solution and dilute to 10 litres with water. Mix well.
6. Standard nitrate solution (100 µg NO_3-N/ml stock solution): Dissolve 0.7221 g KNO_3 (oven dried at 105°C) in water and dilute to 1 litre. Mix thoroughly.

7. Standard nitrate solution (10 µg NO_3-N/ml working solution): Dilute 100 ml of 100 µg NO_3-N/ml stock solution to 1 litre with water. Mix well.
8. Calcium hydroxide, reagent-grade powder (free of NO_3).
9. Magnesium carbonate, reagent-grade powder (free of NO_3).

Procedure

1. Place about 5 g soil in an Erlenmeyer flask.
2. Add 25 ml 2M KCl solution and shake for 10 minutes.
3. Add 0.2 g $Ca(OH)_2$ and shake for 5 minutes.
4. Add 0.5 g $MgCO_3$ and shake for 10-15 minutes.
5. Allow to settle for a few minutes.
6. Filter through a Whatman filter paper No. 42.
7. Pipette 10 ml of the clear filtrate into a 100 ml beaker. Evaporate to dryness on a hot plate at low heat in a fume hood free of HNO_3 fumes. Do not continue heating beyond dryness.
8. Let the beaker cool and add 2 ml phenoldisulfonic acid rapidly (from a burette having the tip cut off or a dispensette) covering the residue quickly. Rotate the beaker so that the reagent comes in contact with all the residual salt. (Caution: the phenoldisulfonic acid is very corrosive).
9. Allow to stand for 10-15 minutes.
10. Add 16.5 ml of cold water. Rotate the beaker to dissolve the residue (stir with a glass rod until the entire residue is in solution).
11. Cool the beaker to room temperature and add dilute NH_4OH slowly until the solution is distinctly alkaline, as indicated by the development of a stable yellow colour (15 ml).
12. After beakers are cool, add 16.5 ml of water (volume becomes = 50 ml). Mix thoroughly.
13. Read the concentration of NO_3-N at 415 nm.
14. Standards: evaporate 0, 2, 5, 8, and 10 ml of the 10 µg NO_3-N/ml working solution after adding 10 ml NO_3-extracting solution in 100 ml beakers and evaporate to dryness. Follow steps 9 to 13. These standard solutions have 0, 0.40, 1.00, 1.60, and 2.00 µg NO_3-N per ml.

Calculation

$$NO_3^- \text{-N in soil } (\mu g/g) =$$

$$NO_3^- \text{-N in test soln. } (\mu g/ml) \times \frac{\text{Vol. after colour developmen t (ml)}}{\text{Vol. evaporated (ml)}} \times \frac{\text{Vol. of extracting soln. (ml)}}{\text{Wt. of oven} - \text{dried soil (g)}}$$

11.2.2. Determination of Nitrate by the Specific Ion Electrode

The concentration of nitrate-nitrogen (NO_3-N) is estimated by comparison of the electromotive force (emf in millivolts) in the unknown with that in the NO_3^--N standards prepared by the same method.

Apparatus

- pH – millivolt meter or specific ion meter, with specific nitrate electrode and reference electrode.

Reagents

1. Standard nitrate-nitrogen (NO_3-N) solutions: Prepare a series of standards in water ranging from 1 to 100 mg NO_3^--N per litre..
2. Ammonium sulphate [$(NH_4)_2SO_4$], 2 M (for ionic strength adjustment): Dissolve 264 g of reagent grade $(NH_4)_2SO_4$ in 1 litre of water.

Procedure

1. Add 20 g of soil and 40 ml of distilled water to a 100 ml beaker. Stir the mixture intermittently for an hour (two to three times).
2. Place the beaker on a magnetic stirrer, insert the electrodes into the suspension and start the stirring. Record the millivolt reading (if using a calibration curve standardization method), or read the concentration directly (if using a specific ion meter calibrated to take into account the 1:2 dilution).

Note: Manufacturer instructions should be consulted for details of electrode assembling, storage and standardization. If interference are suspected (high soluble salts, Cl^- or NO_2^-), specific treatment of the extract may be required. If NH_4^+-N is to be determined by an electrode on the same sample, the analysis must be made before the NO_3^- analysis, because significant sample contamination by the external filling solution of the reference electrode may occur. The presence of soil solids does not markedly affect NO_3^- electrode determinations.

11.3. Extraction of Exchangeable Ammonium and Nitrate

Apparatus

- Erlenmeyer flasks
- Pipettes
- Mechanical shaker

Reagent

- Potassium chloride (KCl) solution, approximately 2 M: Dissolve 150 g of reagent-grade KCl in 1 litre of distilled water.

Procedure

1. Place 10 g of soil in a 250 ml, wide mouth Erlenmeyer, and add 100 ml of 2 M KCl.
2. Stopper and shake the flasks on a mechanical shaker for 1 hour.
3. Allow the soil-KCl suspension to settle and for the supernatant to clear (usually about 30 min).
4. If the KCl extract cannot be analyzed soon after its preparation (within 24 hours), filter the soil-KCl suspension (Whatman no. 42 filter paper) and store in a refrigerator.
5. Aliquots from this extract will be used for the following assays.

11.3.1. Determination of Ammonium by Indophenol Blue Method

The phenol reacts with NH_3 in the presence of an oxidizing agent such as hypochlorite to form a coloured complex in alkaline conditions. The addition of sodium nitroferricyanide dihydrate, also known as sodium nitroprusside as a catalyst in the reaction between phenol and NH_3 increases the sensitivity of the method several folds. The addition of EDTA is necessary to complex divalent and trivalent cations present in the extract. Otherwise, it forms a precipitate at the pH of 11.4–12 used for colour development, and this turbidity would interfere with the formation of the phenol-NH_3 complex.

Apparatus

- Variable wavelength spectrophotometer, equipped with 1 cm light path and capable of measuring absorbance at 636 nm.

Reagents

1. Potassium chloride (KCl) solution, 2 M: Dissolve 150 g reagent-grade KCl in 1 litre of distilled water.
2. Standard ammonium (NH_4^+) solution: Dissolve 0.4717 g of ammonium sulphate $(NH_4)_2SO_4$ in distilled water and dilute to a volume of 1 litre. If pure, dry $(NH_4)_2SO_4$ is used, the solution contains 100 µg of NH_4^+-N/ml. Store the solution in a refrigerator. Immediately before use, dilute 4 ml of the stock NH_4^+ solution to 200 ml. The resulting working solution contains 2 µg of NH_4^+-N/ml.
3. Phenol-nitroprusside reagent: Dissolve 7 g of phenol and 34 mg of sodium nitroprusside [disodium pentacyanonitrosylferrate, $Na_2Fe(CN)_5NO.2H_2O$] in 80 ml of deionised water, and dilute to 100 ml. Mix well and store in a dark-coloured bottle in a refrigerator.
4. Buffered hypochlorite reagent: Dissolve 1.480 g of sodium hydroxide NaOH in 70 ml of deionised water, add 4.98 g of sodium monohydrogen phosphate (Na_2HPO_4) and 20 ml of sodium hypochlorite (NaOCl) solution (5-5.25% NaOCl). Use less or more hypochlorite solution if the NaOCl concentration is higher or lower than that indicated. Check the pH to ensure a value between 11.4 and 12.2. Add a small amount of additional NaOH if required to adjust the pH. Dilute to a final volume of 100 ml.
5. Ethylenediaminetetraacetic acid (EDTA) reagent: Dissolve 6 g of ethylenediaminetetraacetic acid disodium salt (EDTA disodium) in 80 ml of deionised water, adjust to pH 7, mix well, and dilute to a final volume of 100 ml.

Procedure

1. Pipette an aliquot (not more than 5 ml) of the filtered 2 M KCl extract (see 11.3) containing between 0.5 and 12 µg of NH_4^+-N into a 25 ml volumetric flask. Aliquots of $\leq$3 ml normally contain sufficient NH_4^+-N for measurement.
2. Add 1 ml of the EDTA reagent, and mix the contents of the flask.
3. Allow the flask contents to stand for 1 minute, then add 2 ml of the phenol-nitroprusside reagent, followed by 4 ml of the buffered hypochlorite reagent, and immediately make up to volume with deionised water and mix well.
4. Place the flask in a water bath at 40°C for 30 min.
5. Remove the flask from the bath, cool to room temperature, and determine the absorbance of the coloured complex at a wavelength of 636 nm against a reagent blank solution.
6. Determine the NH_4^+-N concentration of the sample by reference to a calibration curve plotted from the results obtained from the measurement of known concentrations of NH_4^+-N.

7. To prepare a standard curve, add 0, 1, 2, 3, 4, 5, and 6 ml of the 2 µg/ml NH_4^+-N solution to the series of 25 ml flasks.
8. Add an appropriate amount of 2 M KCl solution (same volume as that used for aliquots of soil extract) to the 25 ml volumetric flasks.
9. Measure the intensity of blue colour developed with these standards by the procedure described for the analysis of unknown extracts.

11.3.2. Determination of Ammonium by Specific Ion Electrode

Ammonium-N concentration is also estimated by comparison of the electromotive force (emf, in millivolts) in the unknown with that obtained by analysis of NH_4^+-N standards by the same method. The sample or standard is made alkaline by the addition of NaOH (pH 11-12), because the electrode responds only to NH_3 activity.

The meter should be calibrated immediately before each series of analysis. Measurements should be made within 1-2 minutes after the addition of NaOH to ensure no loss of NH_3. If Hg^+ is present in the sample, sodium Iodide (15 g of NaI/l) can be added to the 0.25 M NaOH. Iodide forms complexes with Hg^+. Care must be taken to prevent air bubble entrapment under the electrode. This is easily accomplished by inserting the electrode at about a 20° angle with respect to vertical.

Apparatus

- Ammonia electrode
- pH-millivolt meter with sensitivity of $\pm$ 0.1 mV

Reagents

1. Sodium hydroxide (NaOH), 0.25 M: Dissolve 10 g of NaOH in 800 ml of distilled water and dilute to 1 litre.
2. Standard NH_4^+-N solutions: Prepare a series of standards in 2 M potassium chloride (KCl) ranging from 0.1 to 10 µg of NH_4^+-N/ml (using NH_4 working solution, as described under 11.3.1). If an extract other than 2 M KCl is used, prepare the standards in this solution.

Procedure

1. Place a 20 ml aliquot of the soil extract in a 50 ml beaker containing a Teflon-coated stirring bar.
2. Place the beaker on a magnetic stirrer, add 2 ml of 0.25 M NaOH and insert the NH_3 electrode connected to a pH-millivolt meter.

3. Stir the solution for 1 min., record the electrode potential value and calculate NH_4^+-N in the sample by comparison of this value to a calibration curve (as described under 11.3.1).

12. SOIL PHOSPHOROUS

In general, arid and semi-arid soils are low in available phosphorus and plants respond to application of phosphatic fertilizers. Applied fertilizer phosphate quickly reverts to insoluble forms. The amounts of the various discrete chemical fractions of P, which are formed in soil determine the relative effectiveness of phosphatic fertilizers on crop growth (Lindsay and De Ment, 1961), and are related to the genesis of soils (Westin and Buntley (1966). The retention of phosphorus in soils is the result of chemical precipitation and physico-chemical sorption (Hemwall, 1957). Bashour and Al-Jaloud (2000) studied the fate of applied phosphorus in arid calcareous soils of Saudi Arabia and found that 1/3 of the applied P fertilizers was taken up by plants and about 1/3 was retained in the soil as calcium phosphate. Most of the remaining 1/3 was converted into organic-P and $NaHCO_3$ extractable-P. Sayegh and Abdul Majid (1969) studied phosphorus fractionation and retention in soils of the semi-arid region, and the results are briefly indicated below.

