Techniques for Analysis of Minerals

- Minerals and trace elements are naturally occurring inorganic substance that account for about 4% of total human body mass.
- Its serve as materials and regulators in numerous biological activities in body structure building and needed for good health. Approximately 30 elements have been recognized as essential.
- Minerals are grouped into two main categories: major minerals and trace minerals.
- Major minerals (calcium, potassium, magnesium, phosphorus, sodium, sulphur) are required in higher quantities in daily diet, while trace minerals (chromium, iron, copper, iodine manganese, molybdenum, selenium, zinc) are only needed in smaller amounts.
- Mineral analysis in food samples generally requires sample preparation and can be carried out manually or by using automated or mechanised processes.

- Food samples need to be converted into liquid solution or digested form to enable the samples to be used for analysis with the desired techniques.
- These includes dissolution or homogenisation step (blending, mixing, grinding or slurry preparation) of the sample, then followed by a collection of a representative test portion.
- There are two ways the samples will be digested which remove a large number of potential interferences through acid or alkaline-assisted hot digestion with or without high pressure.
- The final sample digest is commonly diluted in an acidic or alkaline aqueous solution and, as a result, easily amenable to any analytical technique.
- Nowadays, the latest techniques for digestion usually use open vessel which atmospheric pressure digestion is a common approach to sample preparation.
- Another popular approach of digestion is by using microwave assisted-digestion (MW-AD) and microwave induced-combustion (MIC).
- Once the organic matrix has been removed, the inorganic constituents can be measured using a variety of instrumental techniques.

- The exact digestion protocol for complete decomposition varies between food materials, depending on their composition (e.g. liquid or solid).
- **Many minerals possess unique electromagnetic spectra, specific physiochemical characteristics, and will undergo a reaction under specific chemical conditions, and these traits enable minerals to be distinguished from each other, and from other substances in a sample.**
- **However, there are many different methods, from common wet chemistry techniques used in a lab to various types of analytical equipment.**

Wet Chemical Methods

- There are two common ways to detect the presence of minerals using titration methods, and these are by the minerals forming complexes with ethylenediaminetetraacetic acid (EDTA) and through redox reactions.
- Titrations that use EDTA are widely used for calcium-containing and sodium-containing minerals, but it can be used for many metallic minerals.
- EDTA is widely used because once all the metal ions from the mineral have complexed with the EDTA, the EDTA reacts with the indicator to signal the end of the reaction.
- Another wet chemical method used is gravimetric analysis.
- Chemical reagents are added so that the mineral forms a known insoluble complex.
- This precipitate is then removed, dried, rinsed and weighed to determine the amount of mineral present using the chemical formula of the precipitate.
- However, this is a technique that can only be used with large amounts of sample and is not suitable for trace analysis measurements.

Spectroscopy and Spectrometry

- After digestion, the levels of minerals are mostly performed by using by atomic spectrometry and mass spectrometry methods, including:
    - inductively coupled plasma-mass spectrometry (ICP-MS),
    - inductively coupled plasma optical emission spectroscopy (ICP-OES)
    - graphite furnace atomic absorption spectroscopy (GF-AAS)
    - flame atomic absorption spectroscopy (F-AAS)
- Nutrients essential for optimal growth of plants, like K, Mg, Ca, S, Fe and Zn are usually present at relatively high concentrations, while toxic elements as Pb, Cd, Hg and As should be absent, or only present at ultra-trace levels.
- For detection of both plant macro- and micronutrients, as well as possible toxic elements, either ICP-MS or GF-AAS are mostly used as they allow ultra-sensitive detection of elements at parts-per-billion (ppb) levels.
- ICP-OES and FAAS only work for the major/minor plant nutrients as they detect at parts-per-million (ppm) levels, thus at 1000-fold higher.
- ICP-MS is nowadays the most popular technique, as it is both ultra-sensitive and suitable for the simultaneous analysis of series of different elements in a single extract.
- For total N determination, including protein and non-protein N, the classical but rather insensitive Kjeldahl method is still frequently used.
- In this method the plant material is digested in sulphuric acid and the liberated N converted into and distilled as ammonia, which is finally quantified by titration.

