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Abstract: Instrumental Analysis (IA) plays a critical role in different facets of Mineral Exploration – Exploitation (MEE) to establish many important aspects like physical characterization of ore, its mineralogical and chemical composition to establish overall grade, composition of its constituent ore/gangue minerals and beneficiation products, quality assurance and quality control during various operations, value addition, characterization of processed waste and creation of wealth from such waste. IA is carried out by various techniques for different parameters that are broadly of two categories, viz., physical and chemical. For accurate IA, proper and thoroughly cleaned sampling (and sub-sampling) is absolute necessity, as the quality of the sample is the first control on quality of subsequent data, interpretations and decisions. An overview of IA in MEE, covering mainly the salient aspects of commonly adopted instrumental techniques, is presented in this invited lecture.

Keywords: Instrumental Analysis, Mineral Exploration – Exploitation.

1. Introduction

The term *ore* is often loosely used to designate anything that is mined, but technically is an agglomeration of ore (concentrations of formerly diffuse metals, besides a few non-metallic minerals) and gangue (non-metallic minerals or rock matter) minerals. *Mineral Exploration – Exploitation* (MEE) encompasses planning, survey, prospecting, drilling and establishment of an economic deposit of ore mineral(s), followed by its mining and mineral processing for cost-effective utilisation. In different facets of MEE, *Instrumental Analysis* (IA) plays a critical role to establish many important aspects like: a) physical characterization of ore; b) its mineralogical and chemical composition to establish overall grade; c) composition of its constituent ore/gangue minerals and beneficiation products; d) Quality Assurance (QA) and Quality Control (QC) during various operations; e) value addition; f) characterization of processed waste; and g) creation of wealth from such waste. IA is carried out by various techniques that are broadly of two categories, *viz.*, physical [including optical (microscopic), X-ray diffraction, thermal and radiometric] and chemical (for elemental and isotopic analysis). It should be noted that for any accurate analysis, including IA, proper, thoroughly cleaned sampling (and sub-sampling) is absolute necessity, as the quality of the *sample* (a small separated part of the something illustrating the qualities of the mass from which it is taken from) is the first control on quality of subsequent data, interpretations and decisions. Some of the usual procedures employed for proper sampling in

IA include coning and quartering, sampling by Jones riffle or stationary sample splitter, rotary sample divider and core splitter. The present, invited lecture gives an *overview* of IA in MEE and covers mainly the principle, instrumentation, applications and drawbacks, if any, of commonly adopted instrumental techniques.

2. Physical Methods of Instrumental Analysis in MEE

These include for determination of density, porosity, permeability, magnetic susceptibility, mineral – rock – ore characterization by petrological-microscope study, crystal properties by X-ray Diffraction (XRD) study, thermal properties, radioactivity and luminescence of minerals, ores and rocks. Salient aspects of each of these are given in the following.

2.1. Density or Specific Gravity: Density (G: mass of the unit volume, g/cc) or specific gravity [SG: ratio of density of a substance to that of water at 4°C (39.2°F)] is an important physical property of minerals, rocks and ores. G or SG of a solid depends upon the nature of its constituent chemical substances (e.g., all lead compounds with a high SG of ~ 6) and the state of molecular aggregation (e.g., aluminium with SG of 2.5 and its oxide, corundum, with SG of 4). It has many direct applications like in estimation of ore reserves, qualitative evaluation of grade of heavy (SG > 2.89) minerals in mineral-sands, knowing approximate mineralogy (felsic- or mafic-dominant, respectively, with lower and higher values of G) of different types of rocks and ores, state of fresh (higher value for G) or altered (lower value of G) nature within the same type of rock or ore and gravity studies of geophysics. Furthermore, taking advantage of differences in the values of density of rocks, ores and minerals, many instruments of gravity separation are used in MEE, e.g., separation of valuable heavy minerals (ilmenite, rutile, zircon, garnet and sillimanite) from light minerals in mineral sand industry, using spirals and hydro-cyclones; separation of heavy rare minerals like columbite – tantalite from gangue, using tabling; and separation of gold from the rest, using Knelson (gold) concentrator. In geophysical exploration, density-based gravity methods are extensively used. For determination of G or SG, the weight of the solid in air (w) and in water under complete immersion (w’) are determined, and the difference between these weights, i.e., loss by immersion (w-w’), which is the weight of a volume of water equal to that of the solid, is obtained. Then, SG = w / (w-w’). The numerical value of both SG and G is the same, with G is having unit (g/cc) and SG, being a ratio, with no unit. SG or G on geological materials like minerals, rocks and ores is determined by any one of the following methods: (i) weights are measured directly and the volume, determined either by the principle of Archimedes (using a spring, Jolly or Berman balance) or the weight of liquid displaced in a pycnometer, by a few grains of pure minerals; and (ii) by using a ‘Beam Balance’ or Walker’s Steel Yard, especially on rocks and ores. Bulk Density (BD) of mineral sand samples is determined by accurately weighing sand (w) filled fully in a container of known volume (v: 250 or 500 cc), with G being w/v. A list of G of common minerals, rocks and ores is given in Tables 4.1 and 4.2 in Dhana Raju (2009 *a*).

