Hemasree M. et al. / Vol 4 / Issue 2 / 2014 / 125-131.

International Journal of Pharmaceutical Research & Analysis

e-ISSN: 2249 – 7781
Print ISSN: 2249 – 779X

www.ijpra.com

AN OVERVIEW OF ELECTRON PROBE MICROANALYSIS

Hemasree M*[1], Shanti Priya D[1], Raja Shekar S[1], Ajitha A[1], Uma Maheshwara Rao V[1]

[*1]Department of Pharmaceutical Analysis & Quality Assurance, CMR College of Pharmacy JNTU(H) University, Hyderabad, Andhra Pradesh, India.

ABSTRACT

Electron Probe Microanalysis (EPMA) is an analytical technique that is used to establish the composition of small areas on specimens. It's one of the several particle-beam techniques These analytical technique has a high spatial resolution and sensitivity and individual analysis are reasonably short requiring only a minute or two in most cases. The Electron Microprobe can obtain highly magnified secondary and back-scattered electron images of a sample.EPMA is now a vital for condensed matter Physicists working in this field. The characterization is particularly important for thin films and a great deal of work has been devoted to modify them. EPMA correction procedures in order to perform analysis of thin film or layered specimens. At the present time, the instrumentation available for electron probe microanalysis has reached a very high standard of performance and its handling is straightforward as is likely to be achieved. The method offers very great possibilities to analytical chemistry both alone and in combination with other methods indeed, there are few branches of science to which the application of electron probes can bring new and valuable results that could not be achieved by other means.

Keywords: Electron Microprobe, Particle-Beam technique, Back-scattered electron.

INTRODUCTION

Electron probe microanalysis is fairly a mature analytical technique which has been widely used in the fields of geochemistry and material science. The microprobe was described in Castaings 1951 Ph D thesis, in which he laid the foundation of the theory and application of quantitative analysis by electron microprobe. Castaings is considered as the "father of electron microprobe analysis" [1-3].

Theory Involved

A beam of the accelerated electrons is focused on the surface of the specimen using a series of electromagnetic lenses and these energetic electrons produce characteristic X-rays with a small volume (typically 1 to 9 cubic microns) of the specimen. The characteristic X-rays are detected at the particular wavelengths and their intensities are measured to determine concentrations.

The electron microprobe works under the principle that if a solid material is bombarded by an accelerated and focused electron beam, the incident electron beam has the sufficient energy to liberate both matter and energy from the sample. These electron-sample interactions mainly liberate heat, and they also yield both derivative electrons and x-rays. The most common interest in the analysis of geological materials is secondary and back-scattered electrons which are useful for imaging a surface or obtaining an average composition of the material. X-ray generation is produced by in elastic collision of the incident electrons with electrons in the inner shells of the atoms in the sample, when an inner shell electron is ejected from the orbit leaving a vacancy and a higher shell electron falls in to these vacancy and must shed some energy to do so (X-ray). This quantized X-ray is the characteristic of that element [4-8].

Instrumentation

1. An electron source, commonly a W-filament cathode referred to as Gun.
2. The series of electromagnetic lens located in the column of the instrument used to condense and focus the electron beam emanating from the source.

Corresponding Author:- M.Hemasree Email:- hemasree18789@gmail.com

3. A Sample chamber with movable sample stage that is under a vacuum to prevent gas and vapor molecules from interfering with electron beam on its way to the sample.
4. The detectors are arranged around the sample chambers which are used to collect X-rays and electrons emitted from the sample [9].

A pumping system must be employed to remove air from the electron column. In most microprobes and scanning electron microprobes vacuum is achieved through a combination of mechanical and diffusion pumps. These valves allow sequential pumping of the electron column and sample chamber [10-11].

Cameca microprobes have high and low vacuum sections. The wavelength-dispersive spectrometers are separated from the electron column by thin windows made up of polypropylene. The spectrometers are evacuated by the separate mechanical pump and kept at a pressure of about 10^{-3}torr, where as the column is kept at a pressure of about 10^{-6}torr.Polypropylene windows are used on the light element spectrometer because they absorb fewer x-rays. This arrangement using windows allows a smaller volume to be kept at high vacuum additionally they keep the column clean by limiting out gases from gear and fitting oils and detector gas leaking from the spectrometers. The mechanical pumps are further categorized into the Oil Diffusion pump, Turbo molecular pump, Sputter ion pump etc.

