CHAPTER

2

Historical background: milestones in the field of development of analytical instrumentation

Nasrullah Shah[1], *Muhammad Balal Arain*[2] *and Mustafa Soylak*[3]

[1]Department of Chemistry, Abdul Wali Khan University Mardan, Mardan, Pakistan
[2]Department of Chemistry, University of Karachi, Karachi, Pakistan [3]Department of Chemistry, Faculty of Sciences, Erciyes University, Kayseri, Turkey

2.1 Introduction

Quantitative analyses are mainly based on the measurement of (1) the chemical reaction, (2) the electrical property, (3) optical properties, (4) nuclear properties, and (5) thermal properties. Analytical methods are broadly classified as classic and instrumental methods of analysis.

The classical methods of chemical analysis, such as gravimetry, titrimetry, and volumetry, are based on the quantitative completion of chemical reactions. Gravimetry is based on weight measurement, while in volumetry the volume needed for the completion of a reaction is measured. Gravimetry is largely classified as precipitation, volatilization, and electrogravimetry, and voltammetry is broadly consisted of neutralization, complexometric, precipitation, redox, and precipitation titration [1–3].

The methods based on measurement of a property by using an instrument are referred to as instrumental methods. These methods include but are not limited to electroanalytical, spectroscopic, chromatography, thermal, and nuclear techniques of analysis. Voltmeter, ammeter, polarograph, spectrophotometer, and others are the instruments used to measure various properties for analytical purposes [1–3].

Instrumental methods are more sensitive, faster, and have a broad range of applications in industry. The instruments are usually interfaced with a microcomputer, which works as a readout device for digital data, titration curves and polarograms, and other output. In some cases, the instruments are fully automated, and they perform all the functions automatically from sampling to printing the results [1–3].

In chemistry much focus is placed on the theoretical background, applications, and interpretation of data of analytical techniques. In this chapter, the focus is on the historical background of common instrumental analytical

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techniques and the introduction of various types of hyphenated techniques such as HPLC-AAS, HPLC-ICP-MS, HPLC-EC, HPLC-AFS.

2.2 Development in the field of chromatography

Chromatography is an important branch of analytical chemistry. It is a separation technique in which the components of a mixture are separated in a system consisting of two phases: stationary and mobile. Although the term "chromatography" was first introduced by a Russian chemist and botanist Michael Tswett is 1906, the history of chromatographic-like separations is very old, dating back to ancient times. The extraction of natural dyes, food processing, and metal extraction have been done from the early ages of human history [4,5].

In 23–79 BCE, Pliny identified ferrous sulfate by using papyrus soaked with gall nuts, in a process resembling modern-day paper chromatography [6].

In 1834 and 1842 Runge reported a simple spot test for the analysis of bleaching solution using a dyed cotton fabric and a paper soaked with starch and potassium iodide, respectively [7].

In 1850 Runge laid the foundation of paper chromatography by separating the dyes obtained from coal tar using a special type of paper. Runge published his work in 1855 in which described his dye separations on paper [6].

In 1861 Groppelsroeder introduced the term "capillary analysis," as he noticed that dyes became separated on strips of paper due to capillary movement of the water, which was used as a solvent for separation of the dyes. However, he was unable to explain the actual mechanism involved in the separation process in his paper on the chromatographic process [8]. Similarly, S. V. Heins reported in his paper that F. Feigle stated, "It seems not to be known that L. Reed thirteen years before Tswett, discovered that it is possible to separate certain inorganic and organic [alkaloids] by column adsorption [on Kaolin]" [9]. A few other studies also reported that the concept of chromatography was applied by other scientists, such as Reed and Day before Tswett. Reed used a column for separation purposes and described some of his separation work using columns in 1893. In 1897 Day separated a petroleum fraction by using columns. Similarly, Engler and Albrecht also did fractionation while using columns [6].

Due to the introduction of more sophisticated chromatographic methods, the progress and use of paper chromatography declined after 1985 [6].

Beyerinck (1889) and Wijsman (1898), introduced thin layer chromatography (TLC) as they separated the strong acids and enzymes in malt extract using gelatin layers in place of paper. However, the current form of TLC was introduced by Izmailov and Shraiber, who in 1938 analyzed the pharmaceutical tinctures on the glass plates coated with alumina powder used as gelatine stationary phase. Meinhard and Hall (1949) developed their TLC plates by using microscope slides coated with celite and alumina containing starch as a binder. Further development in TLC was made by Kirchner, who in 1951 introduced the ascending TLC techniques. Stahl had compiled a book on TLC in which he described the techniques and various adsorbents used in TLC [5,8,10]. A breakthrough in TLC was observed in 1970s after the introduction of high-performance TLC having efficiency and speed. Heyns and Grutzmacher used a mass spectrometer coupled with TLC for analysis. Similarly, Hutzinger and Jamieson also used TLC coupled with a mass spectrometer (MS) for indole analysis in 1970. TLC coupled with other types of detectors, such as photoacoustic spectrometry and infrared spectroscopy, was also reported [8].

The ion-exchange chromatography was first reported by Taylor and Urey in 1938 for the separation of isotopes of lithium and uranium using zeolite as an ion-exchanger bed. In 1939 Samuelson used synthetic ion-exchanger bed. The progress became much rapid during world war second for separation of transuranium elements. It was in 1980s when the high performance ion-exchange chromatography was introduced and it greatly enhanced the performance of ion-exchange chromatography [8,11].

Size exclusion chromatography was introduced in 1958 when Foldin and Porath produced a cross-linked gel by the reaction of dextrane and epichlorohydrin. More developments were made in size exclusion chromatography by introducing new stationary phases, and it became one of the mostly used chromatographic technique for polymers analysis [8,12].

In 1967 Porath developed affinity chromatography by using peptides and proteins as the stationary phase for the separation of biological molecules [8,13].

In 1903 Michael Tswett presented his work on the effect of different packing materials and their particle sizes on the separation performance of a column at the Warsaw Society of Natural Sciences. However, it did not get much attention until the work of Lederer and others in the field of plant pigments separation in 1930s and the publication of the first book on chromatography by Zechmeister in 1937. Chromatography gained interest among scientists, and Khun, Karrier, and Ruzika won the Nobel Prize in 1937, 1938, and 1939, respectively, for their contributions in chromatography. In 1940s ion-exchange partition and column chromatography led to the initial studies on gas solid chromatography. During this time, liquid adsorption chromatography was at its peak, and it was used as a main chromatographic technique for both analytical and preparative separation purposes. Tiselius (1940) and Claesson (1946) classified chromatography in three broad classes: frontal, displacement, and elution chromatography. In 1948 Tiselius was awarded the Nobel Prize for his achievements in chromatography [6–8,10,14]. The concept of gradient chromatography was introduced in 1950s. In this progressive era of chromatography, Martin and Synge laid the foundation of liquid—liquid chromatography. They were working on the separation of acylated amino acids by using a series of 40 extraction funnels for the separation of different kinds of amino acids. They used water-chloroform as solvent mixture and observed that the amino acids were separated in the extraction funnels according to their distribution ratio and partition coefficients. This was tedious work, and soon they got the idea to utilize the column chromatography using water-containing silica gel as stationary phase with chloroform as a mobile phase for the separation of acylated amino acids. Martin and Synge replaced the silica gel and used cellulose to separate the amino acids without derivatization. They both were awarded the Nobel Prize in 1952. In the 1950s gas chromatography (GC) was developed, and the 1960s saw the development of high-performance liquid chromatography [6,8]. The diagrammatic representations of GC and HPLC are given as Figs. 2.1 and 2.2, respectively.

GC laid the foundation for the modern instrumentation of chromatography. Martin and James were the pioneers in GC as they first used nitrogen gas as a mobile phase for the separation of C2–C4 fatty acids on stearic acid coated celite support as a stationary phase [8]. Although Martin and Synge described their work of gas liquid chromatography in 1941, the first paper on gas liquid chromatography was published by James and Martin in 1952. The first publication on gas solid chromatography was done by Hesse et al. Hesse and his coworkers separated hexanoic acid by using carbon dioxide as the mobile phase and silica gel as the stationary phase. Probably, it was

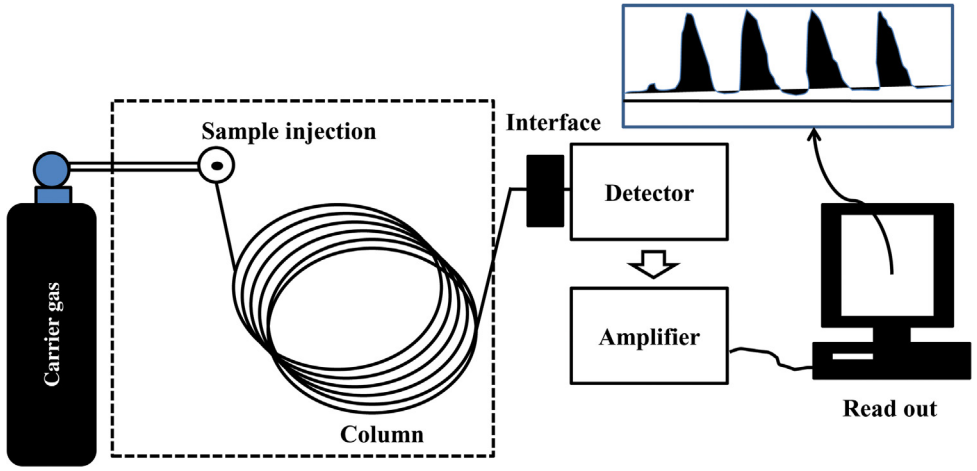

FIGURE 2.1 Schematic diagram of GC.

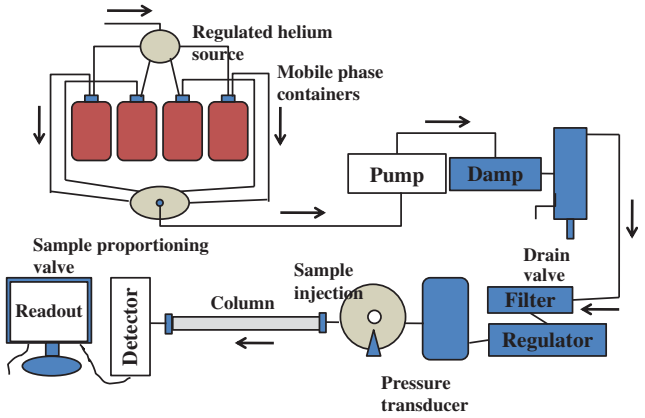

FIGURE 2.2 Schematic diagram of HPLC [15].

Cremer's laboratory that developed the first complete gas chromatograph. Sweeley and Horning reported the use of film-coated inert support for use as the stationary phase. Touchstones reported the separation of estrogens and their detection by using an electron capture detector. Claesson and Ray worked the detector system for GC and reported the use of a thermal conductivity detector. In 1958 Lovlock used an electron capture detector. Harley, Nel, and Pretoriu introduced the flame ionization detector. Lovlock brought an argon ionization detector, which was actually based on the research of Jesse and Sadankis. In 1955 Scott described the hydrogen flame detector. Holmes and Morrell reported the use of the modified mass spectrometer for detection purposes in GC. Similarly, Gohlki used a time-of-flight mass spectrometer as a detector in GC. The use of GC/MS was in practice since 1957. Further, developments were reported in GC instrumentation and applications [6,16].