2.2. Porosity and Permeability: *Porosity* of a rock or an ore is defined as that *percentage of pore space,* out of its total volume, *which is not occupied by solid matter*. This volume of pore space is made up by voids that are generally occupied by liquid or gaseous matter. Rock voids or pores may be interconnected (open pores) or isolated (closed pores). The sum of the volume of open and closed pores is the *total porosity* and the volume of open pores containing free water, oil or natural gas is the *effective porosity* that is responsible for geological reserves of hydrocarbons. As the pore-system constitutes the channel-ways for the passage of fluids through the rock as well as for storage of fluids, porosity and the resulting storage capacity of the rock and its transmissibility are of much importance in study of oil, gas, brines and groundwater. Total porosity ($k_{p,}$ %) of minerals does not generally exceed 1% and in crystalline rocks it is almost nil, whereas in clastic sediments and sedimentary ores, it ranges from 0.2 to 70% (see Table 4.3 in Dhana Raju *a*, 2009 for the list). The original porosity of sediment is affected by size and shape of its grains, method of deposition, packing and compaction during and after deposition. Using a beam balance or a porosimeter, porosity (k_p, %) of a rock can be determined, based on measurements of two of the three volumes, viz., V_f – total volume, V_p – pore volume and V_w – volume of solid matter, with $k_p = V_f – Vp$ or $(V_f – V_w)/V_f$ or $V_p/(V_p + V_w)$. For more details, the reader is referred to Mueller (1967, pp. 238-244).

Permeability is the capacity of rocks for transmitting liquids, gases or their mixtures in the presence of a pressure gradient. It is of two kinds, viz., *absolute* (physical, with respect to a dry gas or single component liquid) and *effective* (definite components like gas – water, oil – water, gas – oil). Effective permeability is characterized by the respective coefficients for gas, oil and water. The permeability of a porous medium can be expressed as the quantity of fluid, Q (cm^3/sec) passing through a given cross section, C (cm^2) and a given length, L (cm). This quantity is directly proportional to the pressure-difference, P (in atmospheres) at the two ends of the system and inversely proportional to the viscosity of the fluid, V (in centi-poises): $Q = K \times CP/VL$, where K is the permeability coefficient (*darcy*). Modern sands have permeability values of 10 to 100 or more darcys, and in most consolidated sandstones, the permeability is < 1 to 2 darcys; and, hence, permeability is usually reported in millidarcys. In the study of oil sands and acquifers, permeability is very important. The permeability of rocks is higher in the direction of stratification, as compared with that at right angles (Kobranova, 1989). Permeability of rocks is determined in laboratories almost exclusively with air as the flowing medium and for details, see Mueller (1967, pp. 244-249).

2.3. Magnetic Susceptibility: Magnetism is the property of rocks to be magnetized by the magnetic field, vary it and sometimes retain the magnetized state after dis-continuing the action of magnetic field. Magnetism shows itself during the interaction of two magnetized rock samples or a rock sample and a conductor through which an electric field flows. Magnetic Susceptibility, *K* of a material is the ratio of the strength of magnetism, *I* induced in it to the strength of magnetization, *μ*, i.e., $K = I/H$. The magnetic permeability, μ and susceptibility, K are connected by the relation, $\mu = 1 + 4pK$. Magnetism of a rock or an ore is governed by their origin and living conditions, and is determined by distribution and concentration in it of dia-, para-, antiferro-, ferro- or more commonly ferri-magnetic components and crystal lattice structure, particularly the type of bonding of atoms or ions in it. Most minerals like principal rock-forming silicates and carbonates, and ores of Au, Cu, Pb, Bi. S, Hg and C (like graphite) are dia- and para-magnetic (with little or almost nil *K*); ore minerals like pyrite, ilmenite and siderite, and clays are para- or paraferrimagnetic (with a little higher value of *K*); pyrolusite and albandite are antiferromagnetic; meteoric iron, alpha-hematite and some hemoilmenite, Ti-magnetite and Fe-hydroxides are ferro-magnetic (with high values of *K*); and magnetite, martite, pyrrhotite, jacobsite, cubanite, etc., are ferri-magnetic (with high to very high values of *K*). Data on magnetic susceptibility of different rocks and ores are listed in Table 4.5 in Dhana Raju *a*, 2009. Magnetic susceptibility is determined by Nagata's ballistic method, Carey Foster's inductance bridge, susceptibility meter (for powdered samples) and Kappameter (for *in-situ* determination on an outcrop). Taking advantage of differences in *K* values of minerals, they are separated from one another, using the equipment like dry ferromagnetic separator, bar magnetic separator and Frantz Isodynamic Magnetic separator in a laboratory, while large-scale dry and wet magnetic separators are used for industrial-scale separation of magnetic, weakly magnetic and non-magnetic minerals like in heavy mineral sand industry to separate magnetite, ilmenite and garnet from non-magnetic rutile, zircon and sillimanite. Furthermore, magnetic and electromagnetic methods are frequently used in geophysical methods of mineral exploration on both surface and in air.

2.4. Thermal Methods: Thermal methods of analysis, used mainly in identification of rock-forming and some ore minerals having characteristic thermal properties (e.g., carbonates, clays, silica, sulphides and oxides), are of two types, viz., Differential Thermal Analysis (DTA) and Thermo-Gravimetric Analysis (TGA). In DTA, the analysis is carried out by heating small quantity of the specimen and an inert reference material (usually alumina) under controlled conditions, and recording the reactions that took place in the specimen during such heating in the form of peaks in a DTA curve. The DTA curve (differential temperature ΔT *vs.* Furnace temperature, t) is fairly reproducible for any mineral on a particular machine under identical operating conditions and can be used for qualitative identification of minerals. Besides, the mass of the reacting material is approximately proportional to the area under the curve, which can be used for quantitative estimation. DTA can quickly identify the presence of small quantities of, for example, carbonate in a rock or kaolinite or other clays, but cannot be considered as the same 'fingerprinting' method that X-ray diffraction is. When a specimen with characteristic thermal properties is heated, two types of chemical reactions may take place, viz., *exothermic* and *endothermic.* Exothermic reaction produces heat, with examples being those involving crystallization, oxidation (e.g., of pyrite) and some other chemical reactions. Endothermic reaction absorbs heat, as is the case in phase-change, dehydration, decomposition and crystalline inversion (e.g., of anglesite). A wide range of DTA instruments (e.g., Stone DTA system) is commercially available. Basically, the system comprises a sample holder, thermocouple, recorder – controller, heating furnace platform and arrangement for dynamic gas flow; there is a choice of sample holders and thermocouples. For a list of DTA reaction peak-temperatures and peak-nature of some common gangue and ore minerals, the reader is referred to Table 12.1 in Dhana Raju *a* (2009). More details on the method of analysis can be had from Hutchison (1973).