Electron Sources

Electron guns provide electrons for the electron beam by allowing them to escape from a cathode material. Electrons with a component of velocity at right angles to the surface and kinetic energy at least equal to the work done in passing through the surface will be emitted. This total energy required for a material to give up electrons is related to its work function it's given by

$$\mathbf{E = E_W + E_f}$$

Where E is the total amount of energy needed to remove an electron to infinity from the lowest free energy state, E_f is the highest free energy state of an electron in the material and Ew is the work required to achieve the difference.

There are three main types of electron sources used in microprobes.

a) Thermionic source in which electrons are produced by heating a conductive material to the point where the outer orbital electron gains sufficient energy to overcome the work function barrier. There are two main types of thermionic sources they are tungsten metal filaments and LaB_6 crystals. They require a vacuum of 10^{-5} and 10^{-7} torr respectively.

b) Field emission source in which a large electrical field 10^5 to 10^8 V/cm is placed between the cathode and anode. This field decreases the Ew of the cathode a phenomenon called the "Schottky effect" it occurs at room temperature and depends very slightly on temperature indicating that it's not a temperature dependant process instead it's a purely quantum mechanical effect. In the Electron Gun alignment the electron gun is aligned by shifting the position of the filament assembly relative to the anode and the column beneath it, to maximize the absorbed current.

Magnetic Lenses

The electron beam is diverged after passing through the anode plate and must be refocused. The simplest types of electron lenses are electrostatic, which deflect beam electrons using electrically charged plates. While a charged particle is in an electrical field, a force acts upon it. The faster the particle smaller will be the accumulated impulse thus substantial lenses are required to deflect a high-voltage electron beam. An additionally electrostatic lens requires a very clean high vacuum environment to prevent arcing across the plates. At present electrostatic lenses are most commonly used to deflect and focus ion beams in mass spectrometers. Electron probes use magnetic lenses [12-15].

The first magnetic electron lenses were developed by M.Knoll & E.Ruska in 1932.Their action is similar to principle of optical lenses, but electron lenses are made only to converge not to diverge. A magnetic lens consists of two circularly symmetric iron-pole pieces with copper windings with a hole in the centre through which beam passes. The magnetic flux diverges along the electron beam axis. Consequently, an off axis electron is acted on by a magnetic force proportional to the cross product of the vectors V & B.

$$F = - eV \times B$$

Where, V= electron velocity, and the B=magnetic field

These forces cause the electron to move perpendicular to the axis of the lens. Electron lenses are not as good as optical lenses in terms of defects of focus called Aberrations. These are of two types Spherical aberrations in which the outer zones of a lens focus more strongly than inner zones, which are most important in magnetic lenses. The result is that electrons that move along the beam axis are deflected less than electrons passing through the beam periphery, yielding more than one focal point. The second type is:

Chromatic aberrations, in which the electrons of slightly different energies are focused differently and are relatively, minor because the electron gun produces electrons with essentially uniform velocities. Spherical aberrations are controlled by placing the Spray Aperture in front of the magnetic lens confining electrons to the centre.

a) Condenser lens

The lens controls the amount of current that passes down the column. It is accomplished by focusing the electron beam on variable degrees on the lower aperture. If the focus is sharper the less of the beam is intercepted by the aperture and higher the current. The ultimate electron beam spot size depends on the beam

current, which is controlled by the condenser lens, and the type of the filament in use. The beam below the condenser lens is again divergent and must be refocused before striking the sample. Before this occurs its useful to be able to monitor and regulate the beam current. Emission from a tungsten filament can vary by up to 1% in 10 minutes, although it seems a small change it will result in unacceptable results. Thus the beam regulation is important in the electron microprobe. Such variations can't be considered in the scanning electron microscope where the primary function is imaging. The beam can be measured by interposing the sensor along its path, the beam is measured before every analysis. This procedure requires that a linear correlation between beam current and x-rays produced from the sample. Beam monitoring is software controlled in the microprobe. A Faraday cup is used to block and measure the electron beam current [16-20].