12.1. Fractionation of Soil Phosphorous

Phosphorus characterization indicated that the water-soluble and easily replaceable P increased while Al-P, Fe-P, reductant soluble Fe-P, and occluded Al-Fe-P decreased with an increase of $CaCO_3$ content. The Ca-P in the soils increased with the increase of $CaCO_3$ content, amounting to 88 percent of the total phosphorus in highly calcareous soils. In the alkaline low calcareous soils Ca-P was the least, amounting to 5 percent, while Fe-P amounted to 19 percent of the total phosphorus suggesting a comparatively high iron content which is supported by the soil analysis and by the dark reddish brown colour. Thus, the considerable differences in the proportions of the various P fractions were associated with the degree of calcareousness.

12.2. Fate of Applied Phosphatic Fertilizer

The applied phosphorus was mainly converted to the forms of Ca-P, water soluble P and easily replaceable P in the highly calcareous soils. In the slightly calcareous soils, the distribution of the applied P was mainly in the forms of Ca-P and Al-P followed by water soluble P. In contrast to the calcareous soils, in the alkaline non-calcareous soils with iron and aluminium oxides, the applied P was distributed in a variety of forms decreasing in the following order: residual-P > Fe-P > Al-P > Ca-P> organic P.

12.3. Influence of Soil Parent Materials on the Distribution of the Inorganic P-fractions

The highly calcareous soils had the highest percentage of Ca-P, and no Fe-P, reductant soluble Fe-P, and occluded Al-Fe-P. In contrast, the soil developed from the hard Eocene calcareous rock had a greater percentage of all the P fractions except for the Ca-P. The soil derived from hard siliceous calcareous beds contained intermediate amounts of P fractions.

12.4. Phosphorous Retention

Phosphorus retention of the soils increased with the increase of iron and aluminium oxides. The retention of P was more rapid in the alkaline non-calcareous soils, which contained larger amounts of iron and aluminium oxides than in the low and high calcareous soils. The slower retention in the calcareous soils might be due to the continued slow precipitation of calcium phosphates in the course of time.

The removal of the amorphous materials from the clay fractions of the low and high calcareous soils increased P retention from 2 to 70 percent upon the addition of 250 µg/g of P, in the highly calcareous soils. The slight difference in the cation exchange capacity between the clays without any amorphous material or clays containing little quantity of amorphous material (partially clean and clean clays) did not appear to provide an adequate explanation for the large difference in phosphorus retention. It was, therefore, postulated that the retention capacity of the Ca-saturated samples was due to a surface reaction, thus the removal of amorphous materials resulted in increased effective surface area and more retention reaction. On the other hand, removal of the amorphous materials from the clay fractions of the non-calcareous soils, which are rich in iron and aluminium oxides, resulted in less P retention. This was attributed to the presence of comparatively high amounts of iron and aluminium in the amorphous materials.

12.5. Iron and Aluminium Amorphous Phosphate in Calcareous Soils

Most text books state that iron phosphates and aluminium phosphates and their intergrades are found in acidic soils where conditions are favourable for the presence of Al and Fe. While in neutral to alkaline soils, calcium phosphate is present where conditions are favourable for the presence of calcium. But they fail to mention the importance of iron and aluminium amorphous materials on phosphorus retention, which coat the clays, silt and sand fractions in the neutral and alkaline soils (Sayegh and Abdul Majid, 1969).

Tisdale and Nelson (1993) reported that in general the inorganic phosphorus content in arid soils is higher than the organic phosphorous content.

Brady (1990) and Soltanpour *et al.* (1988) have reported that the Aridisols and Andisols have 64% and 63% of inorganic phosphorus, respectively.

12.6. Determination of Available Phosphorous (Olsen's method)

Of the many extractants proposed for estimating available soil P, the $NaHCO_3$ solution (Watanabe and Olsen, 1965) is the most commonly used in calcareous soils.

Apparatus

- Mechanical Shaker
- Spectrophotometer
- Funnels and filter papers

Reagents

1. Sodium bicarbonate ($NaHCO_3$) solution, 0.5 M: Dissolve 42.0 g $NaHCO_3$ in 1 litre of distilled water. Before bringing it to volume, adjust pH to 8.5 with 1 M NaOH. This may need about 20 ml/l. Avoid exposure of the solution to air. It can be stored up to 1 month if kept in glass bottle and more than 1 month if stored in polyethylene containers. However, the pH needs to be checked before use.
2. Ammonium molybdate solution: Dissolve 12 g of ammonium molybdate in 250 ml of distilled water, and 0.2908 g of antimony potassium tartrate in 100 ml distilled water. Add both solutions to 1 litre of 2.5 M H_2SO_4 (140 ml conc. H_2SO_4 per litre), mix, make the volume to 2000 ml. Store in a Pyrex bottle in the refrigerator.
3. Ammonium molybdate - ascorbic acid solution: Dissolve 1.056 g of ascorbic acid in 200 ml of ammonium molybdate solution and mix. Prepare only as much as needed, as this solution is not stable for more than 24 hours.
4. Standard phosphate solution: Dissolve 0.4393 g of KH_2PO_4 (dried at 40°C) in distilled water and make the volume to 1 litre. This solution contains 100 µg of P/ml.
5. Working standard (dilute) phosphate solution: Dilute 50 ml of the standard phosphate solution to one litre. This solution contains 5 µg of P/ml.
6. Sulphuric Acid (H_2SO_4), 2.5 M: Add 140 ml of conc. (18 M) H_2SO_4 to 800 ml of distilled water. When cool, make the volume to 1 litre.

Procedure

1. Weigh 5.0 g soil sample in 250 ml Erlenmeyer flask.
2. Add 100 ml of $NaHCO_3$ extracting solution to it.

3. Shake on a mechanical shaker for 30 minutes. (sources of error: the amount of P extracted increases with time and intensity of shaking, and with temperature, 0.4 µg P/g per degree °C).
4. Filter the suspension through Whatman No. 40 filter paper into clean and dry 125 ml Erlenmeyer flask. Shake the suspension by hand immediately before pouring it into the funnel and discard the first 5 to 10 ml of filtrate if turbid.
5. Transfer 10.0 ml of filtrate to a 50 ml volumetric flask; acidify to pH 5 by adding 1.0 ml of 2.5 M H_2SO_4. Swirl carefully in the beginning, then vigorously to remove residual carbonates.
6. Make volume to 40 ml with distilled water; add 8 ml of the ammonium molybdate – ascorbic acid solution. Bring the volume to 50 ml, mix well, and let stand for 10 minutes.
7. Read absorbance at 882 nm on the spectrophotometer. The colour is stable for 24 hours and maximum intensity is obtained in 10 minutes.
8. Determine P concentration of the sample from a calibration curve relating the readings of absorption units to concentration in µg P/ml.
9. Preparation of the standard curve: i) add 0, 2, 5, 10, 15 and 20 ml of 5 µg P/ml standard stock solution to a series of labelled 50 ml volumetric flasks; ii) add 10 ml of the $NaHCO_3$ extracting solution, 1 ml of 2.5 M H_2SO_4, and develop colour as described above

Calculation

$$\text{P µg/g soil} = \text{P (µg/ml)} \; X \; \frac{50 \text{ ml}}{10 \text{ ml}} \; X \; \frac{100 \text{ ml}}{5 \text{ g soil}}$$

13. SOIL POTASSIUM

13.1. Determination of Available Potassium

The determination of plant available K is complicated as, in addition to K soluble in water, it includes part of the exchangeable K. Another factor which complicates the determination of plant available K in arid and semi-arid regions is that extracting solutions used for exchangeable K may also extract part of the non-exchangeable K from K-aluminium silicate clay minerals, like K-feldspars and micas. Plants in the field do not benefit from this form of K. Moreover, moisture content of the soil sample, and the manner of drying the sample also affects K extractability.

In general, routine laboratory tests for determining plant available K do not reflect the true situation under field conditions, because of the variation in the clay mineralogy of the soils.

The following procedure is suggested for determining plant available K in soils of the arid and semi-arid regions, and it may also apply to Ca and Mg.

Apparatus

- Centrifuge
- Round bottom centrifuge tubes - 50 ml
- Mechanical shaker
- Flame photometer

Reagents

1. Ammonium acetate (NH_4OAc), 1.0 M solution: Add 57 ml of conc. acetic acid to 700-800 ml distilled water in a 1-litre beaker. Then, with constant stirring, add 68 ml of conc. ammonium hydroxide. Bring the volume close to 1 litre, and adjust pH to 7.0 by the addition of more ammonium hydroxide or acetic acid. Or, dissolve 77.09 g of ammonium acetate in distilled water and dilute to 1 litre. Adjust pH to 7.0.
2. Potassium chloride (KCl) 0.02 M in 1.0 M ammonium acetate: Dissolve 1.491 g of potassium chloride in one litre of 1.0 M NH_4OAc solution to be used for preparing standard curve.
3. Lithium Chloride (LiCl), 0.05 M: Dissolve 2.12 g of lithium chloride in distilled water and dilute to 1 litre.

Procedure

1. Weigh accurately 5 g of soil and transfer into a 50 ml centrifuge tube.

2. Add 20 ml of 1.0 M ammonium acetate solution to the tube; stopper and shake in a reciprocal shaker for 5 minutes.
3. Centrifuge at 2000 rpm for 5 minutes or until the supernatant is clear.
4. Decant the supernatant into a 100 ml volumetric flask.
5. Repeat steps 2 – 4 three more times.
6. Make up the supernatant volume to 100 ml by adding ammonium acetate solution.
7. Prepare a series of working K standard solutions in the range of 0 – 2 meq/l of K from stock solution of 0.02 M KCl already prepared. For better results, add LiCl in each standard to yield a final concentration of about 5 meq/l of LiCl.
8. Determine K concentration in the extract by flame photometer as in section 6.3.2 and 8.1.

Calculation

$$\text{meq of K/100 g soil} = \text{Reading (meq/l)} \times \frac{100\text{ ml}}{1000\text{ ml}} \times \frac{100\text{ g}}{\text{Wt. of soil (g)}}$$

$$= \frac{\text{R X 10}}{\text{Wt. of soil (g)}}$$

13.2. Determination of Fixed Potassium

Apparatus

- Flame photometer or atomic absorption spectrophotometer.

Reagents

1. Nitric acid (HNO_3), 1.0 M: Dilute approximately 62 ml of conc. HNO_3 to a volume of 1 litre.
2. Nitric acid (HNO_3), 0.1 M: Dilute 6.2 ml of conc. HNO_3 to a volume of 1 litre.
3. Potassium standard solutions in the working linear range of the instrument, like 0.5 – 10 µg K/ml.
4. Lithium Chloride (LiCl), 0.05 M: Dissolve 2.12 g of lithium chloride in distilled water and dilute to 1 litre.

Procedure

1. Weigh accurately 2.5 g of finely ground soil (70 mesh) and transfer into a 200 ml beaker. Add 40 ml of 1.0 M nitric acid to the beaker and place it in

an oil bath at 113°C for about 25 minutes. Remove the beaker and wipe oil from outside.

2. Filter the contents into a 100 ml volumetric flask and wash the soil four times with 10 ml portions of 0.1 M nitric acid, each time filtering into a 100 ml flask. Cool the solution, dilute to volume and mix thoroughly.
3. Prepare K standard solutions in the recommended range of the instrument, like 0, 0.5, 1, 2, 3, 5, 7 and 10 µg K/ml. Add the same volumes of nitric acid solutions that were added in the samples. To suppress ionization and interference, add LiCl solution to yield a final concentration of about 5 meq/l (in case AAS is used, $LaCl_3$ (Lanthanum Chloride) is added as the suppressing agent).
4. Refer to section 6.3.2 for the flame-photometry determination of K.

Calculation

$$\text{Fixed K } (\mu\text{g/g soil}) = \text{K } (\mu\text{g/ml}) \text{ in solution X } \frac{100 \text{ ml}}{2.5 \text{ g soil}}$$

Note: This is in case no dilution was made on the sample prior to K measurement.