Thermo-Gravimetric (TG) analysis deals with studying the loss in weight of a substance as it is being heated. By combining TG technique with DTA, it is possible to distinguish crystalline transitions, second order transitions and solid-phase reactions occurring without weight change on one hand from phenomena such as loss of volatiles and de-hydroxylation involving weight loss or gain on the other. A TG curve records the weight of the specimen in an environment heated or cooled at a controlled linear rate as a function temperature. Several TG instruments are commercially available (e.g., Stone, USA and Shimadzu, Japan). The results of TG determination on a variety of minerals can be shown graphically with temperature (0 – 1000°C) on X-axis and loss in weight % on Y-axis. The TG curves may be compared with DTA peak temperatures of respective minerals. A DTA peak may correlate with a sharp loss of weight on the TG curve, which indicates that the reaction caused a loss of volatiles from the specimen, e.g., chlorite. For more details on operation and other aspects of TG analysis, the reader is referred to Hutchison (1973).

2.5. Microscopic Study: An optical microscope is meant mainly to produce a magnified image of an object, in the range of ~ 10 to 1000 times. In MEE, microscopic study forms an important laboratory technique for both qualitative and quantitative study of various minerals, sands, rocks and ores so as to identify each of these (based on optical properties of minerals, their textures and relative proportion in rocks and ores, and alteration phenomena) as also to examine various products, obtained during ore dressing operations on ores, for determination of grade, nature and quantity of impurities, if any, and during QA and QC operations. This study uses *plane-polarized light* that is propagated by ether-vibrations taking place in *one plane only*. It is carried out in both *transmitted light* to observe the optical features and identification of transparent minerals (mostly gangue and a few ore minerals) and *reflected* or *incident light* to record the optical features and identification of most ore minerals that are opaque in transmitted light. For this study, thin-sections, polished thin-sections and polished slabs/sections of minerals, rocks and ores as well as sands mounted in a liquid medium (e.g., clove oil) on thin sections are used. Details on microscopic study can be had in Chapter 7 of Dhana Raju *a* (2009), in which the diagnostic optical properties of common transparent minerals and ore minerals by which they are identified are listed, respectively, in Tables 7.1 and 7.2.

An advanced version of the optical microscope is the ‘Scanning Electron Microscope’ (SEM), having very high magnification between x20 and x10000. This instrument is not routinely used in MEE and can be rarely used to probe surface-features and qualitative – semi-quantitative elemental composition (SEM in combination with Energy Dispersive X-ray Spectrometer) of sub-microscopic minerals in ores and rocks.

2.6. X-Ray Diffraction (XRD) Study: X-rays or Roentgen rays, discovered in 1895 by Roentgen, are the invisible electromagnetic radiation of short wavelengths of 0.5 to 2.5 Å (1 Å = 10^{-10} m). As the unit-cells or fundamental blocks of crystals that constitute minerals are having dimensions in the order of a few Å, X-rays with comparable wavelengths are the ideal medium to probe crystals and, hence, minerals. X-rays are generated in vacuum (X-ray) tubes in which are sealed two electrodes, viz., anode and cathode. When an electric current of a high voltage is applied, streams of electrons (cathode rays) flow from cathode pass through tube and at high speed strike plate of wolfram or platinum, when X-rays (*to be used with great caution as they may destroy healthy tissues causing genetic damage*) are given off. XRD technique in MEE is used mainly to: (i) identify the ore and gangue minerals in crystalline form, present in a rock or ore, and which could not be normally identified by microscopic methods, e.g., clay minerals and uranyl (U^{6+}) minerals; (ii) confirm the minerals that are suspected by other methods; (iii) probe metamict minerals like niobates and tantaltes containing U, Th, Zr and REE; (iv) undertake crystallographic and related studies of minerals relevant to mineralogy; and (v) rarely to quantify major and minor minerals in simple rock types like granite. Identification of an unknown mineral is done by comparing its XRD data with that in JCPDA/ICDD powder data file. This technique has a limitation in that it *cannot be used in the study of amorphous substances*. For mineralogical studies, camera or powder diffraction (instrument being X-ray diffractometer) techniques are used, with the latter being more common. Details of this technique can be had from Chapter 11 of Dhana Raju *a* (2009).