In 1958 Golay introduced the use of an open tubular column for increasing the efficiency of

gas chromatography. Improvements in GC columns were observed, when in the 1980s, the inner walls of the columns were coated with pure silica, made them sustainable to high temperatures. In the 1960s, Kirkland, Huber, and Horvath published their work on high-speed liquid chromatography, which is known today as high-performance liquid chromatography. Hamilton, Bogue, and Anderson had already reported their work regarding the separation of amino acid by using HPLC in the same year, but that was not much considered [6].

Kirkland had contributed much in terms of introducing new surface-coated porous stationary phases in HPLC. The use of enzymes and proteins as stationary phases in column for affinity HPLC was reported by Walters in 1985 [17]. Katz and Scott introduced the superspeed HPLC, which was able to separate the mixtures in a few seconds [18].

A great contribution was made by the DuPont in the establishment of practical instrumentation for HPLC. Various efforts were made from time to time to improve column efficiency and the detector system in HPLC. The detector used mostly was the UV detector; however, other detectors, such as the refractometer, fluorometer, and electrochemical detectors, were also introduced and used with the HPLC system for analysis [6]. The hyphenated techniques of HPLC such as HPLC-MS, HPLC-FTIR, HPLC-NMR were also reported, bringing tremendous development in the instrumentation and applications of HPLC.

Supercritical fluid was used a mobile phase in chromatography in 1960s, which added a new type of chromatography known as supercritical fluid chromatography [8]. Klesper was the first who reported the use of supercritical fluid chromatography in 1962 [19].

The introduction of fused silica capillary columns in supercritical chromatography has brought much advancement to this technique [20].

Proper instrumentation was available since 1985, which made the supercritical fluid chromatography a practical technique for separation purposes [6].

Among several other techniques of chromatography, countercurrent chromatography was the first reported by Ito and Bauman in 1970 [21], which was actually based on the process of the countercurrent extraction process used by Craig in 1949 [22].

Likewise, the advancement of other chromatographic techniques in the instrumentation and applications of countercurrent chromatography is ongoing, reaching the stage of coupling with advanced detection systems such as the countercurrent mass spectrometer system, as reported in 1990 [23].

2.3 Development in the field of spectroscopy

Spectroscopy is based on the measurement of absorbed or emitted electromagnetic radiation. EMR is divided into several types based on the range of wave length and energy, as well as the effect they cause. Table 2.1 represents different EMR sources along with their properties and effects. Absorption methods are classified as (1) visible spectrophotometry, (2) ultraviolet spectrophotometry, and (3) infrared spectrophotometry. Atomic spectroscopy involves the measurement of absorption or emission of electromagnetic radiations from atomic species [3].

The molecular spectroscopic techniques such as visible, ultraviolet (UV), infrared (IR), and nuclear magnetic resonance (NMR) spectrometry are well-known analytical techniques that measure, both quantitatively and qualitatively, the interaction of electromagnetic radiation with matter, contrary to mass spectrometry, which does not involve a similar interaction. However, in mass spectrometry, the data is presented in the same manner, and

TABLE 2.1 Different EMR sources with their properties and effects [24].

EMR	Wavelength range λ (m)	Energy per mole	Molecular effect
Alpha rays	$\leq 1 \times 10^{-12}$	$\geq 10^6$ kcal	Ionization
Gamma rays	1×10^{-12}	$\sim 10^6$ kcal	Ionization
X-rays	1×10^{-10}	$\sim 10^4$ kcal	Ionization
UV	1×10^{-8}	$\sim 10^2$ kcal	Ionization/electronic transitions
Visible	0.5×10^{-6}	~10 kcal	Electronic transitions
Infrared	1×10^{-5}	~1 kcal	Molecular vibrations
Microwave	1×10^{-2}	$\sim 10^{-2}$ kcal	Rotational motion
Radiowave	1×10^{3}	$\sim 10^{-6}$ kcal	Nuclear spin transitions

MS is therefore also considered a spectroscopic technique.

2.3.1 Development of ultraviolet visible spectrometry

In ultraviolet visible (UV-Vis) spectroscopy, the iteration of UV-Vis radiation with molecules is studied for the purpose of interpreting quantitative and qualitative results. This techniques evolved from ancient observations of colored phenomena. The history of spectroscopy traces back to the study of various colors of the rainbow. The actual history of spectroscopy begins in the 17th century, when in 1666, Sir Isaac Newton attempted to study the nature of light, hoping to determine the origin of the colors of the rainbow that had been under observation for thousands of years. Newton passed a ray of sunlight through a prism and observed the splitting of light into a regular series of various colors, which were again converted into white light by passing it through a prism in the inverted position. From these experiments, Newton concluded that white light was made up of different colors fused together. The word "spectrum" was first coined by Sir Isaac Newton to illustrate the rainbow of colors that mingle to form white light. Joseph von Fraunhofer carried on the experiments with dispersive spectrometers, which enabled spectroscopy to become a more precise and quantitative scientific technique in the early 19th century. The use of a prism by the Romans to generate a rainbow of colors and the works of various scientists such as Athanasius Kircher (1646), Jan Marek Marci (1648), Robert Boyle (1664), and Francesco Maria Grimaldi (1665) provided the basis for Sir Isaac Newton's experiments [24–26]. In 1609 Galileo Galilei made the first telescopic discoveries and reported them in 1610 [27].

In 1802 William Hyde Wollaston improved Newton's model. Wollaston built a spectrometer consisting of a lens and using a narrow slit in place of a round aperture. Wollaston observed that the focused sunlight was split into a series of colors with no uniformity and had dark bands acting as natural boundaries between the colors. However, a decade later, in 1815, this hypothesis was rejected by a German optician, Joseph von Fraunhofer, who studied the dark lines in more detail. Fraunhofer used a convex lens between the prism and slit and achieved a better defined series of images. To study the angular position of the lines precisely, Fraunhoper utilized a telescope to view the spectrum, and this resulted in the

development of the spectroscope. Fraunhoper used this spectroscope for observing the pattern of lines in the light coming from the sun and stars. He observed more than 500 dark lines in the solar spectrum and classified them as A to H for being in the red and in the violet regions, respectively. The work of Fraunhoper was further extended by Anders J. Ångström, who in 1868 measured the wavelength of 1000 Fraunhoper lines and represented them in units of 10^{-10} m—now known as 1 Å (Ångstrom) after his name [27,28].

Spectroscopic techniques were gaining more focus, and other scientists published their work [29]. In the 1820s, John Herschel and William H. F. Talbot did experiments to systematically observe salts using flame spectroscopy. In 1822 Sir John Herschel studied the visible spectra of colored flames and concluded that the color of the flames can be used to analyze different objects. This work formed the basis for the Kirchhoff and Bunsen studies.

In 1835 Charles Wheatstone illustrated that in the emission spectra of various spark metals are bright lines that could easily distinguish the metals, thus introducing another mechanism for flame spectroscopy [30]. In 1849 J. B. L. Foucault reported that for the same materials, the absorption and emission lines appear at the same wavelength. Ångström studied the emission spectrum from hydrogen, later named Balmer lines [31,32]. In 1854 and 1855 David Alter reported his study on the observation of the Balmer lines of hydrogen as well as several metals and gases [33].

In 1859 Gustav Kirchhoff presented a theory to explain the Fraunhofer lines in the sun's continuous spectrum. Kirchhoff drew a conclusion that a substance would absorb and emit light of the same wavelength. While explaining Fraunhofer's lines, he stated that the dark lines in the solar spectrum were due to the absorption of lines matching the emission lines if the gases were otherwise excited [34].

In 1860s Bunsen and Kirchhoff recognized the relation between chemical elements and their unique spectral patterns and hence established the technique of analytical spectroscopy. In 1860 they reported their findings on the spectra of eight elements and their presence in several natural compounds [34].

For instance, in 1861, Kirchhoff and Bunsen discovered cesium and rubidium, and Sir William Crookes discovered thallium. Pierre-Jules-Cesar Janssen observed a new yellow line in the solar spectrum, which was identified as a new color line due to a new element, named helium by Sir Norman Lockyer and chemist Edward Frankland.

In 1885 J. J. Balmer interpreted for the first time that the visible line spectrum of hydrogen has emission wavelengths at 6563, 4861, 4341, 4102, and 3970 A°. In 1913 Niels Bohr proposed the idea of energy in the electronic states. He reported that electrons emit or absorb energy during transition that is equal to the energy difference between the two transition states.

The worth of elucidating visible emission spectroscopy in the electronic structure of matter led to an important breakthrough in analysis. In 1913 August Beer presented his famous law, which defines the relationship between absorption and concentration. The unknown concentration of the colored solutions was derived from the transmitted light by comparing it with standard samples of the same nature. However, the human eye was not accurate enough and was replaced with a detector calorimeter or spectrophotometer in the 1930s [24,27].

In 1801 UV radiation was first observed by a German physicist J. W. Ritter. Ritter was working on the effect of the visible spectrum on silver chloride salt and noticed that violet light caused a darkening of the salt. He further observed that the darkening was more in the region beyond the visible region, and hence he named it the ultraviolet region. In 1947 Varian produced the first combined spectrophotometer, called Cary 11 [27].

In 1895 the X-ray was discovered by the German physicist W. C. Röntgen, which led to

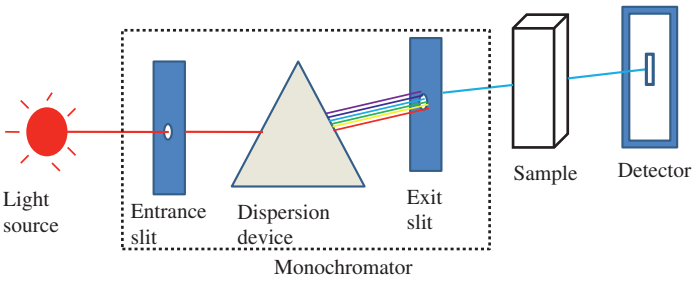

FIGURE 2.3 Schematic diagram of UV-Vis spectroscopy.

TABLE 2.2 The spectral regions of UV-Vis spectroscopy.

Regions	λ(nm)	Absorbing compounds
Far ultraviolet (vacuum UV region)	<190	Saturated and monounsaturated
(Near) ultraviolet	190–380	Polyunsaturated and aromatic
Visible light region	380–780	Colored

X-ray spectroscopy. In 1896 A. H. Becquerel discovered radioactivity, and P. Zeeman observed the splitting of spectral lines by a magnetic field [27].

In 1900 Frank Twyman developed the first commercial quartz prism spectrograph, and in the same year, time-resolved optical emission spectroscopy was reported. In 1947–48 the first commercially available optical emission spectrometers with photomultiplier tubes as detectors were produced. In 1937 the first fully automated spectrometer was developed by E. Lehrer. for more accurately measuring spectral lines. The introduction of more advanced instruments such as photodetectors brought accuracy in the measurement of the specific wavelength of the substances. In 1958 he invention of the laser contributed to the start of modern spectroscopy [27].

In 1963 the invention of annular inductively coupled plasma (ICP) by S. Greenfield and coworkers had an enormous impact on the progress of instrumental analysis. Spectrometers with ICP were commercially available in 1974 [27].

The schematic representation of UV-Vis spectroscopy is given in Fig. 2.3. The purpose of a radiation source is to provide the desired range of radiation necessary for electronic transition.

UV-Vis EMR is classified into different regions shown in Table 2.2. Similarly, various types of transitions caused by UV-Vis EMR in different types of molecules are given in Table 2.3. Stable UV and visible radiation sources with different wavelength ranges have been introduced. Various UV radiation sources are deuterium lamp, hydrogen lamp, tungsten lamp, xenon discharge lamp, and mercury arc lamp. Examples of visible radiation sources are tungsten lamp, mercury vapor lamp, and carbonone lamp.