14. SOIL SULPHUR

Sulphur (S) is present in soils in organic and inorganic forms. Organic S is an important constituent of proteins and amino acids. The major inorganic sources of S include gypsum ($CaSO_4$), and pyrite (Fe_2S). Sulphur is also added to soil as a result of the use of fertilizers containing S, such as K_2SO_4, and some pesticides. It exists in soil and soil solution mainly as the SO_4^{2-} anion in combination with the cations, Ca^{2+}, Mg^{2+}, K^+, Na^+ or NH_4^+. When present in the form of elemental sulphur (S), it will be oxidized under aerobic condition to form SO_4^{2-}. Under anaerobic condition, SO_4^{2-} will be reduced by microorganisms into SO_3^{2-} and S^{2-}. Hydrogen sulphide (H_2S) is formed especially in swamps and other areas with stagnant water. Waterlogged and paddy soils provide a suitable environment for the formation of H_2S. In soils rich in iron, H_2S usually precipitates as FeS, which imparts to soils a black colour. When H_2S is allowed to accumulate, it is not only toxic to soil organisms, but also it creates environmental problems. A group of bacteria present in soils is capable of oxidizing the H_2S into elemental S and SO_4^{2-}.

Away from arid and semi-arid regions, probably in some acid soils, further formation of sulphuric acid (H_2SO_4) will lower soil pH to about 2, resulting in the formation of acid sulphate soils, sometimes called cat-clays. In addition to the toxicity created by the extremely low pH, the acidity will liberate very high levels of Al and Fe, which may reach toxic levels to plant growth.

The total S content in soils varies widely from soil to soil. Sandy soils in the humid regions are generally low in S (0.002%). In contrast, soils in arid regions may contain 5% SO_4^{2-}-S. Plants absorb S mostly in the sulphate SO_4^{2-} form, which is the available form of S. Sulphate is extractable by water, NaCl, $CaCl_2$, NH_4OAC, $NaHCO_3$ and $Ca(H_2PO_4)_2$ solutions.

Concentration of SO_4^{2-} is determined as follows:

Apparatus

- Spectrophotometer
- Mechanical shaker
- Volumetric flask

Reagents

1. Mono-Calcium Phosphate ($Ca(H_2PO_4)_2.H_2O$) solution: Weigh 2.03 g of $Ca(H_2PO_4)_2.H_2O$ and dissolve it in 800 ml distilled water with constant stirring. Transfer to a 1-litre volumetric flask and make up to volume with distilled water. This solution contains 100 mg P/l.
2. Acetic acid (CH_3COOH), 50%: Add 50 ml acetic acid to 50 ml distilled water.

3. Concentrated. Ortho-Phosphoric acid (H_3PO_4).
4. Barium chloride crystals, $BaCl_2$: The crystals are ground to pass a 0.5 mm sieve, and retained on a 0.25 mm sieve.
5. Gum acacia solution, 0.25% (w/v) in water.
6. Standard sulphate solution: Dissolve 147.9 mg anhydrous Na_2SO_4 in distilled water and dilute to 1 litre. This solution contains 100 µg SO_4/ml.

Procedure

1. Weigh 5 g of soil into a 100 ml polyethylene centrifuge tube, add 50 ml $Ca(H_2PO_4)_2$ solution, and shake the mixture for 30 minutes on a mechanical shaker. Filter into 50 ml volumetric flask.
2. Pipette 5 ml of the extract into a 50 ml volumetric flask, add 5 ml of acetic acid, 1 ml of H_3PO_4 and 1 g of $BaCl_2$ crystals. The phosphoric acid will decolourise any Fe present in solution. Mix gently by inverting the flask several times. Add 2 ml of gum acacia solution and make up to volume with distilled water.
3. Mix gently again and at 5 +/- 0.5 minutes, measure $BaSO_4$ turbidity with a spectrophotometer at 420 nm.
4. Estimate SO_4^{2-} concentration in sample by comparing turbidity with a calibration curve prepared by carrying sulphate standards through the entire procedure.

Calculation

$$\text{mg } SO_4/100 \text{ g soil} =$$

$$\text{µg } SO_4/\text{ml in sample} \times 50 \text{ ml} \times \frac{50 \text{ ml}}{5 \text{ ml}} \times \frac{50 \text{ ml}}{5 \text{ ml}} \times \frac{100 \text{ g}}{\text{Wt. of soil (g)}} \times \frac{1 \text{mg}}{1000 \text{ µg/mg}} =$$

$$\text{µg } SO_4/\text{ml in sample} \times \frac{10}{\text{Wt. of soil (g)}}$$

15. GYPSUM REQUIREMENT

Although gypsum is sparingly soluble in water, it is one of the most suitable chemicals used in reclaiming sodic and saline-sodic soils. Its solubility never exceeds 2.4 mg/litre. However, the problem is not mainly concerned with the degree of solubility of calcium sulphate, but to a great extent on the difficulty in replacing sodium by calcium in the colloidal complex. This difficulty is the main problem in the use of gypsum in reclaiming sodic soils, especially in calculating the actual amount of gypsum which should be added to such soils in order to react with Na_2CO_3 and sodium clay so as to bring its pH to about 8, i.e. to reclaim them. This difficulty increases when these soils are rich in soluble salts, i.e. saline-sodic soils.

The common procedure in such cases is to determine the soil content of Na_2CO_3, and then calculate the equivalent amount of calcium sulphate needed to affect the transfer of Na_2CO_3 to Na_2SO_4. This calculation is essentially theoretical and the amount of gypsum thus calculated varies greatly from the actual amount needed to reclaim such soils under field conditions. This is mainly due to the fact that the following factors are usually not taken into consideration:

1. The soluble sodium salts which accumulate in the soil during the process of salinization, eventually leading to alkalinization of such soils.
2. The percentage of exchangeable sodium in the colloidal complex of the soil.
3. The amount of colloidal material in the soil.
4. The calcium carbonate content of the soil.

Therefore, in general, it is recommended to multiply the theoretical quantity of gypsum by three or four to obtain the practical amount of gypsum actually required. A practical method was developed by Schoonover, 1953 to determine gypsum requirement, which is given below.

Apparatus

- Erlenmeyer flasks
- Pipettes
- Filter papers

Reagents

1. Ammonium chloride – ammonium hydroxide buffer solution: Dissolve 6.75 g of ammonium chloride in 57 ml of concentrated ammonium hydroxide and dilute to 100 ml.
2. Saturated gypsum solution: Add about 40 g gypsum ($CaSO_42H_2O$) to 10 litres of water. Allow to stand with occasional shaking for 8 hours or

longer. Let settle until clear or filter. Determine calcium concentration (meq/l) using EDTA trisodium salt ($C_{10}H_{13}N_2Na_3O_8$, commonly known as trisodium versenate) titration method.

3. Trisodium versenate solution (EDTA), 0.03 N: Dissolve 6.0 g of analytical reagent disodium dihydrogen ethylenediaminetetraacetic acid in 1 litre of distilled H_2O. Standardize this solution against standard $CaCl_2$ solution.
4. Eriochrome black T indicator: Dissolve 0.5 g Eriochrome black T and 4.5 g hydroxylamine hydrochloride in 100 ml of 95 percent ethanol.

Procedure

1. Weigh 5 g of soil into a 200 ml Erlenmeyer flask.
2. Add 100 ml saturated gypsum solution, stopper flask, and shake at intervals for 10 minutes.
3. Filter and pipette 10 ml of the filtrate to 200 ml Erlenmeyer flask.
4. Add 50 ml distilled water, 0.5 ml of ammonium chloride-ammonium hydroxide buffer solution, and 4 to 5 drops of Eriochrome black T indicator.
5. Determine calcium plus magnesium in solution by titration with 0.03 N trisodium versenate solution (at the end point, the solution will have a distinct blue colour with no trace of pink or violet). Record the ml of titrant used (V).
6. Titrate 10.0 ml of saturated gypsum solution. Record the ml of titrant used (B).

Calculation

Gypsum meq/100g = (Ca meq/l in gypsum solution) – (Ca + Mg meq/l in filtrate) X 2

$(B - V) \times 0.03\ N \times 382$ = tonnes gypsum/ha (15 cm soil depth)

$(B - V) \times 0.03\ N \times 764$ = tonnes gypsum/ha (30 cm soil depth)

Note: Iron, aluminium, and manganese when present in concentrations greater than 20 mg/kg, and copper in concentrations greater than several tenths of mg/kg, interfere with the performance of the Eriochrome black T indicator. Usually the concentrations of these metals in water and ammonium acetate extracts of soils of arid regions are insufficient to cause interference. If interference is encountered, then Ca and Mg should be determined by atomic absorption spectrophotometer.

16. SOIL MICRONUTRIENTS

16.1. Iron, Zinc, Manganese and Copper

16.1.1. Iron

Iron (Fe) is the third most abundant element in earth crust. The most important iron minerals in soil are *hematite* (Fe_2O_3) and *magnetite* (Fe_3O_4). The hydrated form of hematite is often called *limonite* ($2Fe_2O_3.3H_2O$). Hematite is red in colour and its presence gives the soils a red colour. Magnetite is black in colour and crystalline in nature. It has strong magnetic properties. Another iron mineral is *pyrite* (FeS_2), which occurs in soils as yellow crystals with a metallic luster similar to gold, hence the name *fool's gold*. *Ilmenite* ($FeTiO_3$) is another important iron mineral, and is a valuable source for the production of many industrial products. In addition, Iron occurs in soils in an amorphous form coating soil particles and, also, as organic complexes. The granular soil structure in Oxisols is believed to be stabilized by iron coatings around the structural units.

In soil solution iron exists in two oxidation states, ferrous Fe^{2+} and ferric Fe^{3+}. Under anaerobic conditions, Fe^{2+} is the dominant species, whereas under aerobic conditions Fe^{3+} is the dominant species. The concentration of Fe^{2+} and/or Fe^{3+} in soil solution is very low, due to the highly insoluble nature of Fe_2O_3 minerals. The concentration of soluble Fe in river water and ground water is estimated to range from 0.1 to 10 mg/l (Krauskoph, 1973; Tan, 1994).

Iron is an essential micronutrient for plant growth. It is needed for chlorophyll formation. In animals, iron is present in the blood hemoglobin, which acts as a carrier of oxygen. The normal iron concentration in plant tissue varies considerably with plant species from 100 µg/g dry matter of grasses to 1000 µg/g in alfalfa dry matter. Iron concentration of <20 µg/g in plant tissue is considered deficient, and may result in development of chlorosis, frequently manifested as yellow stripes on young leaves. Iron deficiency in soils can be induced by over-liming, and the presence of high amounts of phosphates. Iron deficiency often occurs on plants growing in alkaline calcareous soils. Therefore, iron deficiency is most likely a problem in the calcareous soils of arid and semiarid regions.

16.1.2. Zinc

Zinc (Zn) is present in small quantities in igneous and sedimentary rocks. Concentration of Zn is usually higher in basic igneous rocks, such as basalt, than in acid igneous rocks, such as granite. The major inorganic sources of Zn are *sphalerite*, ZnS, *smithsonite*, $ZnCO_3$, and *hemimorphite* [$Zn_4(Si_2O_7)(OH)_2.H_2O$]. *Hydrozincite* [$Zn_5(CO_3)_2(OH)_6$] is another Zn mineral frequently mentioned, but

this mineral is considered similar to smithsonite (Hurlbut and Klein, 1977). All the minerals stated above are very rare in soils, and occur only in large amounts as Zn ore deposits.

The concentration of total Zn in soils is approximately in the range of 10 µg to 300 µg/g. The average Zn content in normal agricultural soils is 50 µg/g (Brady, 1990). In soil solution, Zn is present as the divalent Zn^{2+} ion. Most Zn compounds are sparingly soluble in water. Because of its cationic nature, the Zn ion is adsorbed by the negatively charged surfaces of soil colloids, and is then called *exchangeable Zn.* The concentration of Zn ions is dependent upon pH, as is the case with all the other microelements. At low pH, Zn^{2+} concentration is very high in soils, whereas at high pH, Zn^{2+} concentration is low. At pH 9.5, Zn^{2+} exhibits minimum solubility and precipitates as $Zn(OH)_2$. Therefore, high soluble Zn contents occur in acid soils, whereas low soluble Zn contents are found more in basic soils, especially in Aridisols. For example, the concentration of Zn^{2+} ions in neutral and alkaline calcareous soils is in the range of 1×10^{-8} to 1×10^{-10} *M* (Norvell, 1973). Consequently, Zn deficiency is found in alkaline calcareous soils.