2.7. Radiometric Analysis: Radioactivity, discovered in 1896 by Henri Becquerel, is the property possessed by certain elements of high atomic weight like Radium (Ra), Thorium (Th) and Uranium (U) of *spontaneous emission of radiation* of α (${}^{4}_{2}He^{2+}$) particles, β (high energy electrons) particles and γ (high energy, short wavelength X-rays) due to the disintegration of the nuclei of the atoms, e.g., ${}^{238}U \rightarrow {}^{206}Pb$. Of the nearly 100 elements in the Periodic Table, only three, viz., U, Th and K (only ${}^{40}K$) are the naturally occurring radio-elements. In the common rock types, both U and Th usually prefer acidic (with > 62% silica), especially alkali (K and Na)-rich, magmatic rocks; carbonaceous, phosphatic, sandstone and quartz-pebble conglomerate type of sedimentary rocks; and low-grade metamorphic rocks. Radioactive occurrences are located by radioactive anomaly [abnormal content of radioactivity (expressed as x times of background value) due to relatively higher contents of either U or Th or both in rocks and minerals], recorded by γ-sensitive Geiger Muller counter or more sensitive Scintillometer. Airborne radiometric surveys with γ–ray spectrometer speedily help in identification and delineation of radioactive areas within large terrains, while γ–ray logging in a drilled-hole helps to locate radioactive zones at depth. It may be noted that the total content of radio-elements in different rock types is in *ppm* level and is usually < 0.1% eU_3O_8 in ores. Accordingly, the radioactive minerals in rocks and ores are in trace to very minor amounts, due to which it is rather difficult to locate them. For locating and delineating them, techniques like radioluxography, solid state nuclear track detection and chromogram are resorted to. When once they are located, their identification is carried out by microscopic investigation and XRD. There are numerous radioactive minerals, both of primary and secondary origin. Contents of radio-elements, viz., K, U, Th and Total in a sample are determined by radiometric analysis (assuming radioactive equilibrium), using γ-ray spectrometer and measuring the intensity of peaks of 1.46, 1.76, 2.62 and >0.1 MeV (energy), respectively, from ${}^{40}K$, ${}^{214}Bi$ (daughter product of U), ${}^{208}Tl$ (daughter product of Th) and total as counts per second (cps); the contents are obtained by comparing the 'cps' with those of standards containing known quantity of K, U, Th and total of all the three. Details of radioactivity can be had from Chapter 15 of Dhana Raju *a* (2009).

2.8. Luminescence: *Luminescence* is the phenomenon of emission of light or photons, mainly in the visible domain, from a substance, when it is stimulated by any means other than heating to incandescence. There are many types of luminescence and of these, fluorescence – phosphorescence, Cathodo-Luminescence (CL) and Thermo-Luminescence (TL) can be used in MEE. The emission of light from a substance like a mineral, when it is exposed to direct radiation such as ultraviolet light is called *fluorescence* that ceases when radiation stops, whereas the continued emission of light even after exposure to light is termed as *phosphorescence*; these two differ only in the amount of time it takes for electrons to return to their ground state. Both these in different intensity are exhibited by some uranyl (U^{6+}) minerals like autunite and uranophane as well as some non-radioactive minerals like scheelite, barite, halite and fluorite, due to which this technique can be used both as a tool in exploration for these and in their identification before XRD study. When minerals containing impurities like U, Th, Rare Earths and Mn are bombarded in vacuum by an electron-gun, they emit electron-excited luminescence that is termed as CL. This (a) can supplement petrographic observations made by polarizing microscopy; (b) in combination with XRD and SEM, contributes to the phase-characterization of technical products and waste materials; and (c) in combination with image analysis, allows quantification of different minerals in a rock or an ore. TL is the phenomenon of emission of light from a crystal previously irradiated, either by exposure to naturally occurring radioactive minerals in the field (Natural TL, NTL) or by exposure to artificial radioactive sources in laboratory, like ^{60}Co gamma rays (Artificial TL, ATL). TL can be used as a tool in exploration for U, especially to locate concealed contiguous areas of U-mineralization, Rare Metal Pegmatites and to differentiate different rock types containing TL-sensitive minerals. More details of luminescence are given in Chapters 5 and 25 of Dhana Raju *a*, and Dhana Raju (2012).

3. Chemical Methods of Instrumental Analysis in MEE

Chemical analysis of rocks and ores, and their constituent ore-/gangue-minerals and beneficiation products, obtained during their processing, is carried out by diverse instrumental techniques. In MEE, it provides critical information, like (i) *grade of ore samples* (required for calculation of ore reserves); (ii) *chemical nature of rock samples* (as acidic, intermediate, basic and utrabasic); (iii) *chemical composition of rocks and ores* in terms of major (> 1 wt. %), minor (0.1-1 wt. %), trace [< 0.1% (< 1000 – 10 parts per million, ppm or g/ton)] and ultra-trace (< 10 ppm or 10,000 parts per billion, ppb or mg/ton) elements; (iv) *nature of matrix* (e.g., silicate, oxide and carbonate) of analyzed samples; (v) *possible co-/by-products* in ores; (vi) *presence and content of precious metals* like Au, Ag and PGE in ores with no mineralogical expression, e.g., invisible Au and Ag in some sulphides; and (vii) *nature and amount of impurities* in beneficiation products. Chemical analysis of geologic samples is carried out either for elemental (or in oxide form of elements) or isotopic composition, with the latter generally not resorted to in MEE and, hence, is not dealt with here. For elemental (or oxide) composition, the usual chemical methods of analysis are as follows: Gravimetry, Titrimetry, Spectrophotometry, Flame Photometry, Emission Spectrography (DC-arc or AC-spark), Atomic Absorption Spectrometry (AAS), X-Ray Fluorescence Spectrometry (XRFS – either Wavelength- or Energy-Dispersive, W/E D), Instrumental Neutron Activation (INA), Inductively Coupled Plasma - Optical/Atomic Emission

Spectrometry (ICP – O/AES), ICP – MS (Mass Spectrometry), Electron Micro Probe (EMP) and Fluorimetry. Of these, the first two are *absolute* methods and the rest are *comparative* methods that require appropriate standards for calibration and analysis. Depending upon geochemical nature, expected concentration levels and type of matrix of the sample to be analyzed, specific methods amongst the above need to be selected for analysis of its elements. It may be noted that until ~1960s, chemical analysis of geological materials was done by classical and rapid methods, which are based on time-consuming, cumbersome and detailed chemical manipulations. These are superseded by instrumental methods that have revolutionized analytical technology that is possible due to notable advances is micro-miniaturization of electronic and computational technology. Salient aspects of each of the above methods of chemical analysis are given in the following.