Atomic Absorption Spectrometer (AAS)

- AAS is an analytical technique to quantitate the concentration from part per-million (mg/L) level to part-per-billion (µg/L) level of multi-elements in all types of samples including food samples using the absorption of light by free atoms in the gaseous state.
- The analyte concentration is determined from the amount of absorption of specific light at a suitable wavelength.
- AAS instrumentation includes either flame or graphite furnace atomizers.
- Flame atomizers commonly use air–acetylene for atomization of many analytes at a temperature of 2300 $^{\circ}$C, whereas nitrous oxide acetylene is used for selected analytes that require hotter flames of 2900 $^{\circ}$C.
- In contrast, graphite furnace atomizers use a flameless technique where the graphite tubes are heated electrically.
- The graphite furnace technique is mostly automated compared to flame AAS methods and generally about 100–1000 times more sensitive than flame AAS under any given radiation sources.
- The new light path also helps to reduce the size of the instrument. It also uses a stacked design where both flame and graphite furnace can be used on the same instrument.
- This involves a titanium burner that can be easily removed for different analyses. It features a double beam design for quick start-up and long-term stability without the need for recalibration.
- There was new application in analysing food samples using AAS such as determination of meat and baby food samples, infant formula, vegetables, fruit juices, fish fillet and vegetable oils .

Microwave and Inductively Coupled Plasma-Optical Emission Spectrometry/Atomic Emission Spectrometry (ICP-OES/AES)

- OES/AES is based on the principle that when energy is applied to a samples/molecule in the form of light or heat, it will be dissociated into an atom but also cause collisional excitation (and ionization) from a lower energy state to a higher energy state.
- However, at a higher energy state, the molecules are unstable and decay to the lower energy state and thus emitting radiations in the form of photons.
- The specific wavelengths of emitted photons are recorded in the emission spectrometer and used to determine the concentrations of the elements of interest.

ICP

- ICP is the most common excitation process which requires a plasma torch of concentric quartz tubes to induce excitation of samples.
- The process requires argon gas and radiofrequency generator which produces the plasma and the sample particles entering the plasma then undergo desolvation, dissociation, atomization and excitation.
- In the microwave-induce plasma method, a microwave generator will produce a microwave that travels through a cable and is focused via a tuning system where a torch sits in the centre of the cavity.
- Nitrogen gas is used to spark the plasma.
- Cheese was analysed using this method.
- ICP-OES/AES was mostly used to determine the geographical origin of honey, wines, cumin, vinegar, coffee beans, baby foods, vegetables, milk powder for minerals such as Mn, Zn, P, Fe, Cu, Rb, Mo, Ba, Sr and Ni. Slurry sampling had also been applied for the determination of minerals in sugarcane with ICP-OES.
- Soft drinks were successfully analysed for several elements.

Inductively Coupled Plasma-Mass Spectrometer (ICP-MS)

- ICP-MS is a powerful multi-analyte analytical technique used for the quantitation of metals and non-metals in a wide range of digested sample at low concentration, typically parts per billion (ppb) or per trillion (ppt) level.
- Samples will be converted to neutral components in high temperature plasma and identified based on mass to charged ratios.
- There are four mains steps involved in ICP-MS analysis such as sample introduction, aerosol generation, ionization by an argon plasma source, mass discrimination and the detection system.
- There are many complex samples matrix have been successfully analysed using ICP-MS such as honey, rice, cow, goat, buffalo, yak and camel milk, meat, spices and aromatic herbs, honeydew honey, dairy milk and plant based milk and maize.

Energy-Dispersive X-Ray Fluorescence (ED-XRF)

- A non-destructive energy-dispersive X-ray fluorescence (ED-XRF) spectrometry is a nuclear analytical technique was used for macro elements calcium and potassium analysis in food samples such as fruits, vegetables and cumin spice.
- Good comparability with Neutron Activation Analysis (NAA) and AAS showed by statistical results confirming no significant difference between EDXRF and both NAA/AAS methods.