Zinc is a micronutrient to plants, and is needed only in very small amounts. The element functions as a catalyst. It is present in several plant enzymes, e.g. dehydrogenase, proteinase, and peptidase. Zinc is also essential for seed and grain production, and development of growth hormones.

The normal concentration of Zn in most plants ranges on the average from 15 to 125 µg/g. Zn concentration of < 15 µg/g of leaf dry matter cause Zn deficiency, which is manifested as stunted growth. On maize plants, Zn deficiency produces white to yellow leaves with bleached stripes, a symptom known as *white bud* of maize. On the other hand, Zn concentration of > 400 µg/g of leaf dry matter is considered excessive and may induce Zn toxicity. Zinc deficiency is common in the calcareous soils of arid and semiarid regions.

16.1.3. Manganese

Manganese (Mn) is present in small quantities in many rocks. It is released into the soil by rock weathering and is re-deposited in various forms of Mn oxides.

The total Mn content in soils varies considerably from 20 µg/g to 6000 µg/g (Krauskoph, 1973). The element can exist in three oxidation states: Mn^{2+}, Mn^{3+}, and Mn^{4+}. The divalent manganese ion is the main form of Mn in soil solution, especially in reduced soil environment. Because of its cationic nature, Mn^{2+} is usually adsorbed on the negatively charged surfaces of soil colloids. It is then called *exchangeable manganese*. The trivalent form usually exists as Mn_2O_3, which can be found in substantial amounts in acid soils. The trivalent ion itself is unstable in soil solution. The tetravalent form (MnO_2), is perhaps the most stable and inert form of manganese.

The concentration of Mn^{2+} in soil solution is very low, seldom exceeding 0.05 mg/l. Its concentration increases at low pH values, and decreases at high pH values. Therefore, high amounts of manganese may be present in highly

weathered acid soils, such as Ultisols and Oxisols. On the other hand, low amounts of manganese usually occur in Aridisols.

Manganese is an essential micronutrient and is needed by plants to activate a number of enzymes. It also plays an essential role in photochemistry and in N-metabolism and assimilation. Manganese is required for plant growth only in very small amounts. The normal Mn content in plant tissue is 20 - 500 µg/g dry matter. A Mn concentration of < 20 µg/g dry matter is considered deficient and is usually manifested by development of necrotic spots, known as *marsh spots* in pea leaves, and *grey specks* in oat leaves. Soybean and oats are especially sensitive to Mn deficiency. Manganese deficiency is likely to occur in calcareous soils of arid and semiarid regions.

16.1.4. Copper

Copper (Cu), is classified as a *native element,* meaning that it can occur as a native element in the earth crust in contrast to such elements as Al, which exist only in the form of a compound. The most common form of Cu in soils is in the form of minerals, e.g. in the forms of sulphides, sulphates, oxides, carbonates, and silicates. The most common Cu mineral in soils is perhaps chalcopyrite ($CuFeS_2$).

The total Cu content in soils is in the range of 10 µg/g to 80 µg/g (Krauskoph, 1973). In the soil solution, copper exists as Cu^+ (cuprous), or Cu^{2+} (cupric) ions. At concentrations > 10^{-7} mol/l Cu^+ ions are unstable at ordinary temperature. However, it can exist at these conditions as a $CuCl_2^-$ chelate (Krauskoph, 1973). Cuprous ions are so unstable in aqueous solution that they will be automatically affected by the soil redox process, called *auto-reduction-oxidation* reaction, and converted into Cu and Cu^{2+}. Therefore, cupric ions are more stable and are the major copper ions in the soil solution. However, Lindsay (1973) noted that Cu^{2+} is the dominant ion in soils at pH values < 7.3, whereas above this pH, $Cu(OH)^+$ is the major copper ion. The concentration of soluble Cu ions in soils is on the average 20 mg/l. Because of its cationic nature, Cu^{2+} will be adsorbed by negatively charged surfaces of soil colloids, and are then called exchangeable Cu. The concentration of free and exchangeable Cu ions is high in acid soils, and low in basic soils. The Cu^{2+} concentrations in many neutral and calcareous soils are reported to amount only 1×10^{-12} M (Norvell, 1973). Therefore, Cu deficiency is more likely to occur in basic soils, e.g. Aridisols, whereas Cu toxicity may be displayed more by highly weathered acid soils, e.g. Ultisols and Oxisols.

Copper is a micronutrient, and is needed only in small amounts by plants. The element is required for chlorophyll formation, hence Cu affects photosynthesis. It is essential in enzyme reactions, and in the reproductive stages. Cu is noted to be needed in protein and carbohydrate metabolism, and in nitrogen fixation. The normal concentration in plant tissue is approximately 4 - 30 µg Cu/g. Present at concentration < 3 µg/g dry matter, Cu deficiency will occur, which is manifested by yellowing and curling of leaves, stunted growth and development of short

internodes. On the other hand, Cu concentration in leaf tissue of >20 µg/g may result in Cu toxicity, which is manifested by yellowing of leaves, and poorly developed roots with frequently discoloration.

16.2. Determination of Available Micronutrients

Available Fe, Zn, Cu and Mn in soils are extracted with several chelating agents, including EDTA, EDDHA and DTPA. Lindsay and Norvell (1978) developed the DTPA (diethylenetriaminepentaacetic acid) method and reported good correlations between DTPA-extractable micronutrients and plant growth. These elements can also be determined in the soil solution extracted by centrifugation of a moist soil sample collected directly from the field.

16.2.1. DTPA Extraction Method

Reagents

1. Diethylenetriaminepentaacetic acid (DTPA) solution: Weigh 19.67 g DTPA and with constant stirring, dissolve in 1 litre of distilled water. Weigh separately 149.2 g TEA (triethanol amine) and 14.7 g $CaCl_2.2H_2O$, and dissolve in 1 litre of distilled water. Pour under constant stirring the DTPA solution to the TEA-$CaCl_2.2H_2O$ mixture. After the DTPA has dissolved completely, dilute the solution to 9 litres. Adjust the pH to 7.3 with 1:1 HCl (approximately 42 ml required), and make up the volume to 10 litres with distilled water.
2. Standard solutions of Fe, Zn, Cu and Mn: Stock standard solutions containing 1000 mg/l of the metals.

Procedure

1. Weigh 5 g of air-dried soil (<2 mm) in a 100 ml polyethylene centrifuge tube, add 20 ml DTPA solution, and shake for 30 minutes on a mechanical shaker.
2. Centrifuge, and decant into a sample bottle fitted with funnel and filter paper.
3. If needed, dilute the extract so that the reading is in the linear working range of the atomic absorption spectrophotometer.

16.2.2. Measurement of Element Concentration Using Atomic Absorption Spectroscopy

Atomic absorption spectrophotometry has become a common practice in almost all laboratories, especially for the measurement of trace elements (Te) concentration in solution. Each instrument, AA spectrophotometer, has its

instruction manual that guide the user to the adjustment and operation of the instrument, but it is essential to have a general knowledge of the basic principles of the technology.

Atomic absorption spectroscopy (AAS) uses absorption of light to measure the concentration of analyte atoms in a flame or graphite furnace. The light source is usually a hollow-cathode lamp of the element that is being measured. Lamps convert electrical energy into radiation. Atoms absorb the radiation and make transitions to higher energy levels. Light absorption is proportional to the amount of analyte atoms in the path of light. Concentration measurements are determined from a working curve after calibrating the instrument with standards of known concentration.

Atomic absorption spectroscopy requires that the analyte atoms be in the gas phase. Ions or atoms in a sample must undergo vaporization or atomization in a high-temperature source such as a flame or graphite furnace.

Flame AAS uses a slot type burner to increase the path length, and therefore to increase the total absorbance. Sample solutions are usually aspirated with the gas flow into a nebulizing/mixing chamber to form small droplets before entering the flame.

The furnace AAS is a much more efficient atomizer than the flame and can directly accept very small quantities of sample. Samples are placed directly in the graphite tube and the furnace is electrically heated in several steps to dry the sample, ash organic matter, and vaporize the analyte atoms. While flame AAS measures concentration of analyte in µg/ml, furnace AAS detects concentrations in µg/l.

A calibration curve is a plot of the analytical signal (the instrument or detector response) as a function of analyte concentration. These calibration curves are obtained by measuring the signal from a series of standards of known concentration. The calibration curves are then used to determine the concentration of an unknown sample, or to calibrate the linearity of an analytical instrument.

Procedure

1. Prepare an intermediate standard solution by pipetting 10 ml from the 1000 µg/ml Stock solution of the analyte Te into a 200 ml volumetric flask, and dilute to the volume with DTPA solution.
2. Prepare standard solutions in the working range, like 0, 1, 2, 5, 10 µg/ml of the trace metal. Always dilute with the DTPA solution.
3. Now follow the step by step procedure given in the instruction manual to optimize the working condition of the instrument.
4. Measure the signals from the series of working standards of known concentration, and plot the analytical signals (the instrument or detector response) as a function of analyte concentration.

Calculation

$$\mu g\ Te/g\ soil = \mu g\ Te/ml_{sample}\ X \frac{20\ ml}{5\ g\ soil}$$

16.3. DTPA Extractability and Availability for Plant Uptake

Lindsay and Norvell (1978) suggested some critical levels for DTPA extractable micronutrients as a guide to deficiency and availability of these trace elements for plant uptake and growth:

Micronutrients (*µg*/g soil)				
Availability	**Zn**	**Mn**	**Fe**	**Cu**
Very Low	0 – 0.5	0 – 0.5	0 – 2.0	0 – 0.1
Low	0.6 – 1.0	0.5 – 1.2	2.0 – 4.0	0.1 – 0.3
Medium	1.0 – 3.0	1.2 – 3.5	4.0 – 6.0	0.3 – 0.8
High	3.0 – 6.0	3.5 – 6.0	6.0 – 10.0	0.8 – 3.0
Very High	>6.0	>6.0	>10 0	>3.0

17. SOIL BORON

Boron (B) is a non-metal, in contrast to the other micronutrient elements. It is present in small amounts in igneous, sedimentary and metamorphic rocks. In areas with geothermal activity, gases flowing from inner earth contain B. When dissolved in hot springs the element becomes boric acid (H_3BO_3). However, the major inorganic sources of B are borate and boron-silicate minerals. Borate minerals occur mostly in arid regions. They are formed by the evaporation of water in enclosed salt-water lakes and basins in arid regions. The BO_3^{2-} units polymerize and form a variety of borate crystals. Borax is the most common among borate minerals.

Total B content in soils is between 7 and 80 µg/mg soil. It is released by weathering of the minerals in the form of H_3BO_3 and its concentration is usually $<1\times10^{-4}$ M, which equals 0.1 mg/l (Krauskoph, 1973), a very small amount. Concentration of 1–2 mg B/kg soil is perhaps more representative for surface soils. In soil solution, B can exist both as H_3BO_3 and $H_2BO_3^-$. High concentrations of B are found only in seawater, where an average concentration of 4.6 µg/ml has been reported (Krauskoph, 1973). Because of its anionic character, BO_3^{2-} will not be attracted by the negatively charged soil colloids. In humid regions borate ions may tend to leach from soils. Therefore, soluble B concentrations are low in highly leached soils. Since highly leached soils usually exhibit low soil pH, acid soils are deficient in B. On the other hand, soluble B concentrations are expected to be high in soils not affected by leaching. Since arid region soils are usually not affected by leaching, and are, therefore, strongly basic in reaction, they may contain excessive amounts of B for plant growth. Therefore, B deficiency is more likely to occur in Ultisols and Oxisols, whereas B toxicity could be noted in Aridisols. This is in contrast with the other micronutrients.

