

INTRODUCTION

All scientists depend on one form of analysis or the other. This is due to the need to answer questions on the content of the materials with which they work. The methods by which these analyses are carried out are referred to as analytical techniques. The types of analytical techniques may vary from field to field. This variation stems primarily from differences in the nature of materials with which people in each field works.

Soil science is branch of applied sciences that makes use of the principles of physics, chemistry, biology and mathematics in the study of soil. This is because the soil consists of matter (living and non-living) interacting together physically, chemically and biologically to provide ecosystem services at all levels of consideration. For a soil scientist to be able therefore to answer questions on the constituents of soil, he needs to carry out one form of analysis or the other. Methods of analysis in soil science consist of chemical, biological and physical techniques.

A. CHEMICAL TECHNIQUES

The soil is a mixture of elements in various states of occurrence, combination and interaction. Isolation and measurement of components of interest in soil is a major problem. Therefore, chemical analysis is aimed at determination of the component of interest in a soil sample. Chemical analysis has to be carried out in defined steps requiring possession of certain skills.

STEPS IN DETERMINATION OF CONCENTRATION

The final measurement is just only a step in the sequence of operations that are necessary for determination of component of interest (analyte) in a sample. It is therefore relevant to identify the several steps that male up the analytical process, the importance of the steps and the skill needed.

Choice of method

It is a vital step that requires both experience and intuition on the part of the analyst. Choice of method is influenced by factors such as

- the form of component of interest
- desired level of accuracy and economy
- consideration for number of samples
- complexity of the sample to be analysed
- number of components in the sample

Collection and preparation of sample

To obtain meaningful result, analysis has to be performed on soil sample which must be representative of the bulk material (the soil of a plot, field, or an area). Obtaining representative and appropriate form of samples requires knowledge of sampling methods and statistics.

Thorough mixing is needed for bulky and heterogeneous material.

Preparation of sample is to have the sample in the correct form for the analysis. The process may involve drying, homogenization, procuring the amount of the sample by weight, volume or area, having the sample in the correct form for the analysis. Results of quantitative analysis are usually reported in relative terms (quantity of analyte per unit weight or volume of the sample) In order to express the result in meaningful manner, one should know the accurate weight or volume of the sample to be analysed.

Often, an analyte in its matrix is not in the form suitable for the chosen assay method. Bringing the analyte into the best chemical form may involve changes in the analyte or transfer from one matrix to another.

Terms for some of the methods used to optimize chemical forms in soil analysis include the following:

- *Dissolution*: Breaking down of component parts in a liquid. The transformation is driven by the binding of solutes by the solvent.
- *Digestion*: Breaking down into component parts which dissolve in a liquid. It is driven by externally applied energy.
- *Desorption*: Detachment from surface.
- *Vaporization*: Transformation into gaseous form usually by strong heating.
- *Atomization*: breaking a collection of atoms into individual atoms.\
- *Adsorption*: Binding to a surface.
- *Oxidation*: Causing the oxidation state of an element or compound to become more positive.
- *Reduction*: Causing the oxidation state of an element or compound to become more negative.
- *Extraction*: Transferring analyte from one matrix into another. The first matrix is a solid or liquid, the second a fluid.

Knowledge of descriptive chemistry and competitive equilibria are important in preparation of sample in appropriate form for analysis. Sample preparation not only helps in optimizing

chemical forms of analyte but also in eliminating expected interferences (substances that prevent the direct or accurate measurement of the analyte).

Running the assay

All preliminary steps are taken in order to make the final measurement a true estimate of the analyte. The assay may involve measurement of weight or volume which can be directly or indirectly related to the amount of the analyte in the sample. It may be by measurement of some properties of the system containing the analyte, which can then be related to the concentration of the analyte in the sample. To properly relate the property measured with the concentration of analyte requires calibration of standard samples. Running an assay demands that the analyst be skillful in both molecular and elemental methods of analysis.

Calculations and interpretation

The raw data or graphical output obtained as measurement during the assay needed to be rendered in numerical answers. This may involve data reduction, statistical analysis, data transformation, and calculation.

CLASSIFICATION OF ANALYTICAL TECHNIQUES IN SOIL SCIENCE

Analytical techniques are generally divided into two groups:

- Qualitative – identifies the species composition in a sample. It answers the question of the presence or absence of the component of interest without really answering the question of how much is present.
- Quantitative – determines how much of the component of interest in the sample. It does not only indicate the presence or absence of the component of interest but actually specifies the quantity of the component of interest that is present in the sample.