3.1. Gravimetry: This is a tedious, lengthy, classical method of chemical analysis, used until early 1950s for dominant silicate rocks and minerals. It depends on the analytical balance for all the determinations that can be carried out after extensive chemical manipulations (requiring lot of professional skills), intended to isolate quantitatively individual compounds. In this, one gram of finely divided rock powder is fused with 3-5 g anhydrous sodium carbonate in a platinum crucible at 1000 - 1200°C in a muffle furnace. Then the constituents of the sample are separated into 4 groups of elements, viz., SiO_2 (separated by dehydrating silicic acid to insoluble silica); R_2O_3 group of elements comprising Fe_2O_3, Al_2O_3, TiO_2 and P_2O_5 (precipitated as hydroxides, from which silica was removed, is neutralized with ammonia); CaO and SrO (precipitated as insoluble oxalates); and Mg and Mn (precipitated as insoluble phosphates); these insoluble precipitates/residues are ignited and weighed to arrive at the contents of the above radicals. Na and K were determined by igniting the sample with a mixture of ammonium chlorite and calcium carbonate, followed by their leaching and determination after precipitation as insoluble salts.

3.2. Rapid Methods of Analysis: During 1950s, classical gravimetric methods of chemical analysis were revolutionized by 3 developments – 2 instrumental (photometric analysis, using spectrophotometer, and flame photometer) and 1 chemical (use of EDTA for element-specific titrations). These led to development of ‘rapid methods of chemical analysis’ that is still being used in low-budget laboratories, whereas in many geo-analytical laboratories it is superseded by instrumental techniques like XRF, AAS and ICP-AES/MS. In the ‘rapid methods of analysis’, two solutions were commonly used for determination of major elements, viz., Solution A to determine silica and alumina, and Solution B that was subjected to HF/perchloric acid digestion to fume off silica and then total Fe, CaO, MgO, TiO_2, P_2O_5, MnO, Na_2O and K_2O were determined. UV/visible spectrophotometer is used to determine Si, Al, Fe, Ti, Mn and P. It consists of a light source (incandescent tungsten lamp), a sample cell compartment, an optical monochromator and a photomultiplier or photocell detector. The solution quantity (in ml), selected reagents, colour complex and absorption measurement (in nm) for different elements are serially listed in the following: Solution A:- Si – 8, molybdenum blue, blue, 812; Al – 5, Alizarin red S, red, 475; Solution B:- total Fe oxide – 5, 1,10-phenanthroline, red, 508; Ti – 5, tiron, yellow, 380; Mn – 25, oxidize to permanganate, red-purple, 525; P – 25, mixed with sodium-metavanadate and –molybdate solution, yellow,

315. Alkalies (Na and K) are to be determined by a flame photometer. The principle of this is that if a solution is aspired into a flame, any elements that are efficiently excited by the thermal energy of the flame will, on de-excitation, emit light photons that are detected at characteristic wavelengths, with the intensity being proportional to the concentration of the element in the solution. It comprises a burner assembly, into which the sample solution is aspired, and a simple filter photometer, with the intensity of light passing through this filter is measured using a photocell. Na and K emissions are measured, respectively, at 589 and 766 nm. Ca and Mg are determined by EDTA (ethylenediaminetetra-acetic acid) *titration,* with CaO in strongly alkaline solution of 25 ml aliquot of solution B, using murexide as an indicator, while MgO by difference between an EDTA titration for (Ca + Mg) and Ca-determination alone. Ferrous iron (Fe^{2+}) is determined by decomposing 0.5 g of sample powder with H_2SO_4 and HF, and the liberated Fe^{2+} is to be titrated against potassium dichromate solution, using diphenylamine sulfonate as indicator. Loss on Ignition (LoI) is determined gravimetrically by igniting 1g ultrafine sample powder in an unglazed vitreous silica crucible at ~1050°C for about 1 h and determining loss of weight, after cooling. Details of gravimetry and rapid methods of analysis are given in Chapter 5 of Dhana Raju *b* (2009).

3.3. Emission Spectrography (ES): The principle of ES is as follows: Almost all elements, when vaporized or ionized in the intense heat of an electric discharge or other source of energy, emit radiation of characteristic wavelengths from the ultraviolet region (2000 Å), through visible regions (4000 – 7000 Å), up to 10,000 Å, due to electrons refilling the outer electron orbitals; the element can be identified by the emitted wavelength and its quantity can be determined by the intensity of the emitted light. Below 2000 Å, the light is absorbed by air or the photographic emulsion, and above 10,000 Å, there is no photographic response. The instrumental set-up comprises a unit of source of energy (either a d.c. arc or high voltage a.c. spark) for exciting small amount of samples, the prism or grating optics to disperse the radiant energies and a camera to photograph the dispersed beams. The main advantages of ES are the large number of elements (60-70) that can be qualitatively, semi-quantitatively and quantitatively determined simultaneously from ~30 mg of finely powdered (-325 mesh) sample, low detection limits (1-10 ppm) for many elements and low unit cost for large-scale operations in MEE. The disadvantages are problem of signal instability, high cost, need for a trained operator and poor reproducibility, the last can be overcome with plasma sources.