Radiation sources usually emit polychromatic light from which the radiation of a specific wavelength is selected by a filter or monochromator. The monochromator contains entrance and exit slits, collimating and focusing lenses, and a dispersing device, which is usually a prism or grating.

TABLE 2.3 The spectral regions of UV-Vis spectroscopy.

Transition	Molecules
$\sigma \rightarrow \sigma^*$	Alkanes
$\sigma \rightarrow \pi^*$	Carbonyls
$\pi \rightarrow \pi^*$	Unsaturated compounds
$n \rightarrow \sigma^*$	O, N, S, halogen-containing compounds
$n \rightarrow \pi^*$	Carbonyls

The sample is put into a cell made of material that is transparent to UV-Vis radiation. In visible-range glass, cuvettes made of plastic or quartz are used, whereas in UV, only quartz or fused silica is recommended as glass or plastic absorb radiation in the UV range. Although usually cells of rectangular shape with a 1-cm path length are used, they are available in various shapes and sizes.

After passing through the sample container or cell, the radiations are directed toward detectors for measuring the transmittance and absorbance for data acquisition. Three types of detectors are used in UV-Vis spectroscopy, including photovoltaic cells, phototubes, or photoemissive tubes and photomultiplier tubes. The photomultiplier tube is a sensitive detector and is a commonly used detector in UV-Vis spectroscopy [2].

2.3.2 Development of infrared spectrometry

Infrared (IR) spectroscopic techniques are based on the principle that the infrared region EMR (10,000−200 cm^{-1}) are passed through molecules, causing stretching, bending, or rotation of the bonds. This bond length or bond angle variation occurs in various functional groups of molecules at specific frequencies of IR radiation. The characteristic frequencies and the change in bond length and/or angle are used for analytical purposes. The IR radiation lies near the visible range, and, on the basis of this relation, the IR range is divided into three groups: near IR (number ranges from 14,000 to 4000 cm^{-1}, and wavelength ranges from 0.8 to 2.5 mm); mid-IR (wave number 4000 to 400 cm^{-1} and wavelength 2.5 to 25 mm); and far IR (wave number 400 to 10 cm^{-1} and wavelength 25 to 1000 mm). All molecules are not IR active; the only molecules that are IR active are those containing polar bonds, composed of atoms of different elements, and organic compounds and inorganic compounds (H_2O, HCl, salts, NO_2, CO_2) [35,36].

The IR region of EMR was discovered by Herschel in 1800. Herschel observed the presence of radiant heat ahead of the visible region of the solar spectrum. However, Herschel did not study this phenomenon further, and in 1882, Abney and Festing measured the IR absorption spectra for more than 50 compounds and assigned spectral bands to the presence of various organic groups in the molecules. Julius documented the spectra of 20 organic compounds and interpreted that methyl groups absorbed IR at their characteristic wavelengths. Over decades in 1903, W. W. Coblentz performed several measurements and analyzed the IR spectra of hundreds of compounds. However, there were many complications and hurdles in the measurements with IR spectroscopy, which were usually conducted at night due to presence of daylight, and the analysis was very time-consuming as well. This was why IR spectroscopy was not very applicable until the 1940s [35,37,38].

During the late 1930s, Richard S. Perkin and Charles W. Elmer established the Perkin-Elmer Corporation in the United States. In 1937 they constructed optical elements for a prototype IR. The Perkin-Elmer instrument was one of the first infrared spectrometers (Model 12). The Beckman Company also built their Model IR-1 instrument at the same time. Commercially available IR spectrophotometers give the

fingerprints of almost all molecules except for optical isomers.

Different types of IR radiation sources are used based on their range of operation. Silicon carbide is used as a radiation source for measurement in the mid-IR region (5000–400 cm^{-1}). A tungsten halogen lamp is used for near IR radiation (10,000–4000 cm^{-1}). A mercury discharge lamp is used for measurement within the far IR range (200 cm^{-1}).

Pyroelectric detectors are commonly employed in mid-IR spectrometers. Cooled photoelectric detectors are also used that have higher sensitivities and shortened response times. Liquid nitrogen—cooled mercury cadmium telluride detectors are the most widely used in the mid-IR range. Interferometer (Fig. 2.4) is used to obtain interferograms. In the near IR region, uncooled indium gallium arsenide photodiodes are utilized. In the far IR range, liquid helium—cooled silicon or germanium bolometers are the detectors of choice.

Several types of beam splitters are used in IR spectrometers. The KBr-made beam splitter is useful up to 400 cm^{-1}. However, when it is coated with CsI, its range extends to about 200 cm^{-1}. ZnSe-based beam splitters are useful up to the range of 500 cm^{-1}, and these may be effected by water vapor. In the near IR region, the CaF_2-made beam splitter is employed, but its range of use is only up to 1200 cm^{-1}. Far IR beam splitters are generally made of polymer films and are used in a limited wavelength range [35,36].

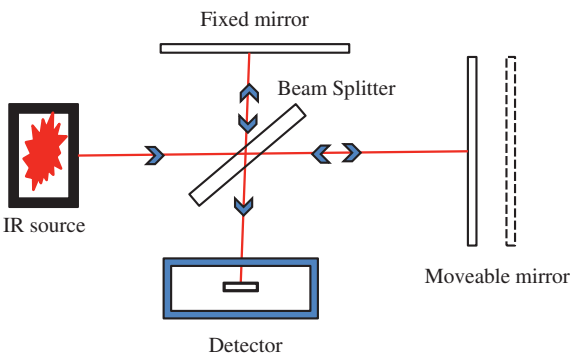

FIGURE 2.4 Diagram of Michelson interferometer using IR spectrophotometer.

2.3.3 Development of nuclear magnetic resonance spectrometry

Nuclear magnetic resonance (NMR) spectroscopy is based on the principle that the sample is placed in a magnetic field that causes excitation of the NMR active nuclei. The changes in the local magnetic field of the nuclei are detected for analytical purposes. The change in resonance frequency appears due the change in the intramolecular magnetic field around an atom in a molecule. These changes are detected for identification of functional groups and the electronic structures of molecules. Proton NMR and ^{13}C NMR are common practices; however, it is applicable to any kind of molecule that has nuclei with spin. The discovery of the Zeeman effect in 1896 laid the foundation of NMR spectroscopy. The concept of NMR development spectroscopy originated in 1924, when Wolfgang Pauli first recognized the magnetic properties of nuclei. It was observed that atoms with nuclei possessing angular momentum had magnetic moment and that they could absorb specific radio frequency waves when kept in an external magnetic field. In 1946 Felix Block at Stanford and Edward Purcell at Harvard conducted the first successful NMR, and both were jointly awarded the Noble prize in 1952. Scientists also tried to determine resonant field-frequency relationships for the calculation of magnetic moments. In this regard, Yu and Proctor measured the magnetic moment of 14 N nuclei and expected the presence of single strong peak, but they observed two peaks of the same intensity. Similarly, Yu and Proctor also observed multiple peaks for antimony while studying its magnetic moment. Hahn and Alichter observed the same phenomenon and coined the term "spin interaction mechanism."

In 1951 the predicted chemical shift phenomenon was verified by Packard and coworkers. They recorded the chemical shift data of ethanol and its interpretation for its structural elucidation. James Shooley recognized the important applications of NMR in chemical analysis. In 1952 Shooley joined the Varian Corporation, and the first commercial 30-MHz NMR instrument HR-30 was produced by Varian Corporation in 1953. Within only five years, other models, such as 40 and 60 MHz, were also introduced. Currently, NMR instruments of various resolutions and natures are commercially available and are considered sophisticated instruments for chemical analysis. The resolution of NMR is dependent on the magnetic strength of the magnet used in the NMR spectrometer. Modern NMR spectrometers have a strong liquid helium—cooled superconducting magnet that is large and very expensive. There are two types of NMR instruments: the continuous wave NMR (CW-NMR) and Fourier transform NMR (FT-NMR). Earlier, the CW-NMR was mostly used; however, after the introduction of the Fourier transform NMR in 1970s, it dominated the market due to its high sensitivity. In CW-NMR, the sample is held in a strong magnetic field, the frequency of the source or the strength of the magnetic field is scanned, and its effect on nuclei spin is noted and the data is generated. FT-NMR records many spectra at a time and transforms them into a single data. This decreases the noise ratio and increases the sensitivity [24,39,40].

A typical NMR instrument consists of a superconducting magnet, sample cell, sweep coil, radio frequency transmitter, radio frequency receiver and amplifier, and readout device.

2.3.4 Development of mass spectrometry

Mass spectrometry (MS) ionizes chemical species and analyzes them by measuring their mass-to-charge ratio. MS is basically used to measure the masses of the analyte species, which are then used for their qualitative analysis. This has a broad history; however, a brief description is given here. Following the cathode ray experiments conducted by Julius Plucker in 1858 and the discovery of electrons in 1886, Eugen Goldstein conducted similar experiments using a perforated evacuated discharge tube. Goldstein noticed a second beam passed straight through the perforated discharge tube. A few years later, Wilhelm Wein clarified the nature of these rays as positively charged particles, which were further studied by J. J. Thomson in 1907. The mass spectrometer origin came in 1912, when Thomson made a positive ray analyzer, or parabola mass spectrograph. In the presence of parallel electric and magnetic fields, the depletion of positive ions was noticed, which was dependent on their mass-to-charge ratio. Thomson was the first to record a mass spectrum. F. W. Aston enhanced the performance of the mass spectrograph by commencing velocity focusing. This development improved resolution, and the spectrograph was able to make isotopic mass measurement more precisely. However, in 1918, Dempster used an entirely different design for his work, which was the first true mass spectrometer. Dempster used a heating filament for bombarding with electrons for ionization purposes, focusing the beam of ions at the detector. Further development was made in mass spectrometry instrumentation to achieve a broad range of analysis [24,41,42].

A typical MS consists of an ionization source, accelerating slits, deflection chamber surrounded by a magnetic field (analyzer), detector, amplifier, and a readout device. The diagrammatic representation of the MS system is given as Fig. 2.5.

- Sample injection: HPLC, GC, syringe, plate, capillary
- Ionization sources: The function of the ion source is to produce gas phase ions. Various ionization sources used are electron

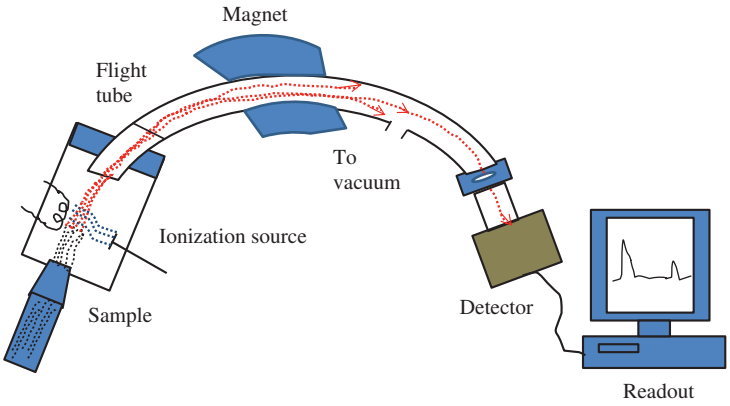

FIGURE 2.5 Diagrammatic representation of a mass spectrometer.

ionization (EI), chemical (CI), spray ionization (APCI, APPI, ESI), desorption ionization (FAB, MALDI, SALDI), gas discharge ion sources (e.g., inductively couple plasma), ambient ionization (DESI, LAESI).