b) Objective Lens

The objective or Probe forming lens is located at the base of the electron column just above the sample. The beam is again divergent after passing through the aperture below the condenser lens and must be refocused. The objective lens focuses the electron beam onto the sample and controls final size and position. Hosted within in it are scanning coils that allow the beam to be rastered across the sample surface, the coils, the beam shift coils and the visible light microscope optics.

SAMPLE CHAMBER

Geological microprobe samples are usually petro graphic thin sections that have been ground flat and polished. The microprobe instrument has a sample chamber just large enough to permit movement of the two entire thin sections under the electron beam. In low vacuum mode the sample chamber pressure is typically 20-30Pa it's maintained at a specific value by a separate extra pump with a large fore line trap. The electron column is separated from the sample chamber by a vacuum orifice that permits the column and objective lens apertures' to be maintained at a high pressure. This mode will allow to study the samples with poor or no electric conductivity.

The sample chamber for a microprobe doesn't need to be large since all samples are flat. The only requirement is the sample chamber has sufficient room for the motors and gearing that allow movement of the sample under the electron beam. Most microprobes can accommodate standard polished thin sections and most permit the examination of the sample with either reflected or transmitted light. The number of sections and the maximum amount of movement depend upon the individual instrument. The X, Y & Z positioning of the sample is accomplished by moving the stage with steeper motors. The microprobe has a light stage installed that can be moved 20 mm in the X-direction and 50mm in the Y-direction. Movement in the Z-direction is limited to avoid striking in the optical system. The microprobes use encoded light bars to control stage movement. In the microprobe the sample changes are accomplished using an air lock to avoid having to vent entire column. The airlock cover plate is removed and a sample change unit is attached. This changer is evacuated to a pressure of about 2 Torr, whereupon the airlock door can be opened and the sample is inserted [21-22].

DETECTORS

The electron microprobe can be used to obtain high resolution of the scanned images of the specimen by rastering the electron beam over an area of the surface. The signal is plotted on the display monitor as the beam scans thus forming a scanning image. Depending on the signal used an image can be scanning electrons image an elemental X-ray map or a cathodoluminescence image. Scanning electron images utilize secondary electrons or back scattered electrons to utilize the characteristic X-rays of elements that may be obtained either through the wavelength dispersive spectrometers or the energy dispersive spectrometer.

a) Backscattered electron detector

The back scattered electron detector is used for imaging the samples because it responds to the average atomic number at the electron beam focus point. Regions with a high average atomic number shown as brighter regions. In silicate rock samples the bright areas are often associated with increasing ion content and the presence of sulphide or metallic ores. Back scattered electrons have high energy when compared with secondary electrons. They are emitted and detected at the higher angles relative to the specimen plane. The emission results from the elastic events among the incident electrons and bound electrons.

b) Cathodoluminescence detector

Many samples produce light when stimulated by electrons, this is called cathodoluminescence. The intensity and color of the light is known by small difference in the trace element content, such as rare earths. Although the electron microprobe doesn't have the sensitivity to measure the trace element directly, distribution can be observed by imaging with light produced by cathodoluminescence. The photomultiplier detector can be placed to either observe light from above the sample using the incident light optical system or from below using the transmitted light optical path. Both positions gather a good percentage of the available light so there are usually no problems with sensitivity. There is chamber to insert a filter for the specific light color of interest .In the longer term a monochromator may be added.

c) X-Ray Detector

An electron microprobe is usually equipped with

energy dispersive spectrometers and several wavelength dispersive spectrometers for X-ray spectrometry. An x-ray detector is a part of it.