3.4. X-Ray Fluorescence Spectrometry (XRFS): XRF analysis is one of the first multi-element instrument-technique, adopted widely in routine geochemical analysis. XRFS determinations can be (i) *Wavelength* or *Energy Dispersive* ((WDXRFS or EDXRFS), with dispersion and subsequent detection based on crystal optics, and (ii) *non-dispersive,* with direct measurement of the energies from the sample with no crystal optics. In XRF analysis, samples are excited by the X-ray spectrum, emitted by an X-ray tube. Interaction of X-ray photons with atoms of the sample causes ionization of inner-shell (K, L) electrons, when the atom, being intrinsically unstable, decays immediately by transition of an outer orbital electron to fill the vacancy created by ionization. During this transition, an electron falls down the potential energy gradient toward the nucleus and looses excess energy by emission of an X-ray fluorescence photon of *characteristic energy*, by which an element is identified, and the intensity of such emission is directly proportional to the amount of that element. For analytical measurements, two ‘line series’, viz., K- and L-line spectra, are important. The instrumentation of WDXRFS comprises an X-ray tube, sample changer and WD spectrometer. WDXRFS can be sequential (for determination of same element in a series of samples) or simultaneous (at a time determination of multi-elements in samples). The advantages of XRFS technique are its: non-destructive, simple nature; orderly regularity of spectra; simple sample preparation (pellet of 1 g -325 mesh sample-powder, mixed with boric acid as backing agent); high precision (reproducibility) for both major and many trance elements; and ability to analyze elements from % to ppm level. The weak points of this technique are: calibrating instrumentation using reference materials and requirement for a correction to be applied to the measured count data to account for matrix-related X-ray absorption/enhancement effects. Portable non-dispersive XRF analyzers with isotope sources are compact, fast and easy to carry in field and, hence, are used much in geochemical exploration and mining for ‘on line’ determination to control grade of ores.

3.5. Neutron Activation Analysis (NAA): NA technique finds wide application, mainly due to its ability to determine simultaneously a range of trace elements, like Ta, Hf, Th, As, Sb, Au, Ag, W and PGE (following Ni sulphide fire assay). It satisfies most of the desired features of the best analytical method like sensitivity, rapidity, non-destructiveness, convenience, economy, accuracy and insensitivity to chemical form of elements like oxidation and bonding effects. Its *limitation is that it requires access to a nuclear reactor to irradiate samples*, although counting and spectrum analysis for isotopes with half-lives longer than ~ 2 days do not have to be undertaken at a reactor. NAA is of 2 modes - Instrumental (INAA) and Radiochemical (RNAA) - and is based on measurement of induced radioactivity that is purely a nuclear phenomenon, brought about due to nuclear interactions, caused by neutrons, such as (n, γ), (n, p), (n, α) and (n, 2n). The activation products of these reactions are the isotopes of the element under activation or its neighbouring elements. When a sample (in a vial) is irradiated in a nuclear reactor by a high flux of neutrons, a number of nuclear transformations can occur. Specific isotopes of many elements undergo (n, γ) reactions during thermal neutron irradiation. A neutron is incorporated into the nucleus of the isotope. Following instantaneous decay of a transient species involving emission of ‘prompt’ gamma rays, the product of this nuclear transformation is almost always radioactive, decaying to a stable daughter with a characteristic half-life that varies from several days to several years for the range of elements of interest in geologic applications. Most radioactive isotopes formed by (n, γ) reactions decay by β-emission. During this decay, the nucleus ejects a β-particle, accompanied by the emission of one or more β rays of energy characteristic of the differences in excited nuclear stated in the transition. INAA involves the measurement of the intensity of these characteristic γ-emissions, as a signal, proportional to the concentration of original elements. Its main instrumentation includes sample vials for irradiation, germanium γ-ray detector with lead-shielding and multi-channel analyzer.

3.6. Electron Probe Micro-Analyzer (EPMA): EPMA is the workhorse of *in-situ* quantitative microanalysis of very small areas of a few microns across. It is the ‘definitive’ technique for accurate determination of major and minor elements in ore and gangue minerals, down to detection limits of the order of 50-200 µg/g (ppm). For analysis by EPMA, specimens of rock or ores must be prepared as polished thin-sections or polished slabs. A thin (20 µm thickness) film of usually carbon or rarely gold is to be coated with a sputter coating machine onto the polished surface to conduct the electron beam to earth; such coating is *not* required in the analysis of metallurgical samples as their metals or alloys are conductive. In this analysis, a focused electron beam (from an electron gun with incandescent tungsten filament) is used to excite the sample, resulting in scattering of the electron beam to form an *excited volume* within the sample. A variety of signals, like *characteristic X-rays* for identification and quantification of different elements (in a manner similar to XRF) and *backscattered- and secondary-electron signals*, respectively, to differentiate minerals based on their mean atomic number and to examine topographic features, is generated within this excited volume. EMP instruments are usually fitted with 2 or more WD X-ray spectrometers (plus 1 EDXRFS), which are to be programmed to measure X-ray intensities at pre-selected peak and background angles, under computer control. After calibration and correction for matrix effects and ZAF, the results are reported.