Boron is an essential micronutrient element for plant growth. It is needed for cell division, hence for the growth of young shoots. It is essential in sugar translocation and in the synthesis of hormones and protein in plants. The normal B concentration in plant tissue is reported to be between 20 and 100 µg/mg dry matter of mature leaves. A boron content of <15 µg/mg indicates B deficiency, whereas a B concentration >200 µg/mg indicates B toxicity. Boron deficiency is usually manifested in formation of white and rolled leaves. In sugar beets, it results in rotting of the shoots, a nutritional disease called *heart rot*.

Boron in soils is primarily of importance in soil fertility and plant nutrition but is not used as a significant parameter in soil characterization, soil genesis and classification.

Methods for determination of total B and available B are described here.

17.1. Total Boron by Na_2CO_3 Fusion

Apparatus

- Platinum crucible
- Bunsen burner
- Beakers, flasks and funnels
- Filter papers

Reagents

1. Sodium Carbonate (Na_2CO_3) anhydrous, solid crystal powder.
2. Sodium Carbonate (Na_2CO_3), 30% solution: Weigh 30 g of Na_2CO_3 in a 100 ml volumetric flask, add 80 ml of distilled water, and dilute to volume. Store in a polyethylene vial.
3. Sulphuric Acid (H_2SO_4), 2 M: Add 12 ml of conc. H_2SO_4 to 800 ml distilled water into a 1 litre volumetric flask, allow the solution to cool and dilute to volume with distilled water.
4. Hydrochloric Acid (HCl), 0.1 M: Add 8.1 ml conc. HCl to 500 ml distilled water in a 1 litre volumetric flask, allow the solution to cool and dilute to volume with distilled water.
5. Ethyl alcohol, 95%.
6. Sodium Hydroxide (NaOH), 0.02 M: Dissolve 800 mg NaOH in a 500 ml distilled water in a one litre volumetric flask, cool, and dilute to volume.
7. Phenolphthalein solution: Weigh 50.0 mg phenolphthalein in a 100 ml volumetric flask, add 50 ml ethyl alcohol and dilute to the volume with distilled water. Shake the flask until the phenolphthalein crystals have dissolved completely.
8. Standard B solution: Pipette 35 ml of a stock solution containing 1000 µg B/ml into a 100 ml volumetric flask, and dilute to volume with ethyl alcohol. This solution, called standard solution, contains 350 µg B/ml.

Procedure

1. Weigh 1.0 g of 100 mesh (2 mm) soil in a platinum crucible.
2. Add 6 g of Na_2CO_3 powder, mix and heat on a Bunsen burner until the sample is completely fused with the Na_2CO_3.
3. Cool to room temperature, add 10 ml of H_2SO_4 to disintegrate and dissolve the melt.
4. Place the crucible on its side in a 250 ml Pyrex beaker, and add 4 ml increments of 2 M H_2SO_4 until the solution pH is 6.0-6.5.
5. Filter the solution into a 500 ml volumetric flask fitted with funnel and filter paper, and wash the contents of the beaker and the crucible with distilled water into the flask, collecting about 150 ml.

6. Dilute with ethyl alcohol to a volume of 400 ml, add a few drops of phenolphthalein and Na_2CO_3 solution (30%) to attain a slightly alkaline reaction, then bring to volume (500 ml) with ethyl alcohol.
7. Prepare a blank by following the same fusion procedure but without soil.

For the measurement of B concentration in the digestion solution, refer to section 17.3.

17.2. Available Boron by Hot Water Extraction

This is the most commonly used method for available B in soil. Extracted B can then be determined by colorimetric methods using reagents such as carmine or azomethine-H. Recently, atomic emission spectrometry or inductive coupled plasma (ICP) is used for boron measurement in laboratories where such equipment is available.

Apparatus

- Boron-free, alkali-resistant glassware or stainless steel
- Water bath
- Rubber policeman

Reagents

1. Calcium hydroxide ($Ca(OH)_2$) suspension: Weigh 400.0 mg $Ca(OH)_2$ into a 100 ml volumetric flask, and dilute to volume with distilled water.
2. Hydrochloric Acid (HCl), 0.1 M: Measure 8.1 ml of conc. HCl (12.4 M) into a 1 litre volumetric flask, add 800 ml of distilled water and allow the solution to cool to room temperature. Dilute to volume with distilled water.
3. Calcium Chloride ($CaCl_2$), 0.01 M: Weigh 1.11 g anhydrous $CaCl_2$ into a 1 litre volumetric flask, add 900 ml distilled water to dissolve under constant stirring, and dilute to volume with distilled water.

Procedure

1. Weigh 20 g of air-dry soil into a 250 ml Erlenmeyer flask, and add 40 ml of hot deionised water (in calcareous soils, dilute 0.01 M $CaCl_2$ is used instead of hot deionised water).
2. Place a refluxing funnel on the Erlenmeyer flask, and heat the mixture to the boiling point, and reflux the suspension for 5 min.
3. Cool and filter the suspension into a 50 ml volumetric flask, and dilute to volume with distilled water.

4. Pipette 25 ml of the filtrate into an evaporating dish, add 2 ml of the $Ca(OH)_2$ suspension and evaporate to dryness on a water bath.
5. Heat the evaporating dish gently over a flame to destroy organic matter.
6. Cool to room temperature, add 5 ml of HCl (0.1 M) and dissolve the digest by rubbing with a rubber policeman.
7. Filter the digest into a 10 ml volumetric flask, and dilute to volume with distilled water.

17.3. Measurement of Concentration by Colorimetric Methods

For the measurement of B concentration in the digestion solution for total boron, or in the hot water extract for available B, colorimetric methods are followed. The following are two procedures, each one of them uses a different compound for colour development.

17.3.1. Colour Development – Carmine Method

In the presence of B, a solution of carmine in concentrated sulphuric acid changes colour from a bright red to a blue, depending on concentration of B in solution.

Apparatus

- Spectrophotometer
- Boron-free, alkali-resistant glassware (flasks, beakers, Pipettes, burettes, etc.

Reagents

1. Hydrochloric acid (HCl) concentrated.
2. Sulphuric acid (H_2SO_4) concentrated.
3. Carmine solution: Dissolve 920 mg carmine in 1 litre concentrated sulphuric acid. Shake until completely dissolved.
4. Standard boric acid stock solution: Dissolve 0.5716 g of recrystallized H_3BO_3 in distilled water and dilute to 1 litre. One ml of this solution contains 0.1 mg (100 µg) of boron.

Procedure

1. Prepare a series of B standard solutions (1.0, 2.5, 5.0, 7.5, and 10 µg B/ml) with distilled water using standard boric acid stock solution.
2. Pipette 2 ml of the sample (digestion solution or water extract), which should contain not more than 0.02 mg B, into a 25 ml volumetric flask.

3. Treat the blank and the calibration standards exactly as the sample.
4. Add 2 drops (0.1ml) conc. HCl, carefully introduce 10.0 ml conc. H_2SO_4, mix, and allow to cool to room temperature.
5. Add 10.0 ml of Carmine reagent, make to volume (25 ml) with deionised water, mix well, and allow to stand for 45 to 60 minutes for colour development, which is bluish or blue depending on the concentration of B in the sample.
6. Prepare a standard curve using the blank as a reference and observe absorbance at 585 nm in a cell of 1 cm or longer light path against each standard sample containing known amount of B (expressed as µg B/ml). Determine the B content (as µg B/ml) in the unknown sample from the standard curve.

Note: Bubbles may form as a result of incomplete mixing. Make sure that there are no bubbles in the optical cell when absorbance readings are being made. Check the calibration daily because the carmine reagent deteriorates.

Calculation

$$\text{B content in } \mu g/100 \text{ g soil} = \frac{\mathbf{X} \times 10 \times 2 \times 100}{20} = \mathbf{X} \times 100$$

Where,

X = Reading in µg/ml from the standard curve

Note:

Weight of the soil taken = 20 g
Vol. of the extract = 50 ml
Vol. taken for estimation = 25 ml (this was reduced to 10 ml)
B content in the reduced sample (µg/ml) = **X**
B content in the 10 ml reduced sample (µg) = **X** x 10 (quantity present in the original 25 ml extract)
B content in 50 ml original extract (quantity in µg present in 20 g soil) = **X** x 10 x 2
B content in 100 g soil (µg) = **X** x 10 x 2 x 100/20

17.3.2. Colour Development – Azomethine-H Method

Apparatus

- Analytical balance
- Flask or beaker
- Volumetric flask
- Funnels

- Whatman No.42 filter paper
- Spectrophotometer

Reagents

- Azomethine-H: Dissolve 0.45 g azomethine-H and 1.0 g L-ascorbic acid in about 100 ml deionised or double-distilled water. If solution is not clear, it should be heated gently in a water bath or under a hot water tap at about 30^0 C till it dissolves. Every week a fresh solution should be prepared and kept in a refrigerator.

- Buffer solution: Dissolve 250 g ammonium acetate in 500 ml deionised or double-distilled water and adjust the pH to about 5.5 by slowly adding approximately 100 ml glacial acetic acid, with constant stirring.

- EDTA solution (0.025 M): Dissolve 9.3 g EDTA in deionised or double-distilled water and make the volume up to 1 litre.

- Standard stock solution: Dissolve 0.8819g Na_2 $B_4O_710H_2O$ AR grade in a small volume of deionised water and make volume to 1 000 ml to obtain a stock solution of 100 μg B/ml.

- Working standard solution: Take 5 ml of stock solution in a 100 ml volumetric flask and dilute it to the mark. This solution contains 5 μg B/ml.

Procedure

1. Take 5 ml of the clear filtered extract in a 25 ml volumetric flask and add 2 ml buffer solution, 2 ml EDTA solution and 2 ml azomethine-H solution.
2. Mix the contents thoroughly after the addition of each reagent.
3. Let the solution stand for 1 hour to allow colour development. Then, the volume is made to the mark.
4. Intensity of colour is measured at 420 nm.
5. The colour thus developed has been found to be stable up to 3-4 hours.
6. Preparation of standard curve: Take 0, 0.25, 0.50, 1.0, 2.0 and 4.0 ml of 5 μg B/ml solution (working standard) to a series of 25 ml volumetric flasks. Add 2 ml each of buffer reagent, EDTA solution and azomethine-H solution. Mix the contents after each addition and allow to stand at room temperature for 30 minutes. Make the volume to 25 ml with deionised or double-distilled water and measure absorbance at 420 nm. This will give reading for standard solution having B concentration 0, 0.05, 0.10, 0.20, 0.40 and 0.80 μg B/ml.

Calculations

Weight of the soil taken	= 25 g
Volume of extractant (water) added	= 50 ml
First dilution	= 2
Volume of the filtrate taken	= 5 ml
Final volume of filtrate after colour development	= 25 ml
Second dilution	= 5
Total dilution	= 2x5 = 10 times
Absorbance of the soil solution as read from the spectrophotometer	= X
Concentration of B as read from the standard curve against X	= C μg/ml
Content of B in the soil (μg /g or mg/kg)	= C x 10

Note:

1. The use of azomethine-H is an improvement over that of carmine, quinalizarin and curcumin, since the procedure involving this chemical does not require the use of concentrated acid.
2. The amount of charcoal added may vary with the organic matter content of the soil and should be just sufficient to produce a colourless extract after 5 min. of boiling on a hot plate. Excess amounts of charcoal can result in loss of extractable B from soils.

18. SOIL MOLYBDENUM

Molybdenum (Mo) is a rare element in soils, and is present only in very small amounts in igneous and sedimentary rocks. The major inorganic source of Mo is molybdenite (MoS_2). The total Mo content in soils is perhaps the lowest of all the micronutrient elements, and is reported to range between 0.2 μg/g and 10 μg/g.