SAMPLE PREPARATION

The volume sampled is typically a few cubic microns at the surface corresponding to the weight of a few pictograms. A sample have to be prepared as clean, flat polished mounts up to 1 inch in diameter or as uncovered petro graphic thin sections and is stable in 5-10 vacuum environments and under electron bombardment. The diameter of the sample has to be 20mm in height including mounting material and wall thickness of the holder. For the best results samples must be polished to within a 0.05 µm flat surface .After the preparation samples are coated with an approximately 200 Angstroms (10nm) layer of carbon using or other conductive material in an evaporator.

PREPARATION TECHNIQUES OF THE SAMPLE

Many different methods are used for the sectioning of materials that is cleaving, fracturing, sawing, cutting and wire EDM. Subsequent operations like grinding and polishing are to be performed in order to remove the damage material [23].

a) Abrasive Cutting

Many types of abrasive wheels are offered by different manufacturers, for precision cutting and for cutting extremely hard materials Diamond-impregnated wheels are preffered.Such a low speed diamond saws cut slowly but as the cut surface is relatively smooth and further preparation time is short. The possibility of the dry cutting prevents the contamination from the lubricant.

b) Wire Saw

The device with highest precision, lowest damage and lowest contamination is the wire-saw, it has a fine diamond-impregnated wire is the cutting tool. Although cutting rates are much lower than those of abrasive wheels the damage produced is negligible and subsequent grinding, polishing is often not necessary, it's nearly contamination free sizing method.

c) Laser Induced Cutting

It can be applied to a metal sheet of which an oxide scale or corrosion products. In order to avoid contamination of the surface and to have a rapid method for preparing a lot of samples, pieces of 1cm x 1.5 cm are cut from the sheet metal by a laser process. Deposition of removed material during the process was avoided by a steady gas flow.

d) Fixing & Mounting

For quantitative x-ray analysis the specimens' surface had to be flat and perpendicular to the electron beam, mounting the specimen is essential for handling of small and oddly shaped specimens during grinding and polishing, and for inserting the specimens in the electron microscope in an acceptable geometry way. The geometry of the mounts depends on the design of the sample holder is an unmounted specimen can be embedded into an Al-foil under the pressure of a dye. For the analysis of a thin film a piece of coated wafer is fixed on a face of a holder by using an adhesive tape or silver paint.

e) Grinding & Polishing

EPMA has to be performed on flat specimens. The erroneous analyses of specimens with rough surfaces are demonstrated by tilting the specimen relative to the direction of the electron beam towards the and straight off the detector. For a material consisting mainly of Fe, the relative x-ray B-Kα, C-Kα, Al-Kα and Ti-Kα plotted versus tilt angle, the incident electron beam energy is 7KV and the detector take off angle is 40^0. In particular for light element analysis where high mass absorption coefficients and low information depths is expected, the relative error is about 50%. In polishing small forces are applied to the individual abrasive particles by the fibers of the cloth. Diamond, alumina and colloidal silica are the most commonly used abrasives for polishing. Colloidal silica is to be avoided when analyzing oxygen since a thin amorphous glass film is deposited on the surface. The Electrolytic polishing is widely used in the preparation of metals or metal alloys which are difficult to polish by mechanical methods. It contains a cathode and anode, the specimen is suspended in a container filled with electrolyte, by applying a voltage a reaction starts between the specimen surface and the electrolyte. The quality of the polishing depends on the current voltage relationship which varies for different analytes and materials [18-19].

WORKING

Electron microprobes contain an electron optical column, which produces the electron beam and controls its diameter when focused on a sample. At the top is an electron gun comprising of tungsten wire bent in to a V-shape and heated with an electric current to about 2700K which free the electrons from the apex of the wire, since electrons are negatively charged which are accelerated by an electron potential between 5 & 30KV. As the electrons are accelerated a pair of electromagnetic lenses focuses the electrons as a convergent lens focusing the light. One lens restricts the number of electrons that passes down the column while the other lens focuses the beam on the sample and controls its diameter. These lenses and a set of apertures can focus the beam to a diameter of 0.1 micron or less. Low energy electrons are evolved from a tungsten filament or lanthanum hex boride crystal cathode and accelerated by a positively biased anode plate to 3 to 30 thousand electron volts (KeV). The anode plate has central aperture and electrons that passes through it are collimated and focused by a series of magnetic lenses and apertures.