- Analyzers: The function of the analyzer is to analyze, or separate, the ions according to their m/z (mass-to-charge) ratio. Commonly used analyzers are sector, quadrupole, TOF, Orbitrap, FTICR.
- Detectors: To convert masses to signals, detectors are used. Photoplate, Faraday cup, electron multipliers (MCP), solid-state, image current are used as detectors in MS.

2.3.5 Development of luminescence spectroscopy

A radiated material emits light either through incandescence (all atoms emit light) or through luminescence (only certain atoms emit light). Luminescence is of two types: fluorescence and phosphorescence. The spectroscopy that is based on type of luminescence is generally known as luminescence spectroscopy. Fig. 2.6 shows the general emission process responsible for the luminescence phenomenon.

Phosphorescence is a form of luminescence that happens when excited electrons of a different multiplicity from those in their ground

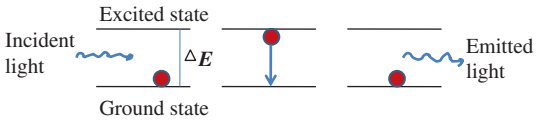

FIGURE 2.6 Phenomenon of emission.

state come back to their ground state through the emission of a photon. It is a spin-forbidden process, but it has applications across several fields.

"*Phosphorus*" was the ancient Greek term stand for "the light bearer," The term "phosphorus" has been used since the Middle Ages to designate materials that glow after exposure to light. A singlet or a triplet state can be created when one couple of electrons in a molecule is excited to a greater energy state. So, in the excited singlet state, the rotation of that excited electron is still contrary to that of the remaining electrons, though the spins of the two electron become unpaired and are thus parallel in the triplet state. Electronic spin states involved in fluorescence and phosphorescence phenomena in molecules are shown as Fig. 2.7. In the ground state, the spins are always paired; thus it is the single state. In the excited level, if this spin remains paired in the excited state, then it is a excited singlet state, but if the spin becomes unpaired, the molecule is in an excited triplet state. The transition of

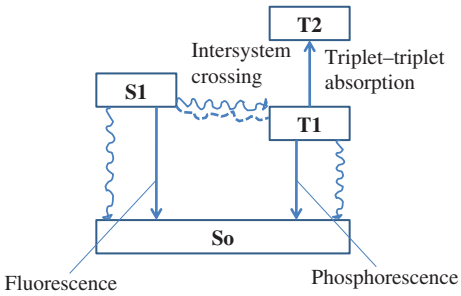

FIGURE 2.7 Mechanisms in luminescence spectroscopy.

electrons from an agitated triplet state to the grounded singlet state produces molecular phosphorescence. Because the triplet—singlet transition produces a change in electron spin, it is much less feasible. As a result, the triplet sate has a much longer lifetime. The long lifetime of phosphorescence is also one of its drawbacks. Because the excited state is relatively long-lived, nonradiational processes have time to compete with phosphorescence for deactivation. Therefore the efficiency of the phosphorescence process, as well as the corresponding phosphorescence intensity, is relatively low. So, of the many of the earliest studies of shining in dark minerals, the best known is that of Bolognian phosphorus (barium sulfide in impure form) studied in 1602 by a cobbler from Bologna, Vincenzo Cascariolo. Later in 1677, a similar designation was allotted to the element phosphorus, separated by Brandt, because, when exposed to air, it burns and releases a shining vapor. Historically, phosphorescence and fluorescence were distinguished by the amount of time after the radiation source was removed that luminescence remained. Fluorescence was defined as short-lived chemiluminescence, whereas phosphorescence was defined as longer-lived chemiluminescence. The instrument used for phosphorescence, called the phosphor scope, was devised in 1857 by Alexander Edmond Becquerel, a pioneer in the field of luminescence. By that time, phosphorescence could persist for seconds through minutes or even longer. The spectrum of phosphorescence is situated at wavelengths greater than the spectrum of fluorescence since the energies of the lower vibrational state of the triplet level T1 is lower than that of singlet level. The basic instrumentation for phosphorescence is similar to that of fluorescence. Two types of phosphoroscrope are used for the measurement of phosphorescence. Rotating disk phosphorescence (RDP) involves two rotating disks with holes, into which the sample is placed to be analyzed. When a beam of light penetrates one of the disks, the sample is electronically excited and can phosphoresce, and a photomultiplier records the intensity of the phosphorescence. The rotating can phosphor scope (RCP) consists of a rotating cylinder with a window to allow the passage of light. The sample is placed at the outside edge of the can, and when the light pass through the window and the sample is excited electronically, the intensity is measure via the photomultiplier. The advantage of RCP or RDP is that, at high speeds, RCP can minimize other types of interferences such as fluorescence, and RDP can minimize Raman and Rayleigh scattering of photons, in a typical phosphorescence-intensity-versus-emission-wavelength spectrum of fluorinated acetophenone compounds [2,43,44].

2.3.6 Development of atomic absorption spectroscopy

The study of EMR interaction with atomic gaseous forms of elements is used for the analysis of numerous metals and scarce nonmetals. Nearly all metal elements can be quantitatively examined by utilizing the spectral absorption features of atoms. This is a very simple and reliable method that can analyze more than 60 elements. In 1860 with the effort of Bunsen and Kirchhoff, spectrochemical examination was invented, but it had comparatively few uses

until the 1930s. Arc and spark emissions and, to some degree, flame emission techniques then became well-known. Due to the efforts of Walsh in 1955, the modern period of atomic absorption spectroscopy started in Australia, due to the work of Alkemade and Miltz in Holland. From 1955, the period can be separated into seven-year periods: the induction time (1955–62) when atomic absorption received rare attention from the public; a growth time (1962–61) when most of what we see nowadays was established; comparative stability (1969–76) when the contribution of atomic absorption was great compared to other methods. So we are today in an era of ongoing change that was initiated around 1976, owing to the impact of computer technologies on laboratory instruments. Currently such technologies are extensively utilized due to their ease of use, efficiency, and relatively lower price. The initial atomic absorption spectrometer was constructed by CSIRO (Commonwealth Scientific and Industrial Research Organization) in 1954 by Alan. The initial marketable atomic absorption spectrometer was presented in 1959. The method used the basic phenomenon that free (gas) atoms are produced in an atomizer and can absorb radiations at precise frequencies. The method qualifies the absorption of the ground-level atoms in gaseous form. The particles absorb visible light or ultraviolet and produce transitions to greater electronic energy states. The concentration of analytes is examined by the quantity of absorption [2,3,27,45,46].

A typical atomic absorption spectrophotometer consists of a radiation source, nebulizer, atomizer, monochromator, detector, and readout device. Fig. 2.8 shows the general mechanism of atomic absorption spectroscopy. Atomic absorption methods are potentially very precise because atomic absorption lines are extraordinarily narrow (0.002–0.005 nm) and, for every element, electronic transition energies are specific. In atomic absorption, the most commonly used two line sources are hollow cathode lamps and electrodeless discharge lamps. The most often used emission of radiations source is the hollow cathode lamp inn atomic absorption spectroscopy. It contains a hollow cylindrical cathode and a tungsten anode consisting of the elements to be examined. These are enclosed in a glass tube occupied by an inactive gas (argon or neon). At a pressure of 1–5 torr. If a 300-V potential difference is applied through the electrodes, then argon ionizes, and the electrons and the cations of argon migrate to the two electrodes, and a current of 5–10 mA is generated. When the potential is great enough, the cathode is struck by the cations with adequate energies to free some of the metal atoms and to form an atomic cloud. This procedure is known as sputtering. These sputtered metal atoms are in agitated states and release their characteristic radiation as they come back to ground level. Eventually, the metal atoms are diffused back to the surface of the cathode or to the walls of the glass tubes and are redeposited. In addition, to hollow cathode lamps, electrodeless discharge

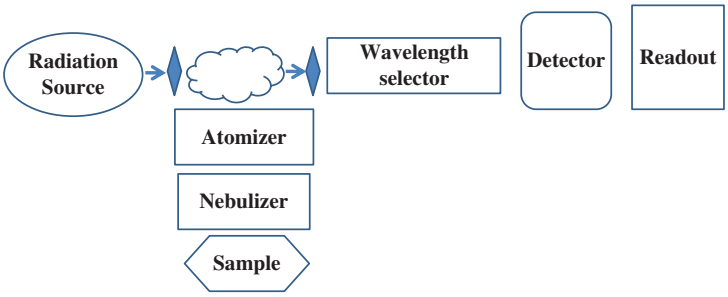

FIGURE 2.8 Flow sheet diagram of atomic absorption spectroscopy.

lamps are valuable in atomic line spectra. A typical electrodeless discharge lamp is built from closed quartz tubes comprising an inactive gas such as argon at a few torr pressure and a lesser amount of analyte metals (or its salt). The lamps contain no electrodes; in their place, the lamp is energized by a penetrating field of microwave radiation or radio frequency. The argon ionizes in this area, so the ions are enhanced through the greater frequencies constituting the field until they achieve adequate energies to agitate the atoms of the analyte metals. Electrode discharge lamp are available commercially for several elements. They are particularly useful for elements such as, Se, and Te, where hollow cathode lamp intensities are low. Every element has its own advance lamp that should be utilized for the analysis. A special high-pressure xenon short arc lamp is also used as a continuous source of radiation. There are numerous significant features of the nebulizing part of the burner arrangement. In order to deliver effective nebulization for every kinds of sample solution, the nebulizer must be adaptable. Stainless steel has been the usual material utilized for the manufacture of the nebulizer. Stainless steel has the benefit of strength and low cost, and it resists corrosion from samples with a great constituent of acid or other corrosive substances. For these issues, vaporizers assembled of a corrosion-resistant material, such as an inactive platinum, plastic, or tantalum, would be used [2,3,27,45,46].

Various types of nebulizers have been introduced such as pneumatic nebulizers, impact bead nebulizers, ultrasonic nebulizers, pulse nebulizers, and Babington nebulizers. The two major types of nebulizer burners used in AAS are the premix nebulizer burner and total consumption burner. In the premix burner, liquid is sprayed into a mixing chamber where the droplets are mixed with the combustion gas and sent to the burner. In the total consumption burner, the nebulizer and burner are combined. This is also called turbulent flow burner. These burners are widely used for atomic emission measurements. The element to be examined needs to be in the atomized state. Atomization is the isolation of elements into separate particles and division of molecules into atoms. It is completed by exposing the analytes to higher temperatures in a graphite furnace or flame. The commonly used vaporizers are flame atomizers and graphite tube atomizers. However, other atomizers, such as electrochemical, hydride, cold vapor, and glow-discharge atomizers, might be used for special purposes. It is very significant portion in AA spectrometers and is used to isolate thousands of lines. The monochromator is utilized to choose the exact wavelength of light that is absorbed through these samples and to eliminate extra wavelengths. The examination of the designated elements in others is found by the selection of precise light. Most commercial AAS instruments use diffraction grating as monochromators. The light chosen through the monochromator is focused on the detector, which is normally a photomultiplier tube, the function of which is to change the light signals into an electrical signal in the direct proportion to the light intensities. The commonly used detector in AAS is the photomultiplier tube. It is a photovoltaic cell consisting of a series of cathodes called dynode and anode. The readout system includes meters, chart recorders, and digital display meters. Modern instruments provide a fast display of experimental conditions, absorbance data, statistical values, calibration curves, and the like [2,3,27,45,46].