In the soil solution, Mo exists mainly as $HMoO_4$ ion under acidic condition, and as MoO_4^{2-} ion under neutral to alkaline conditions. Because of the anionic nature of Mo, its anions will not be attracted much by the negatively charged colloids, and therefore, tend to be leached from the soils in humid region.

Molybdenum can be toxic due to greater solubility in alkaline soils of the arid and semi-arid regions, and deficient in acid soils of the humid regions.

In plants a deficiency of Mo is common at levels of 0.1 μg/g soil or less. Molybdenum toxicity (molybdenosis) is common when cattle graze forage plants with 10-20 μg Mo/g.

Determination of available Mo by ammonium acetate extraction is described here.

Apparatus

- Centrifuge and 50 ml centrifuge tubes

- Automatic shaker
- Atomic Absorption Spectrophotometer

Reagents

1. Ammonium acetate solution (NH_4OAc), 1.0 M: Dissolve 77.09 g of ammonium acetate in 1 litre of distilled water and adjust pH to 7.0.

Procedure

1. Weigh accurately 5 g soil and transfer it into a 50 ml centrifuge tube.
2. Add 33 ml of 1.0 M ammonium acetate solution to the tube, stopper and shake in a mechanical shaker for 5 minutes.
3. Centrifuge at 2000 rpm for 5 minutes or until the supernatant is clear.
4. Decant the solution into a 100 ml volumetric flask.
5. Repeat steps 2 – 4.
6. Make up the volume to 100 ml with ammonium acetate.
7. Determine Mo concentration in the extract by the atomic absorption spectrophotometer, as described under 16.2.2.

19. SOIL SELENIUM

Determination of total selenium (Se) in soils is of little value in predicting Se uptake. Cary and Allaway (1969) have shown that plant uptake of Se is closely correlated to the water-soluble Se fraction in soils high in Se content. This correlation has not been demonstrated for soils low in Se content.

The most commonly used extractants are: Ammonium Bicarbonate – DTPA, hot water, saturated paste extract, DTPA (2 hrs), and 0.5 M Na_2CO_3.

The above five extractants, when tested on soils high in Se, showed high correlation with Se in wheat plant (Jump and Sabey, 1989). However, Se in saturated paste extract expressed as mg Se/l of extract was found to be the best indicator of Se uptake in Se-accumulating plants. The data of Jump and Sabey (1989) suggested that soil or mine-spoil materials that have more than 0.1 mg Se/l of saturated extract might cause Se toxicity in plants.

The ammonium bicarbonate-DTPA method showed that Se in extract correlates better with Se in wheat grain, better when soil samples were taken from the 0 – 90 cm depth as opposed to 0 – 30 cm depth (Soltanpour *et al.*, 1982b). This was found to be particularly useful to screen soils and overburden material for potential toxicity of Se. Concentration of 0.05 µg Se/g or less in feed and forage plants is in the deficient range and-4 – 5 µg Se/g or more are in the toxic range.

Procedure

The ratio of soil to any of the extractant listed above varies from 1:2 to 1:5, and the extraction time from 15 min to 2 hrs. The filtered extract can be analyzed for Se using a hydride generating system attached to an ICP emission spectrometer (Soltanpour *et al.*, 1982 a) or hydride generating system attached to atomic absorption spectrophotometer.

Note:

1. The extracting methods developed for Se have been found to be suitable for predicting the availability of Se in areas where plants suffer Se toxicity. Because of rather small quantities of available Se in Se-deficient areas, no reliable extractant has yet been developed. Therefore, plant Se and total soil Se will continue to serve as the best tools available for testing the Se status of Se-deficient soils.
2. Selenium deficiency has implications with respect to livestock and human nutrition, but not to plant nutrition. So far, there is no known yield response to Se addition on cultivated crops, and its essentiality to plants is not established yet.

20. POTENTIALLY TOXIC ELEMENTS - CD, CR, NI AND PB

As a result of on-land application of certain waste products, like digested sewage sludge contaminated with industrial wastes, soils could become seriously contaminated with certain potentially hazardous products of the industry, like cadmium (Cd), chromium (Cr), nikel (Ni) and lead (Pb). In addition to analysis for plant essential elements, like Fe, Zn, Mn and Cu, soil laboratories are now charged with a new list of metals considered to be potentially toxic elements.

A total elemental analysis of soil for these elements is not necessary for the assessment of risk of soil contamination with potentially toxic elements and its consequent availability for plant uptake. Instead, extraction of a fraction that would indicate the availability of the metal for plant uptake and consequent ecotoxicology should be practised. The DTPA extraction procedure used for Fe, Zn, Mn and Cu is also valid for the assessment of soil contamination with the potentially hazardous heavy elements. In recent publications the EPA methods have also been used to determine these elements, and are described below. Cationic metals are metallic elements that occur predominantly in the soil solution as cations. Examples are Cd^{2+}, Cr^{3+}, Ni^{2+} Pb^{2+}. Oxianions are elements that are combined with oxygen in molecules with overall negative charge such as Chromate ($CrO_4^{-2)}$, which is negatively charged and leachable in the soil solution causing risk to human health and environment (Pierzynski *et al.,* 2000).

The EPA Method (3050)

The United States Environmental Protection Agency (EPA) in 1986 adopted the following acid digestion procedure for total sorbed metals.

Apparatus

- AAS
- Hotplate
- Beakers
- Watch glass
- Filter papers

Reagents

1. Nitric acid (HNO_3) concentrated, and 1:1 dilution in deionised water.
2. 30% hydrogen peroxide (H_2O_2).

3. Hydrochloric acid (HCl) concentrated.

Procedure

1. Add 10 ml of 1:1 HNO_3 to 2 g of air-dried soil (<1 mm) in a 150 ml beaker.
2. Place the sample on a hot plate, cover with a watch glass, and heat (reflux) at 95°C for 15 minutes.
3. Cool the digest and add 5 ml of concentrated HNO_3. Reflux for an additional 30 minutes at 95°C.
4. Repeat the last step, and reduce the solution to about 5 ml without boiling (by only partially covering the beaker).
5. Cool the digest again and add 2 ml of deionised water and 3 ml of 30% H_2O_2.
6. With the beaker covered, heat the sample gently to start the peroxide reaction. If effervescence becomes excessively vigorous, remove the sample from the hot plate. Continue to add 30% H_2O_2 in 1 ml increments, followed by gentle heating until the effervescence subsides.
7. Add 5 ml of concentrated HCl and 10 ml of deionised water and reflux the sample for an additional 15 minutes without boiling.
8. Cool and filter through a Whatman No. 42 filter paper. Dilute to 50 ml with deionised water. Analyze for Cd, Cr, Ni, and Pb by atomic absorption spectrophotometer or inductively coupled plasma (ICP) spectroscopy.

The EPA Method (3052)

The United States Environmental Protection Agency adopted the EPA method No. 3052 for the acid digestion of siliceous and organically based matrices in a closed vessel device using temperature control microwave heating.

Apparatus

- AAS
- Microwave oven
- Flasks

Reagents

1. Nitric Acid (HNO_3), 65%
2. Hydroflouric Acid (HF), 40%

Procedure

1. Weigh 0.5 g of sample in a microwave vessel.

2. Add 9 ml HNO_3 and 3 ml HF acids, then gently swirl the solution to homogenize it.
3. Close the vessel and introduce it into the rotor segment
4. Run the microwave programme to completion as suggested by the microwave manual.
5. Cool the rotor by air or by water until the solution reaches room temperature.
6. Open the vessel and transfer the solution to a marked flask. Analyze for Cd, Cr, Ni, and Pb by atomic absorption spectrophotometer or inductively coupled plasma (ICP) spectroscopy.

Step	Time	Temperature	Microwave power
1	5 min	180 ^{o}C	Up to 1000 watt
2	10 min	180^{o}C	Up to 1000 watt

The EPA Method (3060A) - Alkaline Digestion for Hexavalent Chromium

For the extraction of Cr (VI) the sample is digested using 0.28 M Na_2CO_3 and 0.5 M NaOH solutions and heating at 90 - 95^{o}C for 60 minutes to dissolve the Cr(VI) and stabilize it against reduction to Cr(III). Cr (VI) can be measured in the extract by Atomic Absorption Spectrophotometer or ICPMS or other validated analytical techniques (EPA methods 7196 or 7199).

21. IDENTIFICATION OF CLAY MINERALS BY X-RAY DIFFRACTION (XRD)

The very fine size (<2 microns) of the clay particles give rise to very high specific surface area. Besides, during its formation, substitution of certain elements for some higher valence positively charged elements (isomorphous replacement) occur, and clay particles attain negatively charged surfaces. These phenomena influence the physico-chemical properties of the soil clay fraction. The nature and relative presence of clay minerals determine to a great extent soil properties and characteristics, fertility status, and management practices. For example, phosphorous, potassium and ammonium retention showed a direct relationship with the type of clay minerals present in soil (Sayegh and Abdul Majed, 1969; Sayegh and Rehman, 1969; Schwertmann, 1962; Bajwa, 1980 and Carson and Dixon, 1972). This is why the U.S. system of soil taxonomy includes the identification of clay minerals.

Clay minerals are crystalline in structure and built of several planes. Mineralogical analysis is based on the principle that x-rays will be diffracted by these planes. Type of clay minerals can then be identified by measuring this diffraction at different angles. Each mineral type is characterized, depending on pre-treatment, by a certain pattern of spacing between planes. The diffraction pattern serves as a *fingerprint* of each mineral.

The common unit for the measurement of the distance between planes, known as *lattice spacing* or *intermicellar spacing*, is the angstrom unit (1Å = 0.1 nm), which corresponds to the unit of x-ray wavelength. A spacing of 0.715 nm is characteristic for kaolinite, 1.0–1.2 nm for montmorillonite, and 1.4 nm for vermicullite. Pre-treatment of the clay sample, like saturation of the mineral with K, Mg or Mg plus glycolation, and heating at 500^0C, effects certain shifts in spacing that are characteristic of the type of mineral.

When a beam of x-rays hits a crystal, x-rays are scattered. A crystal plane is composed of a systematic and/or periodic arrangement of atoms in space. This kind of arrangement of atoms is called a *crystal lattice.* Each atom in the lattice serves as a scattering point. The coherently scattered waves may constructively interfere with each other, producing diffraction maxima.

Prior to running an XRD, and in order to enhance the diffraction peaks, organic matter is removed by treating the clay samples with H_2O_2. Removal of $CaCO_3$ is done by an acid treatment. Amorphous and free iron may be present as coatings. The removal of these compounds is usually performed by the dithionite-citrate-bicarbonate (DCB) method (Jackson, 1956).

For the identification of minerals, a number of XRD runs are made on differently pre-treated samples. Potassium saturation and glycolation of Mg-saturated samples are used to distinguish between expanding and non-expanding minerals. Saturation with K will normally effect a collapse of

intermicellar spacing, and the value for d-spacing of 2.0-1.7 nm exhibited by smectite collapse to 1.0 nm. Reconstitution of the d-spacing to 1.7 nm is achieved by the glycolation procedure. None of these treatments will have any effect on the d-spacing of non-expanding minerals, e.g., kaolinite. Table 3 presents the intermicellar spacing for some common clay minerals under different conditions of pre-treatment.

Table 3. Effect of pre-treatments on the d-spacing of selected clay minerals

d-spacing nm	**Clay minerals**
	K-saturated samples
1.4	Vermiculite, chlorite
1.0-1.2	Smectite, illite
0.72-0.75	Halloysite, metahalloysite
0.715	Kaolinite, chlorite
	Mg-saturated samples
1.4	Vermiculite, chlorite, smectite and illite
1.0-1.2	Illite, halloysite
0.72-0.75	Kaolinite, chlorite
	Mg-saturated + glycolation
1.7-1.8	Smectite
1.4	Vermiculite
1.0-1.2	Illite, halloysite
0.715	Kaolinite
	Heat at 500 °C
1.4	Chlorites
1.0	Vermiculites
0.70	Chlorites (kaolinite and sesquioxides become amorphous)

The diffractogram is composed of a series of diffraction peaks printed with the beam angles (2θ) on the abscissa, and radiation counts or peak intensities in

the y-axis. The position of the diffraction peaks corresponds directly to the d-spacing. Peaks serve as fingerprints for the identification of the mineral species. The following illustrations serve as examples (Tan, 1995).