Two types of electrons were liberated during this process they are the Secondary electrons and Back-scattered electrons. Secondary electrons are a result of inner shell ionization. These electrons have lower energy which are very sensitive to surface topography and they can be utilized to acquire images of a sample similar to those collected by SEM. Back-scattered electrons are the electrons that have been scattered back toward the surface of the sample which are collected by the detector and these electrons have the energies greater than the secondary electrons so they are less sensitive to topography. The back-scattered electrons are influenced by the atomic numbers of the elements in the interaction volume. In heavier elements electrons are back-scattered as a result of single deflection and the electrons retain there much of their original energies, in lighter elements electron is more likely to suffer small deflections and loose more energy to before it re-emerges, this effect results to produce images called Back-scattered images that show compositional information. The image shows bright areas where the atomic number is high and dark areas where the mean atomic number is low [17-20].

PHARMACEUTICAL APPLICATIONS OF EPMA

In Qualitative analysis

1. Secondary electron imaging (SE) it provides topographic images with a magnification range from 63x to 10000 x, online gray and false color imaging.
2. Back-scatter electron imaging it provides average atomic number contrast images and topographic images with a magnification in the range of 63x to 10000 x.
3. Qualitative X-ray imaging provides X-ray mapping of sample surface for up to 4 elements.
4. Wavelength spectrometer scanning it gives the simultaneous wavelength scan acquisition on 4 spectrophotometers, online data base for peak identification with a publication of quality graphical output.

In Quantitative analysis

1. Quantitative analysis generally involves the use of calibration standards and correction for dead time, background and interference effects in both the standards and unknown sample.
2. In Quantitative Elemental analysis simultaneous analysis of four elements up to a maximum, from C to U elements.
3. Trace element procedure for low concentration elements.
4. Full automation for unknown and standard data acquisition.
5. Good results in elemental and oxide weight percent, mole percent, formula atoms etc
6. Statistics on detection limits, sample homogenesity and analytical sensitivity.

In Quantitative X-ray Imaging

The software provides automatic acquisition of rectangular and irregular polygon areas for up to 10,000 analyses. Larger area mapping up to 25mm and more.

OTHER APPLICATIONS

Material science and Engineering

The technique is commonly used for analyzing the chemical composition of metals, alloys, ceramics and glasses. It is particularly useful for assessing the composition of individual particles or grains and chemical changes on the scale of a few micrometers to millimeters.

Mineralogy and Petrology

Most rocks are aggregates of small mineral grains. These grains will preserve the chemical information adopted during their formation and subsequent alteration. This information may illuminate geologic processes such as crystallization, lithification, volcanism, and metamorphism. This technique is also used for the study of extraterrestrial rocks and provides chemical data which is vital to understanding the evolution of the planets, asteroids, and comets.

Paleontology

In exceptionally preserved fossils, such as those of the burgess shale, soft parts of the organism are preserved, a famous example is that of triangular extensions in opabinia which were interpretated as either legs or extensions of the gut.

Stereometric analysis

The application of microprobe to these three dimensional analysis, it has been proved to be a very valuable tool for the determination of chemical composition of phases and it has nearly the same spatial resolution as the light microscope. The scanning microprobe design offers the possibility for scanning the sample in straight lines. Thus the most sophisticated method of stereometric analysis, linear analysis can be obtained with the microprobe [12].

RECENT TECHNOLOGICAL DEVELOPMENT IN EPMA

1. Development in electron guns (field emission guns)
2. Development in X-ray Detectors
3. Development in image detectors
4. Software development

This type of electron gun uses a very small source and requires only simple optics to obtain much narrower and brighter beams. It is very useful in the high resolution imaging at lower voltages. They provide nanometer probes with nano ampere current. The most interesting technological evolution can probably found in the energy dispersive spectrometers which can detect the X-ray from lighter elements for particle analysis.