Both qualitative and quantitative analyses

— Require measurement of some chemical or physical properties of the system which can be related to the desired information.

— Require preliminary treatments and procedures to ensure measurement of analyte (component of interest)

However, quantitative analysis further requires that

- the analyst works with the aim of keeping loss of components to the barest minimum
- the reaction on which the analysis is based proceeds to completion with formation of a single product
- there is reproducible relationship between the property or quantity being measured and the analyte
- systematic and orderly work habits be development of, and intellectually honest observations

QUANTITATIVE ANALYSIS

In every quantitative analysis, there is a final measurement which can be related in magnitude to the quantity of the analyte. Quantitative analysis can be generally classified on the basis of this final measurement. Majority of early analytical techniques involved weight and volume as their final measurement. These techniques are generally referred to as *classical methods* of analysis. Other methods that were later developed based on the measurement of some properties of the analyte (or the matrix containing the analyte). These methods which relate the properties of the analyte such as optical, thermal and electrical are termed instrumental methods.

Both classical and instrumental methods involve correlation of a physical measurement with the concentration of the analyte. Both methods also involve the use of instruments, and preliminary steps in the process of analysis

Classical Analytical techniques

a. **Gravimetric techniques** involve weight as the final measurement

Direct method – involves weighing of compound that contains the analyte. For example, in determination of carbon by Dumas method, CO_2 is weighed.

Indirect method – involves loss of weight due to combustion or volatilization. Example is determination of CO_2 in CaCO_3 by addition of HCl.

b. **Volumetric techniques** – (also titrimetric techniques) involve measurement of volume of solution that is equivalent to the analyte. Titrimetric techniques include acid-base titration, redox titration, complexometric titration and precipitation titration

Instrumental techniques

a. Spectrophotometric techniques – involve measurements based on interaction of electromagnetic waves with analyte.

b. Electroanalytical techniques – involve measurement of electrical properties of the chemical system containing the analyte in relation to the analyte. Electrical properties measured include potential differences, amount of charges, current, resistance and conductivity.

Electroanalytical techniques include

Potentiometric technique relates the concentration of analyte to its potential difference as compared to that of reference system.

Conductimetric technique – involves measurement of changes in resistance of electrolyte (solution containing the analyte) with changes in concentration of the analyte. Conductance = $1/R$ where R is the resistance

Coulometric technique – relates the number of moles of analyte oxidized or reduced to total electrical charge. When electrical current is the property measured the technique is referred to as *amperometry*

Voltametric technique – combines the measurement of potential, current and time i.e. the change in current (over time) while the voltage applied to the system is changed in a precisely controlled manner.

c. Separation techniques –

Solvent extraction

Chromatographic techniques – Chromatographic techniques generally include the paper, thin layer chromatography (TLC), gas liquid chromatography (GLC), column chromatography, ion exchange chromatography, and electrophoresis.

TITRIMETRIC AND GRAVIMETRIC TECHNIQUES IN SOIL ANALYSIS

Titrimetric techniques

There are four types of titrimetric techniques: Acid-base, potentiometric, precipitation and complexiometric titrations.

Acid-base titration

These are titrations that are based on the neutralization reaction. Acid-base titrations can be used to determine most strong monoprotic acids. Acid-base titration can be used to determine concentration of hydrochloric acid, sulfuric acid, acetic acid, as well as bases - like sodium hydroxide, ammonia and so on. In some particular cases, when solution contains mixture of acids or bases of different strengths, it is even possible to determine in one titration composition of a mixture - for example determination of exchangeable acidity (H^+ and Al^{3+}) in soil.

Most commonly used reagents are hydrochloric acid and sodium hydroxide. Solutions of hydrochloric acid are stable; solutions of sodium hydroxide can dissolve glass and absorb carbon dioxide from the air, so they should be not stored for long periods of time.

Type of indicator depends on several factors including the equivalence point pH.

Potentiometric titration

Potentiometric titrations are based on redox reactions.

There are many redox reagents used in redox titrations. For example, potassium permanganate is used for determination of Fe^{2+} , H_2O_2 and oxalic acid, potassium dichromate for determination of Fe^{2+} and Cu in CuCl. Determination of organic matter in soil is achieved by redox titration of Ferrous sulphate with excess potassium dichromate after oxidation of soil organic matter with dichromate –acid mixture.