Figure 9, exhibits a diffractogram characteristic of kaolinite clay mineral characterized by a first-order x-ray diffraction peak of 0.713 nm, which does not change with pre-treatment.

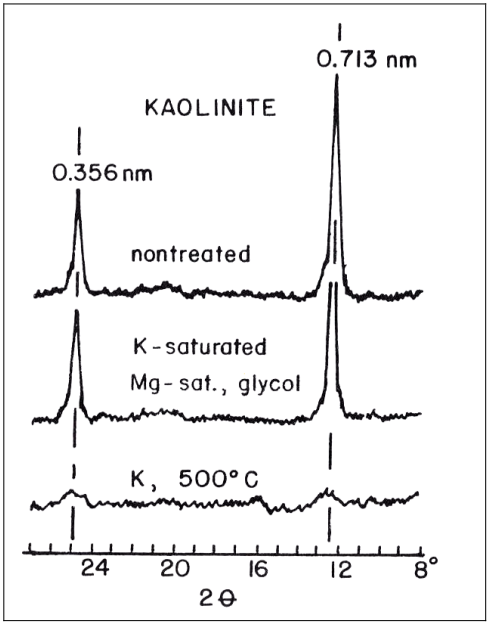

Figure 9. Identification of kaolinite using its characteristic XRD patterns
(Source: Tan, 1995)

Smectite or montmorillonite mineral type is characterized by a first-order x-ray diffraction peak of 1.23 nm that shifts to 1.73 nm after solvation or glycolation of the sample. Saturation with K produces a shift of the peak to 1.0 nm (Figure 10).

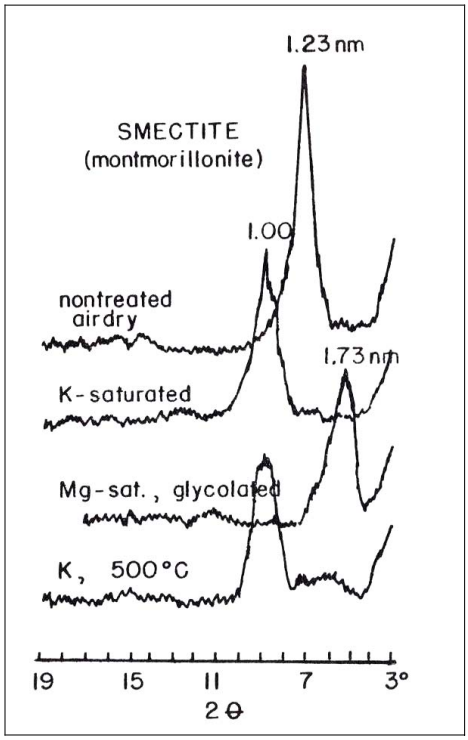

Figure 10. Identification of smectite using its characteristic XRD patterns
(Source: Tan, 1995)

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Appendix A. List of the atomic weights of the elements

Element	Symbol	Atomic Number	Atomic Weight	Element	Symbol	Atomic Number	Atomic Weight
Actinium	Ac	89	(227)	Mercury	Hg	80	200.59
Aluminium	Al	13	26.98	Molybdenum	Mo	42	95.94
Americium	Am	95	(243)	Neodymium	Nd	60	144.24
Antimony	Sb	51	121.75	Neon	Ne	10	20.183
Argon	Ar	18	39.948	Neptunium	Np	93	(237)
Arsenic	As	33	74.92	Nickel	Ni	28	58.71
Astatine	At	85	(210)	Niobium	Nb	41	92.91
Barium	Ba	56	137.34	Nitrogen	N	7	14.007
Berkelium	Bk	97	(249)	Nobelium	No	102	(253)
Beryllium	Be	4	9.012	Osmium	Os	76	190.2
Bismuth	Bi	83	208.98	Oxygen	O	8	15.9994
Boron	B	5	10.81	Palladium	Pd	46	106.4
Bromine	Br	35	79.909	Phosphorus	P	15	30.974
Cadmium	Cd	48	112.40	Platinum	Pt	78	195.09
Calcium	Ca	20	40.08	Plutonium	Pu	94	(242)
Californium	Cf	98	(251)	Polonium	Po	84	(210)
Carbon	C	6	12.011	Potassium	K	19	39.102
Cerium	Ce	58	140.12	Praseodymium	Pr	59	140.91
Cesium	Cs	55	132.91	Promethium	Pm	61	(147)
Chlorine	Cl	17	35.453	Protactinium	Pa	91	(231)
Chromium	Cr	24	52.00	Radium	Ra	88	(226)
Cobalt	Co	27	58.93	Radon	Rn	86	(222)
Copper	Cu	29	63.54	Rhenium	Re	75	186.23
Curium	Cm	96	(247)	Rhodium	Rh	45	102.91
Dysprosium	Dy	66	162.50	Rubidium	Rb	37	85.47
Einsteinium	Es	99	(254)	Ruthenium	Ru	44	101.1
Erbium	Er	68	167.26	Samarium	Sm	62	150.35
Europium	Eu	63	151.96	Scandium	Sc	21	44.96
Fermium	Fm	100	(253)	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.09
Francium	Fr	87	(223)	Silver	Ag	47	107.870
Gadolinium	Gd	64	157.25	Sodium	Na	11	22.9898
Gallium	Ga	31	69.72	Strontium	Sr	38	87.62
Germanium	Ge	32	72.59	Sulfur	S	16	32.064
Gold	Au	79	196.97	Tantalum	Ta	73	180.95
Hafnium	Hf	72	178.49	Technetium	Tc	43	(99)
Helium	He	2	4.003	Tellurium	Te	52	127.60
Holmium	Ho	67	164.93	Terbium	Tb	65	158.92
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.37
Indium	In	49	114.82	Thorium	Th	90	232.04
Iodine	I	53	126.90	Thulium	Tm	69	168.93
Iridium	Ir	77	192.2	Tin	Sn	50	118.69
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.80	Tungsten	W	74	183.85
Lanthanum	La	57	138.91	Uranium	U	92	238.03
Lawrencium	Lw	103	(257)	Vanadium	V	23	50.94
Lead	Pb	82	207.19	Xenon	Xe	54	131.30
Lithium	Li	3	6.939	Ytterbium	Yb	70	173.04
Lutetium	Lu	71	174.97	Yttrium	Y	39	88.91
Magnesium	Mg	12	24.312	Zinc	Zn	30	65.37
Manganese	Mn	25	54.94	Zirconium	Zr	40	91.22
Mendelevium	Md	101	(256)				

Numbers in parentheses indicate mass of most stable known isotopes.

Appendix B. pH indicators[1]

pH Indicators	pH transition intervals			
Name	**Colour**	**pH**	**pH**	**Colour**
Cresol red	pink	0.2	1.8	yellow
m-Cresol purple	red	1.2	2.8	yellow
Thymol blue	red	1.2	2.8	yellow
p-Xylenol blue	red	1.2	2.8	yellow
Triphenylcarbinol	red	1.2	3.2	Colourless
2,4-Dinitrophenol	Colourless	2.8	4.7	Yellow
4-Dimethylaminoazobenzene	Red	2.9	4.0	Yellow-orange
Bromochlorophenol blue	Yellow	3.0	4.6	Purple
Bromophenol blue	Yellow	3.0	4.6	Purple
Methyl orange	Red	3.1	4.4	Yellow-orange
Bromocresol green	Yellow	3.8	5.4	Blue
2,5-Dinitrophenol	Colourless	4.0	5.8	Yellow
Alizarinsulfonic acid sodium salt	Yellow	4.3	6.3	Violet
Methyl red	Red	4.4	6.2	Yellow-orange
Methyl red sodium salt	Red	4.4	6.2	Yellow-orange
Chlorophenol red	Yellow	4.8	6.4	Purple
Hematoxylin	Yellow	5.0	7.2	Violet
Litmus extra pure	Red	5.0	8.0	Blue
Bromophenol red	Orange-yellow	5.2	6.8	Purple
Bromocresol purple	Yellow	5.2	6.8	Purple
4-Nitrophenol	Colourless	5.4	7.5	Yellow
Bromoxylenol blue	Yellow	5.7	7.4	Blue
Alizarin	Yellow	5.8	7.2	Red
Bromothymol blue	Yellow	6.0	7.6	Blue
Phenol red	Yellow	6.4	8.2	Red
3-Nitrophenol	Colourless	6.6	8.6	Yellow-orange
Neutral red	Bluish-red	6.8	8.0	Orange-yellow
4,5,6,7-Tetrabromophenolphthalein	Colourless	7.0	8.0	Purple
Cresol red	Orange	7.0	8.8	Purple
1-Naphtholphthalein	Brownish	7.1	8.3	Blue-green
m-Cresol purple	Yellow	7.4	9.0	Purple
Thymol blue	Yellow	8.0	9.6	Blue
P-Xylenol blue	Yellow	8.0	9.6	Blue
Phenolphthalein	Colourless	8.2	9.8	Red-violet
Thymolphthalein	Colourless	9.3	10.5	Blue
Alizarin yellow GG	Light yellow	10.2	12.1	Brownish-yellow
Epsilon blue	Orange	11.6	13.0	Violet

[1] Adapted from pH Indicators, E. Merck and Co.

Appendix C. Properties of laboratory materials

Material	Max. Working Temperature, °C	Sensitivity to Thermal Shock	Chemical Inertness	Notes
Borosilicate glass	200	150°C change OK	Attacked to certain degree by alkali solutions while heating	Trademarks: pyrex (Corning Glass Works) Kimax (Owens-Illinois)
Soft glass		Low	Attacked by alkali solutions	
Alkali-resistant glass		More sensitive than borosilicate		Boron-free. Trademark: Corning
Fused quartz	1050	Very High	Resistant to most acids, halogens	Quartz crucibles used for fusions
High-silica glass	1000	Very High	More resistant to alkalis than borosilicate	Similar to fused quartz Trademark: Vycor (Corning)
Porcelain	1100 (glazed) 1400 (unglazed)	High	High	
Platinum	1500		Resistant to most acids, molten salts. Attacked by *aqua regia*, fused nitrates, cyanides, chlorides at >1000°C. Alloys with gold, silver, and other metals	Usually alloyed with iridium or rhodium to increase hardness. Platinum crucibles for fusions and treatment with HF
Nickel and iron			Fused samples contaminated with the metal	Ni and Fe crucibles used for peroxide fusions
Stainless steel	400-500	High	Not attacked by alkalis and acids except conc. HCI, dil. H_2SO_4, and boiling conc. HNO_3	
Polyethylene	115		Not attacked by alkali solutions or HF. Attacked by many organic solvents (acetone, ethanol OK)	Flexible plastic
Polystyrene	70		Not attacked by HF. Attacked by many organic solvents	Somewhat brittle
Teflon	250		Inert to most chemicals	Useful for storage of solutions and reagents for trace metal analysis

Appendix D. Grades of chemicals

Grade	Purity	Notes
Technical or commercial	Indeterminate quality	May be used in preparation of cleaning solution only
C.P. (Chemically pure)	More refined, but still unknown quality	
U.S.P.	Meets minimum purity standards	Conforms to tolerance set by the United States Pharmacopoeia for contaminants dangerous to health
A.C.S. reagent Reagent grade	High purity	Conforms to minimum specifications set by the Reagent Chemicals Committee of the American Chemical Society
Primary standard Analytical grade	Highest purity	Required for accurate volumetric analysis (for standard solutions)

Concentrations of Commercial Reagent-Grade Acids and bases[a]

Reagent	F. Wt.[b]	M[c]	% by Wt.	Density (20°), g/cm^3
H_2SO_4	98.08	17.6	94.0	1.831
$HClO_4$	100.5	11.6	70.0	1.668
HCl	36.46	12.4	38.0	1.188
HNO_3	63.01	15.4	69.0	1.409
H_3PO_4	98.00	14.7	85.0	1.689
$HC_2H_3O_2$	60.05	17.4	99.5	1.051
NH_3	17.03	14.8	28.0	0.898

[a]These are approximate concentrations and cannot be used for preparing standard solutions.
[b]Formula weight.
[c]Molarity.