2.3.7 Development of atomic emission spectroscopy

When energies in the form of heat or light are applied, the molecules are motivated to high-energy states and move from lowest-energy states to the highest-energy states, so

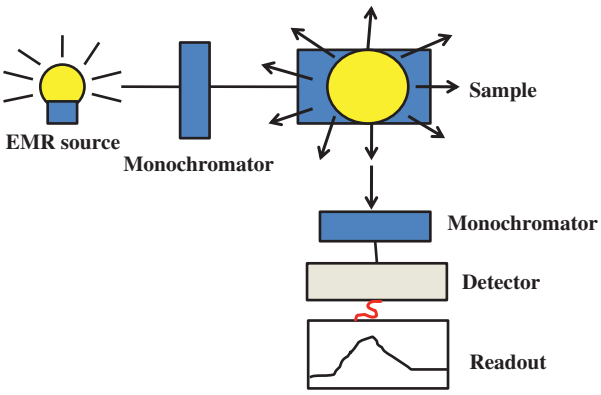

FIGURE 2.9 Flow sheet diagram of fluorescence spectroscopy.

molecules are unstable at this level. Consequently, the agitated molecules jump from the highest-energy states to the lowest-energy states, releasing radiation. The energies are emitted in the form of photons. The radiations are noted in the emission spectrometer. The change among the constituents in the agitated and lowest level is the level of emissions of a substance. Every element has a distinct and specific level of emission that benefits the experts in identifying the elements. In the 20th century, Max plank decided that energies might be emitted or absorbed irregularly in the form of packs of energies called quantas. A photon of energy is released when the particle jumps down from the highest-energy state to the lowest-energy state. The spectra gained are named "emission spectra," and the spectroscopy is called atomic emission spectroscopy (EAS). Fig. 2.9 shows the simplified mechanism of AES. AES is a method used to examine the component amounts in the samples by means of the intensities of light released by spark, flame, plasma, or arc. In AES, the samples are useful with light or heat energies. The sources of energies could be plasma, flame, or electric arc. Every component has dissimilar emission levels and provides the forecast of the dissimilar elements in the sample. Lines of emission from hot gases were initially studied by Ångstrom, and the method was then advanced by Robert Bunsen and David Alter Gustav Kirchhoff [2,24,27].

Atomic emission spectroscopy has a long history. In 1550 qualitative applications of atomic emission spectroscopy produced in the color of flames were cast off for the first time in the smelting of raw material. They were then completely established with the studies of atomic spectra produced on spark emissions and flame emissions in 1830. Quantifiable uses of atomic emission spectroscopy based on the electric spark were established by Lockyer in 1870. Quantitative uses of flame emission established in 1930 were found by Lundegardh. Atomic emission established upon production from plasma was presented in 1964 [2,27,45].

Atomic emission has been used dependent only on flame arc or spark excitation sources. Improvement is made by the introduction of noncombustion plasma source.

Instrumentation:

Light source: DC arc, AC arc, spark, ICP
Spectrometer: Monochromator optical-direct read spectrometer, polychromatic optical—direct read spectrometer
Detector: Spectrograph, photomultiplier tube (PMT), segmented-array charge-coupled detector (SCD)
Readout: Gives signals or peaks

The instrument used for recording a spectrum is known as a spectrometer or spectrophotometer. The first step is atomization or excitation. In this step, a solid liquid or solution is converted into gaseous atoms. The sample is excited by absorbing energy and then emits it by releasing radiation in the form of electromagnetic radiation, which may be thermal or electrical. It is necessary that only the emitted radiation is collected and analyzed and then recorded. In case of emission spectrometer no analyzer is necessary, the source being its own analyzer. A monochromator is employed to separate radiations into individual wavelengths. The dispersing element used is a prism. The detector is the device that converts spectral radiation into an electrical signal that is transmitted to a recording device, called a recorder. The recorder prints the chart. It is essential that the detector does not receive radiation directly from the exciting beam and that the two are placed at right angles. A modulator is placed between the source of excitation and the sample, its function being only that the emission that directly arises from the excitation is recorded [2,45,47].

2.3.8 Development of plasma emission spectroscopy

This emission spectroscopy utilizes plasma as a source of atomization, and it is known as plasma emission spectroscopy. It has greatly enhanced the application of atomic emission spectroscopy. Plasma is a fog of extremely ionized gases, consisting of electrons, ions, and neutral species. Ions represent about 1% of the total proportion. Argon gases are commonly ionized by a sturdy electrical ground. The produced plasma may be inductively coupled plasma (ICP) or direct current plasma (DCP) depending on the source of the electric field. In DCP, the ionization is done in a discharge tube with a two- or three-electrode system. In ICP, three silica quartz tubes are utilized in which argon gas transmits the samples in the aerosol form. The radio frequency power is applied to the system to ionize the gas and produce plasma. ICP has more of a detection limit than DCP. Compared to flam emission spectroscopy, the plasma substance produces a large quantity of agitated released atoms in the UV range. Plasma emission spectroscopy results in better atomization conditions than arc and spark spectroscopy. Plasma spectroscopy can be used for multielement determinations on a broad concentration range. The sample solution is injected into the system through a nebulization system that is usually a cross-flow nebulizer or Babington-type nebulizer. Basically two types of spectrometers are utilized in plasma emission studies: the concurrent and the successive multielement spectrometers [2,3].

2.3.9 Development of atomic fluorescence spectrometry

An atom comprises a set of quantized energy states that can be attained by electrons depending on their energies. When atoms in ground state absorb EMR, they are excited toward the higher-energy level, or excited state. Then, after excitation, these electrons seek to relax back toward ground state by the emission of emitted radiations. In AFS, both absorption and emission occur in the UV range. AFS occurs in two steps: absorption and emission. In AFS, the minimum amount of analysis can be detected by the detector, which is in the range of femtograms to attograms. AFS is based on fluorescence phenomena introduced by Wood in 1905. Later in the development of AFS, an analytical method is attributed to West and Wineforder, who did the initial work in this area. The intensity of emitted light is measured with the help of the detector, which is placed in a direction perpendicular to

that of the radiation source. A spectrofluorometer or fluorimeter is used in AFS. In the spectrofluorometer, a monochromator is used (as wavelength selector) to quantify the intensities of released energy, whereas in the fluorimeter, a filter is used as a (wavelength selector) to quantify the intensities of released radiations. The sample solution (analyte) is thoroughly associated with electrogravimetry in coulometry, which is also founded on Faraday's law; the initial uses include examination of atomic weight and of tinny metal coatings. The amount of electric charge is a very ancient, possibly the oldest measurable "electroanalytical" technique; originally, electrolytic deposition electrolysis was designed for the quantification of currents or electric charges by the measurement of the number of electrolysis product(s) according to Faraday's law. A primary tool for this determination is using the electrolysis of water, as proposed by Michael Faraday himself and known as volta-electrometer. A coulometer is a tool utilized for determining the amount of electricity required to carry out a chemical alteration of the analytes. The usual exercise in coulometry is to insert the ammeter (which quantifies the current in electrical trials) with a coulometer. Iodine coulometer is a type of a titration coulometer in which an anodic alloy produced iodine is titrated with arsenic (III) or thiosulphate solutions. This is used in the study of the Faraday constant. Another example is the colorimetric coulometer, which is built on the principle of dying species with a substance with a metal ion that should be stripped anodically. For example, a cobalt ion species dyed with nitroso-R-salt and the quantification of absorbance with a spectrophotometer. Coulometry has progressed extensively and is categorized as follows: controlled-current coulometry (amperostatic), primary source coulometry, and secondary source coulometry-controlled potential (potentiostat) coulometric titration. See Fig. 2.10 for a schematic diagram of various kinds of cuolometric procedures. In

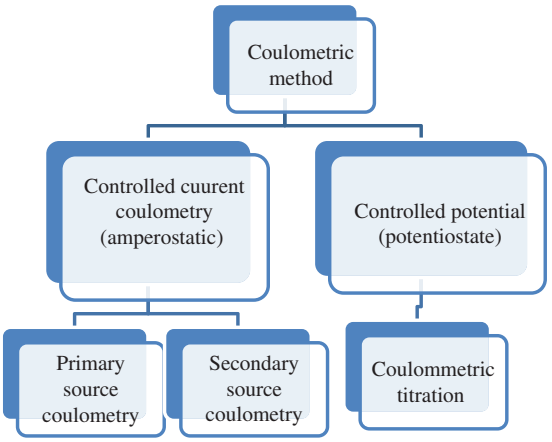

FIGURE 2.10 Schematic diagram of the various types of cuolometric methods.

controlled potential coulometry, the potential is kept constant in order to get maximum current efficiency so that the analytes react completely without involving interfering species. With progress in electrolysis, the concentration of analyte and the current decrease with time. The curve of current time is plotted and integrated. A three-electrode potentiostat is utilized to make the potential in controlled-potential coulometry [2,48–50].

2.4 Development of electroanalytical techniques

In 1801 William Cruikshank was doing electrolysis of aqueous solutions of copper salts and suggested the possibility of using current as a parameter for the analysis of metals. In 1830 A. C. Becquerel suggested the use of anodic deposition for the detection of lead and manganese. Buchner used galvanic electricity or electric discharge for analysis at almost the same time in the 19th century. In 1861 and 1865 Weyl developed quantitative electroanalytical procedures for the determination of carbon amounts in pig iron and steel. Jaroslav was awarded the Nobel

prize in 1959 for his discovery of and contributions to polarography. Faraday's law, the pH scale by Sorensen, the work of Haber and Klemensiewicz on glass electrodes, and the introduction of the carbon paste electrode by Ralph Adams have contributed much in the development of electroanalytical techniques [51,52].

2.4.1 Electrogravimetry

Elecrogravimetry is a quantitative electroanalytical technique. In electroanalytical techniques, the concept of quantitative analysis was started with the work of Wolcott Gibbs for the determination of copper and nickel using the electroanalytical precipitation method reported in 1865. This method was used for the determination of copper in copper nickel coins. This work was followed by Carl Luckow, who in 1865 separated and determined copper in the presence of Zn, Co, Ni, Mn, and Fe by the electrodeposition method. Although these were the initially reported methods for the quantitative determination of metals using electrogravimetry concepts, they were called electroanalysis, electrochemical analysis, or electrolytic analysis [51].

With the passage of time, modifications in the nature and construction of electrodes were made by different scientists. Nikolai Klobukov used the rotating electrode to save time. Heinrich Paweck and Clemens introduced the net-shaped platinum electrode. Gibbs suggested the mercury electrode, which was used by Luckow. The concepts of electrode potential for analytical purposes was studied by Hermann Freudenberg. In 1907 Henry Sand and Arthur Fischer introduced electrogravimetry with manually controlled potential. Alexander Claessens wrote the first book on electrogravimetry in 1882. Similarly, in 1890 E. F. Smith published a monograph with the name *Electrochemical Analysis* [51,53].

2.4.2 Coulometry

Coulometry is the name given to the group of analytical technique used to determine the amount of matter transferred during an electrolytic reaction by measuring the amount of current or electricity produced or consumed. Alternatively, the quantity of electrical charge to convert the sample analyte qualitatively to another oxidation state is measured. The coulometric method is usually rapid and does not require the product of the electrochemical reaction be a weighable solid. Closely related to electrogravimetry is coulometry, which is also based on Faraday's law; early applications include determinations of atomic masses and of thin metal layers. The measurement of electric charges is a very old, perhaps the oldest quantitative "electroanalytical" method, but originally electrolytic deposition electrolysis was aimed at the quantification of electric charges or currents by the measurement of the amount of electrolysis product(s) according to Faraday's law. A first instrument for this purpose utilizing the electrolysis of water was suggested by Michael Faraday himself, called volta-electrometer [51,52,54].