Commonly used indicators are substances that can exist in two forms - oxidized and reduced - that differ in color. Potential at which the substance changes color must be such that the change occurs close to the equivalence point. Examples of such substances are ferroin, diphenylamine or Nile blue.

Complexiometric titration

Complexiometric titration can be used to determine metal concentration in soil extract with the use of Ethylenediaminetetraacetic acid (EDTA) as the reagent. The reagent acts as a chelating agent as it forms a complex with the metal. There are also other similar chelating agents used in complexiometric analysis, but the common one in soil analysis is EDTA.

In the determination of metals, detection of the endpoint is mainly based on substances that change color when creating complexes with determined metals. One of these indicators is Eriochrome Black (a substance that in pH between 7 and 11 is blue when free, and black when forms a complex with metals). This method can be employed in the determination of Ca and Mg.

Precipitation Titration

This is typified by titration of chloride with silver. It is rarely applied directly to soil, but can be applied to soil extract because of interferences.

SPECTROPHOTOMETRIC TECHNIQUES

These are techniques based on the theory and principles of spectroscopy. Spectroscopy studies the interaction of electromagnetic radiation with matter in its entire ramification.

Electromagnetic radiation has both the wave and particle properties.

Wave properties

Electromagnetic radiation as waves have wavelength varying from 10^3 m to 10^{-14} m and frequencies varying from 10^3 KHz to 10^{21} KHz. Various bands from the infra red to x-ray are employed in soil analytical techniques.

Particle property

According to Albert Eistein, the energy given by electromagnetic radiation is quantized (in form of particles) referred to as photon. The energy generated by the photon is

$$E = hc$$

Where h = planck's constant, and c = velocity of light

The form of interaction between electromagnetic waves and matter (analyte) include absorption, emission, diffraction, reflection, scattering and fluorescence.

Absorption Spectrophotometric techniques

Absorption spectrophotometry involves relating characteristic electromagnetic waves absorbed by analyte to its concentration. The forms include :

- (1) Ultra violet/visible spectrometry
- (2) Atomic absorption spectrophotometry:

Ultra violet/visible spectrometry (Colorimetric technique)

This is based on two laws – The Beer's Law, and Lambert's Law.

Beer's Law states that when a monochromatic radiation passes through an absorbing medium, the intensity decreases exponentially with increase in the concentration of the absorbing medium.

Lambert's Law state that when a monochromatic radiation passes through an absorbing medium, the intensity decreases exponentially with the path-length of the absorbing medium.

When other variables are held constant, the concentration of the analyte (absorbing medium) is related to light absorbance or transmittance.

Atomic absorption spectrophotometry (AAS)

AAS makes use of the principle that atoms at a ground-state energy level can absorb electromagnetic radiation when radiation of appropriate wavelengths is focused upon them.

Measurements made when the analyte or calibration (standard samples) are placed in the path of the radiation are compared with blank. The ratio of the sample's measurement to the blank can be expressed in transmittance ($T = P/P_0$), Percent transmittance ($\%T = T \times 100$), or absorbance (negative log of T)

Differences in ability and scope of AAS is due to the excitation sources which include: air-acetylene flame, acetylene-nitrous oxide, and hydrogen flames (for determination of K, Ca, Mg, Fe, Na, Mn, Cu, and Zn); graphite flame (a flameless excitation source for Cr, N, Cd, Al, Mo, Pb and Co); flame devices such as cathode sputtering, tantalum ribbon, and cold vapour.

Atomic emission spectrophotometry

Atomic emission spectrophotometry is based on the principle that excited atoms emit electromagnetic energy of specific wavelengths upon returning to ground state which is proportional to the concentration of the excited atoms.

The radiation is measured by a detection system. The intensity of the radiation is directly proportional to the elemental concentration of the analyte.

Excitation sources for emission spectrometry include: flame sources (flame photometer for determination of K, Na, Ca and Mg); arc (e.g. Graphite electrode); spark; and plasma (hot gas in which a high percentage of atoms have been ionized). Different kinds of plasma sources used in multi-element analysis include Direct Current Plasma (DCP), Capacitatively Coupled Microwave Plasma (CMP), Radio frequency Inductively Coupled Plasma (ICAP), and Microwave Induced Plasma (MIP).