3.7. Atomic Absorption Spectrophotometry (AAS): This technique, with *sample in solution form*, was introduced during late 1950’s. It started an instrumental revolution in wet chemical laboratories and almost replaced the use of gravimetric (classical) and colorimetric (rapid methods) techniques. By this, major elements and a range of trace elements in geological samples can be determined. Though this technique is replaced during last few decades by more powerful atomic spectroscopic techniques like ICP-AES and –MS, still AAS is widely used in analytical service laboratories (especially of low-cost and those not supported by an extended infrastructure) due to its cheap, simple and robust instrumentation, adaptability in both field/mobile and stationary laboratories, and highly cost-effective method of analysis. The capabilities of conventional flame AAS are considerably extended by the hydride generator accessory (for determination of hydride-forming elements like As, Sb, Se, Sn and Bi), cold vapour generator (for determination of Hg) and by the option of the higher sensitive graphite furnace (replacing flame) AAS (gf-AAS). In AAS, atomic absorption effect involves the absorption of light photons in the UV-visible region of the spectrum by atoms of a designated element. Absorption causes excitation of outer orbital electrons from one electronic state to another. The most effective means of measuring the atomic absorption signal is to excite an atomized sample with the atomic emission spectrum of the element to be determined. The atom cell used is a flame into which the sample solution is nebulized. The light source is the hollow cathode lamp, chosen to emit the atomic spectrum of the element of interest. Selected emission lines in the spectrum of the hollow cathode lamp have exactly the correct energy to excite the electronic transitions in corresponding analyte (species for which determination is sought) atoms. The degree of absorption of an atomic emission line is measured using an optical monochromator, tuned to the selected wavelength. The degree of absorption is related to concentration of analyte in the atom cell by the Beer’s law. By comparing the absorption of sample and standard solutions, the concentration of analyte can be determined. Although a wide range of elements can be determined by AAS, notable exceptions are electronegative non-metals that do not possess suitable atomic absorption lines in UV-visible region of the spectrum. The highest sensitivity is obtained from lighter elements in the periodic table, up to and including the first-row transition series.

3.8. Inductively Coupled Plasma – Atomic/Optical Emission Spectrometry (ICP–A/O ES): This *high-cost* technique, with *sample in solution form* like in AAS, was introduced during mid 1970s. Compared to the techniques of AAS, XRF and INAA, it has many advantages like (i) *less interferences* in determination of alkali metals and refractory elements, which affect AAS; (ii) *high sensitivity* for a wide range of trace elements, including B, Be and Li, which cannot be detected by XRF or INAA techniques; (iii) offering a *linear calibration response over concentration ranges extending over 5 or 6 orders of magnitude;* and (iv) *capability to determine both REE* (following an ion-exchange separation) and *PGEs* (following fire assay and solution chemistry). These are possible due to *inductively coupled plasma* (plasma is an ionized gas in which positive and negative ion concentrations are equal), which is a powerful excitation (optical emission) source that is resilient to most chemical interference effects. In this technique, the plasma is propagated at the end of a quartz glass torch by radio-frequency (RF) power, coupled into the plasma through a copper work coil, surrounding the end of the torch. The concentric nozzles of the torch are supplied with argon gas at appropriate flow rate. When argon gas at the end of the torch is seeded with electrons, the intense RF field, generated by work coil, induces violet oscillations in these charged species leading to collisional ionization of the atoms of argon gas. These ions are also subjected to RF oscillations. The net consequence is an ohmic heating effect that creates a localized plasma fireball at the end of the torch, with temperatures of up to 10,000 K. A high flow rate of coolant argon gas is required to prevent the quartz glass torch from melting. Sample solutions are introduced into the plasma as an aerosol (colloid in which the dispersion medium is a gas, e.g., smoke, mist), using argon as carrier gas. This sample aerosol is delivered to the central capillary of the torch, where it punches a hole through core of the plasma fireball. During the 2 µs taken by the aerosol to pass through the fireball, its temperature is raised to ~ 8,000 K by conduction, convection and radiation effects. Thermal energy available in the plasma is sufficient to (i) efficiently dissociate the aerosol into atoms (overcoming many of the chemical interferences encountered in the flame AAS), (ii) excite atomic species and (iii) ionize many elements and create ionic species with very short lifetimes. Analytical determinations are made by measuring the intensity of optical emission at characteristic wavelengths of both atomic and ionic species in the tail flame of the plasma. In assessing the most sensitive lines for analysis, ion emission lines are preferred for many elements. The main components of an ICP – AES instrument are: sample changer, nebulizer, cloud chamber, torch comprising 3 concentric tubes (to serves as injector supply, auxiliary supply and coolant supply), work coil assembly connected to RF generator and optical monochromator to measure optical emissions in the tail flame. The drawbacks of this technique include presence of some matrix effects, matrix interference in the plasma, spectral interference, high running cost (due to consumption of costly argon gas), less precision in determination of major elements (as compared to XRF) and low sensitivity in determination of Rb and K.

3.9. ICP – Mass Spectrometry (ICP – MS): Mass spectrometry, based on the atomic mass of the elements and optical spectrometry, originated in the early 20th century, with its main application being isotopic study. During the early 1950's, it (with static mass analyzers for separation of ions, based on their mass to charge ratio) was applied to organic chemistry, particularly in petroleum industry. In ICP-MS, two major innovations took place, viz., dynamic mass spectrometer (quadrupole mass analyzer) that operates at ultra-high vacuum and its interface with inductively coupled argon plasma (propagated at atmospheric pressure) as source of ions. The mass spectrometer offers highly favourable analytical performance, with both very *high sensitivity* that can be tuned to detect full range of most of the elements in the periodic table and low background levels facilitating *low detection limits*. All elements, except In (Indium), possess at least one isotope that is free of interference from the isotopes of other elements in the periodic table. The technique, with sample in solution form, is capable of direct determination of the REEs in many samples and of the PGE, after fire-assay pre-concentration. The first commercial ICP-MS instrument was introduced in 1983. The principal area of innovation is in design of a suitable interface for sampling ions from the plasma into the MS, with initial designs using a pinhole (50-80 µm in dia.) to sample plasma gases directly into the MS. Recent instruments use a modified sample interface design in which the plasma gases are sampled through large (0.8-1 mm) aperture into an expansion stage, held at intermediate vacuum (~ 0.0 torr). Ions entering the expansion stage are then sampled through a second skimmer aperture into MS itself, thereby avoiding effects of boundary layer without causing discharge phenomena. Instrumentation-wise, the ICP-MS system comprises mainly sample introduction system, plasma torch, quadrupole mass analyzer and electron multiplier detector in which signal is measured as counts per second (*cps*). The raw data in the form of *cps* are obtained, either by continuous scanning (for qualitative identification of elements in the sample solution) or by peak-hopping method (for quantitative analysis of elements). The interferences in this system are poly-atomic, isobaric, formation of oxide and double charged ions in the plasma, presence of abundant mass peaks and high salt content and TDS. To obtain accurate analysis by ICP-MS technique and to overcome the above interferences, the following factors are to be taken care of: selection of alternate isotope, use of highly pure acid and water for preparation of sample solutions, employing proper dissolution procedure, using multi-variant correction methods for inter-elemental effects, reducing TDS by sufficiently diluting samples, reducing oxide and double charged ions by adjusting gas flows and other parameters, use of matrix-matching standards for calibration and periodical cleaning of cones, nebulisation and spray chamber system. Drawbacks of this technique include limited tolerance to acid strength exceeding 2-5% and TDS exceeding ~0.1% and not for routine determination of major elements in silicate rocks due to (i) isobaric artifacts that cause troublesome interferences and (ii) less precision, as compared to that of ICP-AES and XRF.