Michael Faraday introduced the first voltage measuring device, the volta-electrometer. Similarly, A. C. Becquerel and Johann Christian Poggendorff introduced the metal voltmeter for copper and silver, respectively. In mid-19th century, coulometry progressed when Hampe and Pfeiffer determined the atomic masses of elements by measuring their deposited masses as specific electric charges were applied. In 1893 Freudenberg, with the help of Max Le Blanc, introduced the electrolytic cell incorporated with silver voltmeter. Heinrich Danneel worked on the use of the coulometer for the determination of metals, but his work did not get much attention. Coulometric determination of the tin layer on copper wire was used by Grower in 1917. In this case, Grower used electrolytic cells,

coupled with a coulometer, for determination of free tin and alloyed tin on the surface of copper wire. This was followed by the work of Zbinden who in 1931 used stripping analysis while employing the electrolytic cell, coupled with a coulometer, to determine trace amounts of copper. In 1938 László Szebelledy and Zoltan Somogyi published their work of titration involving coulometric analysis. In 1942 Archie Hickling introduced the potentiostat, which resulted in rapid progress in the use of coulometry for analysis. In the 1960s, Claassen, Milner, and Philiphs worked on analytical coulometry and published the first monograph [51,54].

A coulometer is a device used for measuring the quantity of electricity required to bring about a chemical change in the analyte. It is usual practice in coulometry to substitute the ammeter (which measures current in electrical experiments) with a coulometer.

The iodine coulometer is an example of a titration coulometer in which anodically generated iodine is titrated with thiosulphate or arsenic (III) solution. This has been used in the determination of the Faraday constant.

Another example is the colorimetric coulometer, which is based on the principle of developing a colored species with a reagent with a metal ion that may be anodically stripped. For example, a colored species might be formed for a cobalt ion with nitroso-R-salt and measurement of absorbance with a spectrophotometer.

Coulometry has progressed extensively and is classified by the categories shown in Fig. 2.10.

In controlled potential coulometry, the potential is kept constant in order to achieve maximum current efficiency so that the analyte reacts completely without involving interfering species. With progress in electrolysis, the concentration of analyte, as well the current, decreases with time. The curve of current—time is plotted and integrated. A three-electrode potentiostat is used to set the potential.

In controlled current coulometry, the measurement is performed at a constant current instead of a constant potential. The relationship is drawn as a curve between current and time. Controlled current coulometry is advantageous over controlled potential coulometry in terms of taking less time and not needing the integration of the current—time curve [2,51,52,54].

2.4.3 Conductometry

Conductometry is used to analyze ionic species and to monitor a chemical reaction by studying the electrolytic conductivity of the reacting species or the resultant products. It has notable applications in analytical chemistry. Conductivity measurement can be performed directly by using a conductivity meter or by performing conductometric titration. Conductometric analysis of electrolytes is a long-time practice. Henry Cavendish and Andreas Baumgartner reported the analysis of mineral waters and salt solutions by using conductometric methods. Georg Quincke and Emil Warburg checked the water solubility of glasses. In the early stages, direct current conductometry was utilized, but that had the drawbacks of electrode polarization, and hence alternating current was used. Kohlrausch and Nippoldt used alternating current and took conductometric measurements without polarizing electrodes. Alternating current was applied for the determination of electrolytes in water, mineral waters, acids, and sugars. Kohlrausch and Berthelot used conductometric measurements to study chemical reactions. Whitney used conductometry to determine the end point in volumetric analysis. Kolthoff summarized the studies related to end point detection by using conductometric analysis. A special type of conductometric analysis, called telephone analysis was introduced by Bouty. In this type of conductometric analysis,

different electrolytic mixtures, including KCl, KI, K2SO4, among others, were studied using the telephone as the indicator. Kohlrausch, Holborn, and Kolthoff published early monographs on conductometric analysis [2,51,52,55].

2.4.4 Potentiometry

Nernst used potentiometric analysis in 1889 based on his famous equation regarding potentiometry. Behrend used potentiometry for the detection of end points in his volumetric analysis, working the titration of chloride and bromide with mercury nitrate. Bottger and Crotogino used the potentiometric method for end point determination of acid base and redox titrations, respectively. Ostwald's laboratory was mainly used for such experiments. The use of glass membrane electrodes led to much development to potentiometry. Cremer, Haber, and Klemenciewics studied the relation between the concentration of hydrogen ions and the potential across a glass membrane in 1909. This was followed by the introduction of the pH equation by Søren Peter Lauritz Sørensen in the same year. In 1937 Nikosky depicted the response of an ion-selective electrode for target ions in the presence of interfering ions. Michaelis, Kolthoff Clarke, Muller, Furman, and Jorgensen performed work on the determination of pH using potentiometry and reported their work in the first half of the 20th century. Jagner and Graneli introduced chronopotentiometric stripping analysis in 1976. Ernst Salomon studied and published the current–voltage curve in 1896. The current–voltage curve brought on much development in utilizing voltametry for analytical purposes. Salomon studied the relation between concentration and residual current. Nernst and Merriam described the theory of residual current and interpreted that the limiting current in the stirred solution corresponds to the diffusion current. Nernst and Brunner introduced the concept of limiting current, which is very important for analysis in voltametry, polarography, and amperometry [51,56].

2.4.5 Voltammetry

Voltammetry is a category of electroanalytical methods used in analytical chemistry and several industrial processes. In voltammetry, information about an analyte is obtained by measuring the current as the potential is changed. The result comes from the voltametric experiment in the form of voltammogram, which is plot of the current versus the potential of the working electrode. Voltammetry experiments investigate the half-cell reactivity of an analyte. Voltammetry is the study of current as a function of applied potential. These curves, $I = f(E)$, are called voltammograms. The potential is varied arbitrarily either step by step or continuously, or the actual current value is measured as the dependent variable. The shape of the curves depends on the speed of potential variation (nature of driving force) and on whether the solution is stirred or quiescent (mass transfer). Most experiments control the potential (volts) of an electrode in contact with the analyte while measuring the resulting current (amperes).

A number of voltammetric electrodes or cells are introduced and are used in industry and research. These electrodes are referred to as sensors, which are used for the analysis of various types of analytes in different media. Glucose sensors and oxygen electrodes are examples.

Voltametry has developed very rapidly, and several types have been introduced with high efficiency, sensitivity, and selectivities. Among several types, a few examples are linear sweep. cyclic, staircase, square wave, stripping, normal pulse, differential pulse, direct current, alternating current, polarography, and the like [2,51,57].

2.4.6 Polarography and analytical voltammetry

The voltametric technique uses droping mercury electrode (DME) as an indicator or a working electrode is known as polarography. It was first introduced by Jaroslav Heyrovsky in 1922 and earned the Nobel prize in chemistry in 1959. However, its development starts with the study of electrocapillary phenomena, where DME was used as the measurement. Jaroslav Heyrovsky and Masuro Skikata developed the first automated instrument, the polarograph, for analytical purposes. The polarograph was used for automatic recording of the current–voltage curve. Matheson and Nichols used the oscillograph for recording the current–voltage curve in 1938. Oscillograph was used for studying the potential–time curve in polarography. Although the term "oscillographic polarography" was given by Heyrovsky and Forejt, later literature reported this as chronopotentiometry. With the passage of time, differential polarography and derivative polarography were introduced for better analysis of analytes in the presence of interfering species. Different other modern polarographic techniques, such as cyclic, square wave, pulse, and differential polarography, were developed for analytical purposes. The use of stripping voltametry employing stationary DME was used for trace element analysis, starting in the 1950s. Heinz Gerischer used stationary DME in 1953 for electroanalytical purposes. The hanging DME (Kemula type) was introduced by Kemula and Kublik in 1956. Metallic substrates with mercury film were also used as electrodes. The carbon paste electrode was introduced by Adams in 1958. Analytical voltametry was promoted with the introduction of wax graphite, pyrolytic graphite, and glassy carbon electrodes by Miller and Zittelin in 1963 and 1965. The development of square-wave and pulse voltametry increased the sensitivity of voltametric techniques up to the nanomolar range. In these techniques, a two-step process is performed; in the first step, preconcentration of the analyte is done, followed by analysis. The preconcentration of methylene blue was performed by Kemula and his coworkers in 1961, and with this they determined its concentration in the range of $10-8$ M while working with DME. The preconcentration process prior to voltametric analysis was practically done by several researchers for both organic and inorganic species. The use of modified surface electrodes for analytical purposes was started in the 1970s. Cheek and Nelson used the carbon paste electrode for the determination of $Ag+$, and Oyama and Anson utilized the platinum electrode, modified with a polymer film, for analysis. Ravichandran and Baldwin were the first to float the idea of carbon paste electrodes for analytical purposes. A modified glassy carbon electrode has been employed for preconcentration and analysis of uranium (VI) [2,51,52,58,59].

2.4.7 Amperometry

In this type of electroanalytical technique, the current produced during a redox reaction is observed at a constant potential. Amperometry is conducted in a three-electrode system. Every analyte has a fixed potential for undergoing a redox activity. The potential required is applied, and the resultant current is measured. Amperometric titration is done in the same manner. At the fixed potential, the changes in current are measured as the titrant is added to the analyte solution. Sharp changes are observed at the end point. The concept of amperometry was strengthened after the work of Nernest and his coworkers on diffusion current and limiting current. Amperometry was used for oxygen determination in the 1930s and 1940s. With the passage of time, much progress has been made in the amperometric method of analysis. Different types of

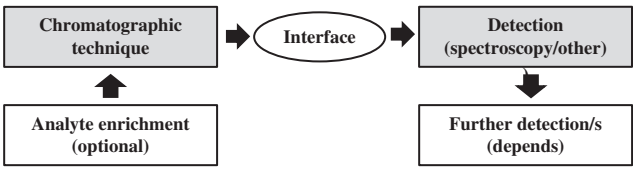

FIGURE 2.11 Block diagram of a dual-hyphenated technique [61].

amperometric methods have been introduced, such as single-potential or DC amperometry, pulsed amperometric detection (PAD), integrated amperometry. For amperometric titration, drop mercury electrode (DME), rotating platinum electrode (RPE), or twin polarized microelectrode (TPME) is used as the indicator electrode, while usually the saturated calomal electrode is used as the reference electrode. Various types of commercially available amperometers are vintage amperometers (about 1950) and (mechanical gauge) amperometers. Two types of detection methods are used in amperometery: single-potential amperometry or direct current amperometry and pulsed amperometry [2,51,59,60].

2.5 Hyphenated techniques

These techniques involve the coupling of chromatographic techniques with an online detection system, mostly spectroscopic methods, and they are called hyphenated techniques. Hirsch Feld in 1980 adapted the term "hyphenation" for two- or multiple-instrument techniques for analysis in a single run. The basic aim was to achieve purification, identification, and quantification simultaneously [2,61–65].

These techniques were developed to achieve quantification results and detection simultaneously. They have the advantage that, in a single run, separation as well as identification of the analyte is done. Hyphenated techniques are mostly automated, fast, and reliable compared to using chromatography followed by spectroscopy. A generalized diagram for hyphenated techniques is given as Fig. 2.11. The results are also mostly free from interference and are reproducible. Initially, double-instrument hyphenated techniques were introduced. However, over time, triple-hyphenated techniques were developed to get more reliable and accurate results for quantification and identification. Among the double-hyphenated techniques are LC-MS, LC-NMR, LC-IR, CE-MS, GC-IR, GC-MS, HPLC-DAD, and GC-FTIR, while triple- or multiple-hyphenated techniques include but not limited to LC-API-MS, APCI-MS-MS, ESI-MS-MS, LVI-GC-MS, LC-ESI-MS, LC-UV-NMR-MS-ESI, LC-MS-TSPLC-UV-NMR-MS, LC-NMR-MS, LC-DAD-API-MS, LC-PDA-MS, LC-PDA-NMR-MS, and SPE-LC-MS [61–63,66].