NBS Tolerances for Volumetric Glassware, Class A[a]

Capacity, ml (Less than and Including)	Tolerances, ml		
	Volumetric Flasks	Transfer Pipettes	Burettes
1000	±0.30		
500	±0.15		
100	±0.08	±0.08	±0.10
50	±0.05	±0.05	±0.05
25	±0.03	±0.03	±0.03
10	±0.02	±0.02	±0.02
5	±0.02	±0.01	±0.01
2		±0.006	

[a] Corning Pyrex glassware and Kimball KIMAX, Class A, conform to these tolerances.

Appendix E. Nutrient range in soils, mg/kg (Bashour, 2001)

Nutrient	Very Low	Low	Medium	High	Very High
Nitrate, NO_3-N	0 – 5	5 – 15	15 – 30	30 – 40	>40
Phosphorus *Olson method*	0 – 3	3 – 8	8 – 14	4 – 20	>20
Potassium *NH4OAC- extractable*	0 – 85	85 – 150	150 – 250	250 – 450	>450
Magnesium *Exchangeable*	0 – 85	85 – 180	180 – 300	300 – 500	>500
Calcium *Exchangeable*	0 – 500	500 – 1200	1200 – 2500	2500 – 3500	>3500
Sulphur *Water soluble*	0 – 10	10 – 20	20 – 35	35 – 45	>45
Sodium *Water Soluble*	0 – 300				>300

Appendix F. Temperature factors (f_t) for correcting resistance and conductivity data on soil extracts to the standard temperature of 25°C

$$EC_{25} = EC_t \times f_t;\ EC_{25} = (k/R_t) \times f_t;\ R_{25} = R_t/f_t$$

°C	°F.	f_t	°C	°F.	f_t	°C	°F.	f_t
3.0	37.4	1.709	22.0	71.6	1.064	29.0	84.2	0.925
4.0	39.2	1.660	22.2	72.0	1.060	29.2	84.6	0.921
5.0	41.0	1.613	22.4	72.3	1.055	29.4	84.9	0.918
6.0	42.8	1.569	22.6	72.7	1.051	29.6	85.3	0.914
7.0	44.6	1.528	22.8	73.0	1.047	29.8	85.6	0.911
8.0	46.4	1.488	23.0	73.4	1.043	30.0	86.0	0.907
9.0	48.2	1.488	23.2	73.8	1.038	30.2	86.4	0.904
10.0	50.0	1.411	23.4	74.1	1.034	30.4	86.7	0.901
11.0	51.8	1.375	23.6	74.5	1.029	30.6	87.1	0.897
12.0	53.6	1.341	23.8	74.8	1.025	30.8	87.4	0.894
13.0	55.4	1.309	24.0	75.2	1.020	31.0	87.8	0.890
14.0	57.2	1.277	24.2	75.6	1.016	31.2	88.2	0.887
15.0	59.0	1.247	24.4	75.9	1.012	31.4	88.5	0.884
16.0	60.8	1.218	24.6	76.3	1.008	31.6	88.9	0.880
17.0	62.6	1.189	24.8	76.6	1.004	31.8	89.2	0.877
18.0	64.4	1.163	25.0	77.0	1.000	32.0	89.6	0.873
18.2	64.8	1.157	25.2	77.4	0.996	32.2	90.0	0.870
18.4	65.1	1.152	25.4	77.7	0.992	32.4	90.3	0.867
18.6	65.5	1.147	25.6	78.1	0.988	32.6	90.7	0.864
18.8	65.8	1.142	25.8	78.5	0.983	32.8	91.0	0.861
19.0	66.2	1.136	26.0	78.8	0.979	33.0	91.4	0.858
19.2	66.6	1.131	26.2	79.2	0.975	34.0	93.2	0.843
19.4	66.9	1.127	26.4	79.5	0.971	35.0	95.0	0.829
19.6	67.3	1.122	26.6	79.9	0.967	36.0	96.8	0.815
19.8	67.6	1.117	26.8	80.2	0.964	37.0	98.6	0.801
20.0	68.0	1.112	27.0	80.6	0.960	38.0	100.2	0.788
20.2	68.4	1.107	27.2	81.0	0.956	39.0	102.2	0.775
20.4	68.7	1.102	27.4	81.3	0.953	40.0	104.0	0.763
20.6	69.1	1.097	27.6	81.7	0.950	41.0	105.8	0.750
20.8	69.4	1.092	27.8	82.0	0.947	42.0	107.6	0.739
21.0	69.8	1.087	28.0	82.4	0.943	43.0	109.4	0.727
21.2	70.2	1.082	28.2	82.8	0.940	44.0	111.2	0.716
21.4	70.5	1.078	28.4	83.1	0.936	45.0	113.0	0.705
21.6	70.9	1.073	28.6	83.5	0.932	46.0	114.8	0.694
21.8	71.2	1.068	28.8	83.8	0.929	47.0	116.6	0.683

Source: Agricultural Handbook 60, U.S. Dept of Agriculture

Appendix G. Conversion factors for SI and non-SI units (Soil Science Society of America Journal)

To convert Column 1 into Column 2, multiply by	Column 1 SI Unit	Column 2 Non-SI Unit	To convert Column 2 into Column 1 multiply by
	Length		
0.621	kilometer, km (10^3 m)	mile, mi	1.609
1.094	meter, m	yard, yd	0.914
3.28	meter, m	foot, ft	0.304
1.0	micrometer, μm (10^{-6} m)	micron, μ	1.0
3.94×10^{-2}	millimeter, mm (10^{-3} m)	inch, in	25.4
10	nanometer, nm (19^{-9} m)	angstrom, å	0.1
	Area		
2.47	hectare, ha	acre	0.405
247	square kilometer, km^2 (10^3 m)^2	acre	4.05×10^{-3}
0.386	square kilometer, km^2 (10^3 m)^2	square mile, mi^2	2.590
2.47×10^{-4}	square meter, m^2	acre	4.05×10^3
10.76	square meter, m^2	square foot, ft^2	9.29×10^{-2}
1.55×10^{-3}	square millimeter, mm^2 (10^{-3} m)^2	square inch, in^2	645
	Volume		
9.73×10^{-3}	cubic meter, m^3	acre-inch	102.8
35.3	cubic meter, m^3	cubic foot, ft^3	2.83×10^{-2}
6.10×10^4	cubic meter, m^3	cubic inch, in^3	1.64×10^{-5}
2.84×10^{-2}	liter, L (10^{-3} m^3)	bushel, bu	35.24
1.057	liter, L (10^{-3} m^3)	quart (liquid), qt	0.946
3.53×10^{-2}	liter, L (10^{-3} m^3)	cubic foot, ft^3	28.3
0.265	liter, L (10^{-3} m^3)	gallon	3.78
33.78	liter, L (10^{-3} m^3)	pint (fluid), pt	0.473
	Mass		
2.20×10^{-3}	gram, g (10^{-3} kg)	pound, lb	454
3.52×10^{-2}	gram, g (10^{-3} kg)	ounce (avdp), oz	28.4
2.205	kilogram, kg	pound, lb	0.454
0.01	kilogram, kg	quintal (metric), q	100
1.10×10^{-3}	kilogram, kg	ton (2000 lb), ton	907
1.102	megagram, Mg (tonne)	ton (U.S.), ton	0.907
1.102	tonne, t	ton (U.S.), ton	0.907
	Yield and Rate		
0.893	kilogram per hectare, kg ha^{-1}	pound per acre, lb $acre^{-1}$	1.12
7.77×10^{-2}	kilogram per cubic meter, kg m^{-3}	pound per bushel, lb bu^{-1}	12.87
1.49×10^{-2}	kilogram per hectare, kg ha^{-1}	bushel per acre, 60 lb	67.19
1.59×10^{-2}	kilogram per hectare, kg ha^{-2}	bushel per acre, 56 lb	62.71
1.86×10^{-2}	kilogram per hectare, kg ha^{-1}	bushel per acre, 48 lb	53.75
0.107	liter per hectare, L ha^{-1}	gallon per acre	9.35
893	tonnes per hectare, t ha^{-1}	pound per acre, lb $acre^{-1}$	1.12×10^{-3}
893	megagram per hectare, Mg ha^{-1}	pound per acre, lb $acre^{-1}$	1.12×10^{-3}
0.446	megagram per hectare, Mg ha^{-1}	ton (2000 lb) per acre, ton $acre^{-1}$	2.24
2.24	meter per second, m s^{-1}	mile per hour	0.447

APPENDIX G. (*continued*)

To convert Column 1 into Column 2, multiply by	Column 1 SI Unit	Column 2 Non-SI Unit	To convert Column 2 into Column 1 multiply by
	Specific Surface		
10	square meter per kilogram, $m^2\ kg^{-1}$	square centimeter per gram, $cm^2\ g^{-1}$	0.1
1000	square meter per kilogram, $m^2\ kg^{-1}$	square millimeter per gram, $mm^2 g^{-1}$	0.001
	Pressure		
9.90	megapascal, MPa (10^6 Pa)	atmosphere	0.101
10	megapascal, MPa (10^6 Pa)	bar	0.1
1.00	megagram per cubic meter, Mg m^{-3}	gram per cubic centimeter, g cm^{-3}	1.00
2.09×10^{-2}	pascal, Pa	pound per square foot, lb ft^{-2}	47.9
1.45×10^{-4}	pascal, Pa	pound per square inch, lb in^{-2}	6.90×10^3
	Temperature		
1.00 (K - 273)	Kelvin, K	Celsius, °C	1.00 (°C + 273)
(9/5 °C) + 32	Celsius, °C	Fahrenheit, °F	5/9 (°F - 32)
	Plane Angle		
57.3	radian, rad	degrees (angle), °	1.75×10^{-2}
	Electrical Conductivity, Electricity, and Magnetism		
10	siemen per meter, S m^{-1}	millimho per centimeter, mmho cm^{-1}	0.1
10^4	tesla, T	gauss, G	10^{-4}
	Water Measurement		
9.73×10^{-3}	cubic meter, m^3	acre-inches, acre-in	102.8
9.81×10^{-3}	cubic meter per hour, $m^3\ h^{-1}$	cubic feet per second, $ft^3\ s^{-1}$	101.9
4.40	cubic meter per hour, $m^3\ h^{-1}$	U.S. gallons per minutes, gal min^{-1}	0.227
8.11	hectare-meters, ha-m	acre-feet, acre-ft	0.123
97.28	hectare-meters, ha-m	acre-inches, acre-in	1.03×10^{-2}
8.1×10^{-2}	hectare-centimeters, ha-cm	acre-feet, acre-ft	12.33
	Concentrations		
1	centimole per kilogram, cmol kg^{-1} (ion exchange capacity)	milliequivalents per 100 grams, meq 100 g^{-1}	1
0.1	gram per kilogram, g kg^{-1}	percent, %	10
1	milligram per kilogram, mg kg^{-1}	parts per million, ppm	1
	Radioactivity		
2.7×10^{-11}	becquerel, Bq	curie, Ci	3.7×10^{10}
2.7×10^{-2}	becquerel per kilogram, Bq kg^{-1}	picocurie per gram, pCi g^{-1}	37
100	gray, Gy (absorbed dose)	rad, rd	0.01
100	sievert, Sv (equivalent dose)	rem (roentgen equivalent man)	0.01
	Plant Nutrient Conversion		
	Element	***Oxide***	
2.29	P	P_2O_5	0.437
1.20	K	K_2O	0.830
1.39	Ca	CaO	0.715
1.66	Mg	MgO	0.602

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