3.10. Fluorimetry/Laser Fluorimetry: Determination of U in rocks and ores is carried out by gamma-ray spectrometry (see section 2.7 above), assuming equilibrium between the parent ^{238}U and its daughter product, ^{214}Bi. However, in many samples the equilibrium is not attained, with disequilibrium operating in favour of either parent or daughter, thereby making the radiometrically determined U being different from the actual content in the sample and, hence, it is always recommended to determine chemically the U-content in the samples for correct evaluation during exploration for U. Of different methods to determine U content chemically, the best is fluorimetry and better laser fluorimetry, especially for very low contents of ppm to ppb levels, normally encountered in water samples. In the fluorimetric method of determination of U, uranyl nitrate is extracted from nitric acid solution with ethyl acetate, using aluminium nitrate as salting out agent. A portion of the extract is evaporated in a platinum dish and the residue is fused with sodium fluoride flux to prepare a fluorescent melt. The extraction separates U from many elements that quench its fluorescence in the melt. The relative yellow green fluorescence (560 µm) in UV light radiation of the prepared sample is determined in a pellet fluorimeter, calibrated with known amounts of U-standards. Using the technique of laser fluorimetry and with addition of the fluorescence enhancing buffers (like sodium pyrophosphate), a rapid method of determining U with > 5 ppb was developed for determination of U in natural waters and brines.

Apart from the analysis of minerals, rocks and ores, the above methods of IA can be applied for *value addition* (e.g., preparation of synthetic rutile and other Ti-products from ilmenite) and *creation of wealth from waste* (e.g., production of valuable Mo and V, as by-products from the waste, obtained after extraction of U in the Tummalapalle U-deposit).

Depending upon the geochemical nature, concentration levels of different elements and the type of matrix of sample (minerals, rocks, ores and process products), specific methods amongst the above are to be selected for analysis of particular elements. As a general guide, chemical methods that are usually adopted for the analysis of various radicals in geologic samples are listed in Table 1. For details of the above chemical methods of analysis, the reader is referred to Part I of Dhana Raju *b* (2009) and the references therein.

4. Conclusions

Mineral Exploration – Exploitation (MEE) is a multi-disciplinary, multi-faceted and multi-dimensional economic programme, involving geo-scientists, drilling engineers, mining engineers and mineral technologists. During multi-stage operations of MEE, Instrumental Analysis (IA) plays a critical role to establish many important aspects like characterization of ore, its mineralogical and chemical composition, overall grade, nature and composition of its constituent ore/gangue minerals and beneficiation products, QA and QC during various operations, value addition, characterization of waste obtained during its processing and creation of wealth from such waste. IA in MEE is carried out by many physical and chemical techniques. Salient aspects, including principles, instrumentation, applications and draw-backs, of the commonly used techniques of IA in MEE are presented in this overview.

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Table 1. Chemical methods, usually adopted for analysis of various radicals in geologic samples

Sl. No.	Method	For determination of elements or radicals
1.	Spectrophotometry (UV-VIS)	Si, P, Ti, V, Mn and Th
2.	Titrimetry	Fe^{2+}, Sn^{2+}, Cl^-, SO_4^-, CO_3^-, HCO_3^-, Ca, Mg
3.	Flame Photometry	Na, K
4.	Flame Atomic Absorption Spectrophotometry (F-AAS)	Li, Rb, Cs, Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn, Cd, Au, Ag, Pd, Al, In, Pb
5.	ICP – AES or better –MS for low to very low contents	REE, Y, Sc, Zr, Hf, W, Nb, Ta, Be, Sr, Ba, V, Cr, Mo, B, Ga, In, Sn, As, Th, PGE
6.	Fluorimetry (Laser Fluorimetry for ppb levels)	U
7.	Gamma-ray Spectrometry	U, Th, K
8.	DC-Arc Emission Spectrograph	Pb, Ga, Cu, Ni, Co, Cr, V
9.	Wavelength Dispersive X-ray Fluorescence Spectrometry (WDXRFS)	Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, V, Cr, Co, Ni, Cu, Zn, Ge, Ga, Rb, Sr,Y, Zr, Mo, Sn, Nb, Ba, W, Ta, Pb, Re, Os, Bi, Th, U (with Rh, W and Au tubes)
10.	Instrumental Neutron Activation Analysis (INAA)	REE, Au, Ag, Sc, Hg, Ta, Zr, Hf, Cs, Th, U, Co
11.	Electron Probe Micro Analysis (EPMA)	*In-situ* analysis of a few microns area in minerals and ores for major and minor elements