2.5.1 GC-NMR

The GC-NMR technique was introduced in the 1960s. In its early stages, the separated components of the sample coming from GC (gas chromatography) were introduced into an NMR (nuclear magnetic resonance) glass microtube through a syringe. In the 1970s, GC-NMR system was improved by flow cell NMR tubes for the introduction of separated sample components from GC into NMR. Although these two were not really hyphenated techniques, the first GC-NMR hyphenated technique was introduced in 1980 by Buddrus and Hertzog. In this attempt, the NMR tube was used in the form of a flow cell with both sides open, connecting GC with NMR. Over time, much development followed, and the on-flow and stop-flow modes were introduced [61,63].

2.5.2 LC-NMR

The LC-NMR system is used for the simultaneous separation and identification of NMR-active compounds present in complex mixtures of all types. LC-NMR has been recognized since the 1970s. Watanabe and Niki reported the first paper on LC-NMR in 1978. They used a stop-flow mode of LC-NMR for the qualitative analysis of a mixture of compounds. The first online LC-NMR was reported in the 1980s, and its implementation as a common laboratory technique of analysis was started in 1990s. The LC-NMR system works in two modes: continuous and stop-flow. Along with the NMR detection system, a UV-Vis detector is also used as a primary detector with the LC system for primary operations [61,63,67].

2.5.3 GPC-NMR

The hyphenation of on-flow or online gel permeation chromatography (GPC) with NMR, an GPC-NMR system, has been practiced widely to study the molecular weight and structure of polymers. The molecular weight and polymer size of poly(methyl methacrylate) (PMMA) and poly(butyl methacrylate) copolymers were determined by Hatada et al. using on-flow GPC-NMR. Similarly, other polymers such as polystyrene, polybutadiene, and poly (butyl acrylate) (pBA) mixtures have been examined effectively via GPC-NMR. This technique is also useful in determining the tacticity of polymers. GPC-NMR is rapid in response; however, compared to other analytical techniques, the GPC-NMR has low sensitivity, and it requires several scans of analysis for obtaining data with a low signal-to-noise ratio [67].

2.5.4 CE-NMR

Capillary electrophoresis (CE) is used to separate ions based on their electrophoretic movement under the influence of applied voltage. The ionic mobility is dependent on the mass-to-charge ratio, viscosity, and pH. CE is carried out in the submillimeter-diameter capillaries and in micro- and nanofluidic channels. The hyphenation of CE with NMR makes for a highly sensitive detection method as the volume size is reduced from microliters to nanoliters. Special small NMR flow cells are used for CE-NMR. Wu et al. used CE-NMR for the detection of amino acids by using a fused-silica capillary NMR flow cell with an RF microcoil directly around the cell. The sensitivity was below 50 ng. Both on-flow and stop-flow experiments have been reported for CE-NMR. CE-NMR is a promising technique that presents a huge number of potential applications in analyzing the structure of compounds very sensitively in the micro- and nanogram ranges [67].

2.5.5 SFC-NMR

The combination of supercritical fluid chromatography (SFC) with NMR is more advantageous than ordinary LC-NMR. The use of supercritical fluid as a mobile phase does not require the suppression of solvent, and when supercritical CO_2 is used as the mobile phase, it does not interfere with $_1$HMR results. SFC-NMR needs special flow cells to carry out the analysis because the SFC system creates high pressure that cannot be handled by ordinary NMR flow cells. Different studies have been reported using SFC-NMR. Studies of monomeric acrylates, hydrocarbons, and cis/trans isomers of vitamin A via on-flow SFC-NMR have already been reported. SFC-NMR has been used to perform on-flow data for the NMR analysis of ethylbenzene and of a mixture of dibutyl and diallyl phthalate. SFC-NMR has its applications in food analysis as well [67].

2.5.6 SFE-NMR

Similarly to SFC-NMR, the hyphenation of supercritical fluid extraction (SFE) with NMR is considered an ideal analytical technique in both on-flow and stop-flow modes. The use of proton-free CO_2 as the eluent of extraction is very compatible with $_1$HNMR. The hyphenation of SFE with NMR (SFE-NMR) is more sensitive and effective compared to conventional LC-NMR with the only need being a high-pressure NMR flow cell, as with SFC-NMR. Various studies, such as the study of the composition of coffee and black pepper extract in the on-flow and stop-flow modes with 2D COSY NMR, have been reported. Similarly, plastifiers from poly (vinyl chloride) have also been studied using SFE-NMR [67].

2.5.7 GC-MS

Gas chromatography coupled with mass spectrometry (shown in Fig. 2.12) is used for the analysis of volatile compounds. The two techniques are highly compatible with each other. However, there is the pressure difference between the two. GC operates at 760 torr, while MS works in an inert environment at only 5–7 torr. The two techniques are interlinked through an interface such as a jet/orifice separator, effusion separator, or membrane separator [61,64].

2.5.8 LC-MS

The hyphenation of LC with MS has broad applicability and is used for the simultaneous separation and identification of compounds. Automated LC-MS assembly consists of a double three-way diverter connecting the autosampler, chromatographic system (LC), and MS. The diverter works automatically for controlling the sample volume and passage to the LC-MS system. Various types of interfaces are used to connect the LC with the MS system. Interfaces in LC-MS are designed to perform nebulization, vaporization, ionization, and control of the delivery of ions into the MS system. Among various common interfaces, atmospheric pressure chemical ionization and electrospray ionization are usually used for natural products analysis. In case of LC-UV-MS thermospray and continuous-flow FAB interfaces are also used [61,64].

2.5.9 CE-MS

Capillary electrophoresis (CE) was developed in the early 1990s. In CE, separation is achieved under the influence of an electric field, which is used to separate charged particles and have them move toward respective electrodes according to their mass-to-charge (m/z) ratios. The separation is achieved due to a change in migration rate. In the CE-MS hyphenated system, CE works for the

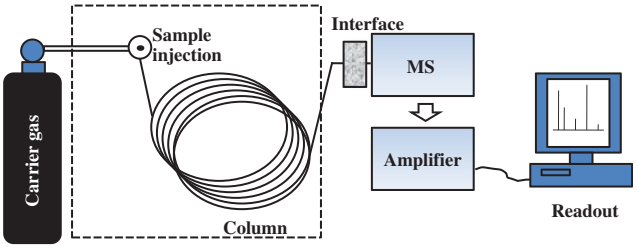

FIGURE 2.12 GC-MS system [61].

separation or purification of components, which are detected through an online MS detector. Hence the simultaneous purification and data acquisition are accomplished [61,64].

2.5.10 GC-ICP-MS

The GC system is used mostly for volatile compounds. The detectors of GC need a sample to be in volatile or gaseous form. Nonvolatile compounds can also be analyzed by GC after making them volatile by derivatization or pyrolysis. Although GC has several detectors systems, the hyphenation of GC with ICP-MS enables it to analyze volatile organic or organometallic compounds with high specificity and sensitivity. IC-MS is very sensitive and specific in elemental analysis when coupled with GC [68–70].

2.5.11 HPLC-ICP-MS

In this hyphenated technique, HPLC is used for separation purposes while ICP-MS is used as a detection system. HPLC may separate the components of a mixture through an adsorption, partition, ion-exchange, or size exclusion mechanism. HPLC is very useful for nonvolatile compounds. The mobile phase composition is gradient or isocratic. The eluted separated components are entered into an ICP-MS detection system connected through an interface with an HPLC system. ICP-MS acts as an universal, element-specific detector for HPLC with several applications. This system is useful in the analysis of organic, inorganic, and biological molecules [70–72].

2.5.12 CE-ICP-MS

Capillary electrophores (CE) are coupled with ICP-MS to perform simultaneous separation and detection of the electrically active components of a mixture. CE is not a chromatographic technique; however, it functions in the same manner as any good chromatographic method does. In CE, the separation of components occurs according to their m/z ratio under the influence of an electric field applied through electrodes. CE is applicable to ionic or charged species from small cations to large biomolecules. Once the separation is achieved, the components are detected through an ICP-MS detection system, which is connected through a special type of interface with CE [73–75].

2.6 Advancement in sampling systems for analytical instruments

Sampling plays an important role in any kind of analysis. It is very difficult to achieve accurate results without proper sampling. As a sample is a representative part of some material under investigation, it should be given great care. Various types of treatments are available to prepare a sample for analysis. For example, for an organic sample to be analyzed through GC, HPLC, GC/MS, or LC/MS, various processes such as extraction, concentration, purification and sometimes derivatization are necessary. For metal metals analysis through atomic spectroscopy (AA), graphite furnace atomic spectroscopy (GFAA), ICP, ICP/MS, extraction, concentration, and speciation are conducted. For metals analysis through UV-Vis, molecular spectrophotometry and ion chromatography, extraction, derivatization, concentration, and speciation are performed. Ions are initially extracted, concentrated, and derivatized prior to ion chromatography (IC) and UV-Vis spectrophotometry. For DNA/RNA, cell lysis and extraction are done to analyze through PCR electrophoresis, UV-Vis, and florescence spectrometry. For amino acids, fats, and carbohydrates, the extraction and cleanup processes are done to make them suitable for

analysis through GC, HPLC, and EC. For microstructure analysis through microscopy and surface spectroscopy, various sample preparation techniques such as, polishing, etching, ion bombardments, reactive ion techniques, and the like are done. Once the sample is ready, proper loading to the instrument is also very important. For this purpose, sampling loading systems are specially designed to load the proper amounts of sample with small or no loss and reproducible results. Sample loading systems are researched progressively, and they have shifted from manual to automated in many instrumental techniques [8,76,77].

2.7 Conclusion

Various analytical techniques have been practiced since ancient times. Chromatography, spectroscopy, and electroanalytical techniques are commonly used for routine as well high priority research purposes. The analytical techniques discussed here have emerged as efficient after continuous development in the related methods and instrumentation. Chromatography is mainly used for separation, purification, and preconcentration, while electroanalytics is mostly and spectroscopy generally used for detection. Prior to any analysis, the separation or preconcentration of the target species is an important step that is usually performed via chromatography, extraction, or electrophorisis techniques. After separation and purification, the analytes or mixtures containing analytes are passed through a detection system. The combination of chromatography with the detection system, such as spectroscopy, has resulted in hyphenated techniques that perform separation and/or purification and analysis simultaneously in a single run. The historical background and development of chromatography, spectroscopy, electroanalytical techniques, hyphenated techniques, as well as the development in sampling systems for these techniques, have evolved through continuous research contributions. The era from less efficient classic to more efficient sophisticated modern instrumentation has seen enormous developments and has not ended in the search for further improvements.

References

[1] G. Svehla, Vogel's Qualitative Inorganic Analysis, 7/e, Pearson Education, India, 2008.
[2] D.A. Skoog, F.J. Holler, S.R. Crouch, Principles of Instrumental Analysis, Cengage Learning, 2017.
[3] J. Mendham, Vogels Textbook of Quantitative Chemical Analysis, Pearson Education, India, 2006.
[4] A. Braithwaite, J. Smith, Chromatographic Methods, Springer Science & Business Media, 2012.
[5] T. Beesley, Evolution of chromatography: one scientist's 51-year journey, LC GC North. Am. 28 (11) (2010).
[6] J.C. Touchstone, History of chromatography, J. Liq. Chromatogr. Relat. Technol. 16 (8) (1993) 1647–1665.
[7] H. Weil, T.I. Williams, Early history of chromatography, Nature 167 (4257) (1951) 906.
[8] R.M. Smith, Before the injection—modern methods of sample preparation for separation techniques, J. Chromatogr. A 1000 (1–2) (2003) 3–27.
[9] S. Heines, Three who pioneered in chromatography, J. Chem. Educ. 46 (5) (1969) 315.
[10] L. Zechmeister, History, scope, and methods of chromatography, Ann. N. Y. Acad. Sci. 49 (2) (1948) 145–160.
[11] W. Russell, D. Papanastassiou, Calcium isotope fractionation in ion-exchange chromatography, Anal. Chem. 50 (8) (1978) 1151–1154.
[12] S. Mori, H.G. Barth, Size Exclusion Chromatography, Springer Science & Business Media, 2013.
[13] K. Mondal, M.N. Gupta, The affinity concept in bioseparation: evolving paradigms and expanding range of applications, Biomol. Eng. 23 (2–3) (2006) 59–76.
[14] J. Farradane, History of chromatography, Nature 167 (4238) (1951) 120.
[15] D.A. Skoog, F.J. Holler, S.R. Crouch, Principles of instrumental analysis sixth edition, Thompson Brooks/Cole 10 (1998) S0003–S2670.
[16] K.D. Bartle, P. Myers, History of gas chromatography, TrAC. Trends Anal. Chem. 21 (9–10) (2002) 547–557.

[17] K. Ernst-Cabrera, M. Wilchek, High-performance affinity chromatography, TrAC. Trends Anal. Chem. 7 (2) (1988) 58–63.
[18] E. Katz, R. Scott, Liquid chromatography system for fast, accurate analysis, J. Chromatogr. A. 253 (1982) 159–178.
[19] M.J. Telepchak, T.F. August, G. Chaney, Introduction to solid phase extraction, Forensic and Clinical Applications of Solid Phase Extraction, Springer, 2004, pp. 1–39.
[20] D.R. Gere, R. Board, D. McManigill, Supercritical fluid chromatography with small particle diameter packed columns, Anal. Chem. 54 (4) (1982) 736–740.
[21] T. Tanimura, et al., Droplet countercurrent chromatography, Science 169 (3940) (1970) 54–56.
[22] L.C. Craig, O. Post, Apparatus for countercurrent distribution, Anal. Chem. 21 (4) (1949) 500–504.
[23] Y.-W. Lee, et al., Application of high speed countercurrent chromatography/thermospray mass spectrometry for the analysis of bio-active triterpenoic acids from Boswellia Carterh, J. Liq. Chromatogr. 13 (12) (1990) 2389–2398.
[24] N.C. Thomas, The early history of spectroscopy, J. Chem. Educ. 68 (8) (1991) 631.
[25] J. Brand, S. Mason, Lines of light: the sources of dispersive spectroscopy, 1800-1930, Nature 381 (6582) (1996). p. 488-488.
[26] D.T. Burns, Aspects of the development of colorimetric analysis and quantitative molecular spectroscopy in the ultraviolet-visible region, Analytical Spectroscopy Library, Elsevier, 1987, pp. 1–19.
[27] V. Thomsen, A timeline of atomic spectroscopy, Spectroscopy 21 (10) (2006) 32.
[28] A. Leitner, The life and work of Joseph Fraunhofer (1787 – 1826), Am. J. Phys. 43 (1) (1975) 59–68.
[29] G. Gore, The Art of Scientific Discovery: Or, The General Conditions and Methods of Research in Physics and Chemistry, Longmans, Green, and Company, 1878.
[30] B. Bowers, Sir Charles Wheatstone FRS: 1802–1875, IET, 2001.
[31] R.J. Tilley, Colour and the Optical Properties of Materials: An Exploration of the Relationship Between Light, the Optical Properties of Materials and Colour, John Wiley & Sons, 2010.
[32] H. Wagner, Early spectroscopy and the Balmer lines of hydrogen, J. Chem. Educ. 82 (3) (2005) 380.
[33] H. Retcofsky, Spectrum analysis discoverer? J. Chem. Educ. 80 (9) (2003) 1003.
[34] G. Kirchhoff, R. Bunsen, Chemische analyse durch spectralbeobachtungen, Annalen Der. Phys. 186 (6) (1860) 161–189.
[35] H. Günzler, H.-U. Gremlich, IR spectroscopy. An introduction. 2002, 374 p; Wiley-VCH; Weinheim (Germany).
[36] Q. Williams, T. Ahrens, Infrared, Raman and optical spectroscopy of Earth materials, Miner. Phys. Crystallography: A Handb. Phys. Constants (1995) 291–302.
[37] E. Libowitzky, A. Beran, IR spectroscopic characterisation of hydrous species in minerals, Spectrosc Methods Mineralogy 6 (2004) 227–279.
[38] P.F. McMillan, A. Hofmeister, Infrared and Raman spectroscopy, Rev. Mineralogy Geochem. 18 (1) (1988) 99–159.
[39] R.L. Kleinberg, J.A. Jackson, An introduction to the history of NMR well logging, Concepts Magnetic Reson. 13 (6) (2001) 340–342.
[40] J.K. Sanders, B.K. Hunter, Modern NMR Spectroscopy: A Guide for Chemists, Oxford University Press., 1988.
[41] E. De Hoffmann, Mass spectrometry, in: Kirk-Othmer Encyclopedia of Chemical Technology, 2000, John Wiley & Sons, Inc.
[42] A.G. Harrison, Chemical Ionization Mass Spectrometry, Routledge, 2018.
[43] B. Valeur, M.N. Berberan-Santos, A brief history of fluorescence and phosphorescence before the emergence of quantum theory, J. Chem. Educ. 88 (6) (2011) 731–738.
[44] E.P. Kirby, Fluorescence instrumentation and methodology, Excited States of Proteins and Nucleic Acids, Springer, 1971, pp. 31–56.
[45] J.W. Robinson, Atomic Spectroscopy., CRC Press, 1996.
[46] R.D. Beaty, J.D. Kerber, Concepts, Instrumentation and Techniques in Atomic Absorption Spectrophotometry, Perkin-Elmer, USA, 1978.
[47] J. Broekaert, Atomic emission spectroscopy instrumentation, Spectrochimica Acta 37 (1982) 727.
[48] D.C. Harris, Quantitative Chemical Analysis, Macmillan, 2010.
[49] J.D. Winefordner, R.C. Elser, Atomic fluorescence spectrometry, Anal. Chem. 43 (4) (1971) 24A–42A.
[50] N. Omenetto, J.D. Winefordner, Atomic Fluorescence Spectrometry: Basic Principles and Applications, Pergamon, 1979.
[51] K.H. Lubert, K. Kalcher, History of electroanalytical methods, Electroanalysis 22 (17–18) (2010) 1937–1946.
[52] D.R. Crow, Principles and Applications of Electrochemistry, Routledge, 2017.
[53] A.R. Hillman, The EQCM: electrogravimetry with a light touch, J. Solid. State Electrochem. 15 (7–8) (2011) 1647–1660.
[54] D.D. DeFord, R.C. Bowers, Electroanalysis and coulometric analysis, Anal. Chem. 30 (4) (1958) 613–619.
[55] D. Harvey, Modern Analytical Chemistry, McGraw-Hill Companies, Inc, Boston, MA, 2000.
[56] E. Bakker, E. Pretsch, Advances in potentiometry, Electroanalytical Chemistry., CRC Press, 2016, pp. 16–89.
[57] S.P. Kounaves, Voltammetric Techniques, Prentice Hall, Upper Saddle River, NJ, 1997, pp. 709–726.

[58] I.M. Kolthoff, J.J. Lingane, Polarography: polarographic analysis and voltammetry, amperometric titrations, 1946, Food and Agriculture Organization of the United States.
[59] J. Barek, J. Zima, Eighty years of polarography—history and future, Electroanalysis 15 (5—6) (2003) 467—472.
[60] T.J. Roussel, et al., Amperometric techniques, Encyclopedia of Microfluidics and Nanofluidics (2013) 1—11.
[61] S. Nagajyothi, et al., Hyphenated techniques-a comprehensive, 2017, International Journal of Advanced Research and Development, 2 (4), (2017) 63—71.
[62] J. Szpunar, R. Lobinski, Hyphenated Techniques in Speciation Analysis, vol. 8, Royal Society of Chemistry, 2003.
[63] I. Wilson, U.T. Brinkman, Hyphenation and hypernation: the practice and prospects of multiple hyphenation, J. Chromatogr. A 1000 (1—2) (2003) 325—356.
[64] K.N. Patel, et al., Introduction to hyphenated techniques and their applications in pharmacy, Pharm. Methods 1 (1) (2010) 2—13.
[65] C.L. Wilson, D.W. Wilson, C.R.N. Strouts, Comprehensive Analytical Chemistry, Elsevier, 1964.
[66] T. Hyötyläinen, M.-L. Riekkola, On-line coupled liquid chromatography—gas chromatography, J. Chromatogr. A 1000 (1—2) (2003) 357—384.
[67] M.V.S. Elipe, LC-NMR and Other Hyphenated NMR Techniques: Overview and Applications, John Wiley & Sons, 2011.
[68] M.M. Bayón, et al., An alternative GC-ICP-MS interface design for trace element speciation, J. Anal. At. Spectrometry 14 (9) (1999) 1317—1322.
[69] S. Wehmeier, R. Ellam, J. Feldmann, Isotope ratio determination of antimony from the transient signal of trimethylstibine by GC-MC-ICP-MS and GC-ICP-TOF-MS, J. Anal. At. Spectrometry 18 (9) (2003) 1001—1007.
[70] M. Moldovan, et al., High resolution sector field ICP-MS and multicollector ICP-MS as tools for trace metal speciation in environmental studies: a review, J. Anal. At. Spectrometry 19 (7) (2004) 815—822.
[71] Ma Montes-Bayón, K. DeNicola, J.A. Caruso, Liquid chromatography—inductively coupled plasma mass spectrometry, J. Chromatogr. A 1000 (1—2) (2003) 457—476.
[72] L. Rottmann, K.G. Heumann, Development of an on-line isotope dilution technique with HPLC/ICP-MS for the accurate determination of elemental species, Fresenius' J. Anal. Chem. 350 (4—5) (1994) 221—227.
[73] A. Prange, D. Pröfrock, Application of CE—ICP—MS and CE—ESI—MS in metalloproteomics: challenges, developments, and limitations, Anal. Bioanal. Chem. 383 (3) (2005) 372—389.
[74] B. Michalke, O. Schramel, A. Kettrup, Capillary electrophoresis coupled to inductively coupled plasma mass spectrometry (CE/ICP-MS) and to electrospray ionization mass spectrometry (CE/ESI-MS): An approach for maximum species information in speciation of selenium, Fresenius' J. Anal. Chem. 363 (5—6) (1999) 456—459.
[75] V. Majidi, et al., Improving sensitivity for CE-ICP-MS using multicapillary parallel separation, J. Anal. At. Spectrometry 14 (12) (1999) 1933—1935.
[76] J. Rosenfeld, Sample Preparation for Hyphenated Analytical Techniques, John Wiley & Sons, 2009.
[77] S. Mitra, Sample Preparation Techniques in Analytical Chemistry, vol. 237, John Wiley & Sons, 2004.