The improved detectors can detect the X-rays from light elements. The advantages of it are better geometry and quantum efficiency. The improved kinds of energy dispersive detectors have been fully commercialized and the example is the THIN WINDOW ELECTRON PROBE MICROANALYSIS (TW-EPMA). Another very recent kind of energy dispersive type detector is the Micro Calorimeter combines the advantages of both the above mentioned detectors that allow straight forward identification of closely spaced X-ray peaks in complicated spectra at fast operation times.

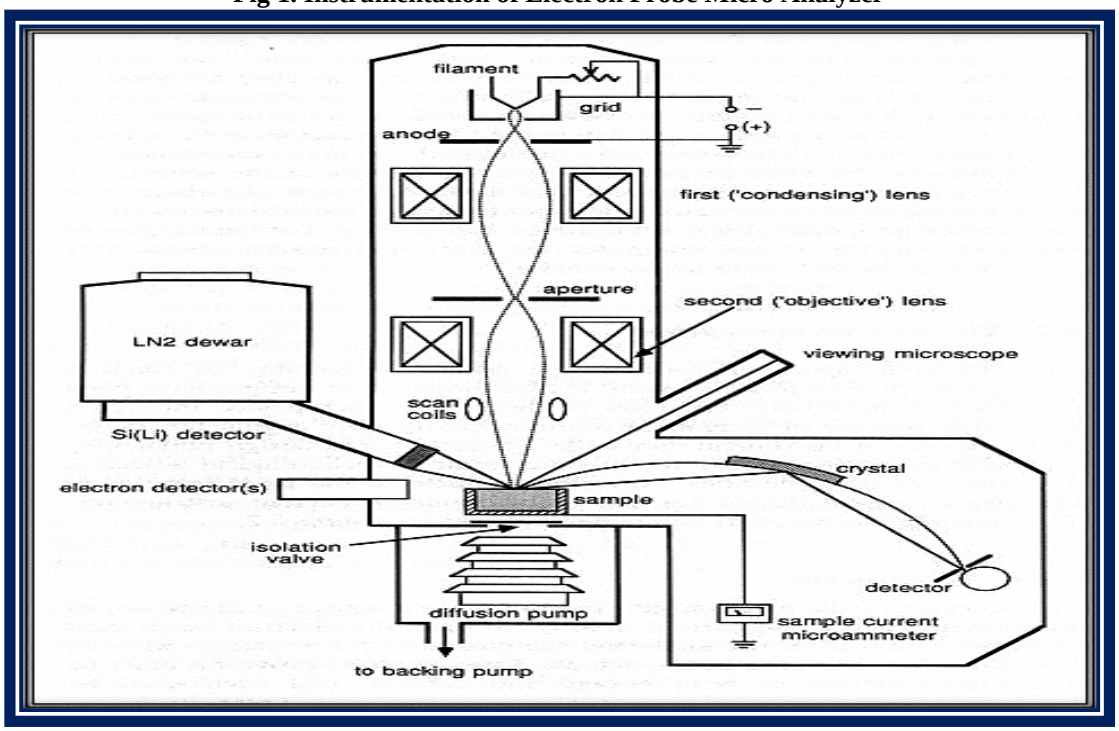
One of the most recent developments in the detectors is the VARIABLE PRESSURE SECONDARY ELECTRON DETECTOR that can withstand the typical environment pressure (2-133pa). ANNULAR IN LENS SECONDARY ELECTRON DETECTOR was also recently introduced it shows high resolution information, an increased signal to ratio, an improved dynamic range and prevention of the aging effects on the detectors material.

Single particle analysis often requires fast and automated analysis of huge number of particles, which means that analyst need specific software to locate and analyze the particles in a computer controlled way. Mi TAC developed its own particle analysis program mostly based on the back scattered electron signal. Recently developed software called Feature Analysis as having the same principle as the Mi TAC [14].

LIMITATIONS

1) Although an electron probe has the ability to analyze for almost all elements, they are unable to detect the lightest elements (H.He & li).
2) Some elements generate X-Rays with overlapping peak positions that are to be separated.
3) Microprobe analyses are reported as oxides of elements, not as cations therefore cation proportions and mineral formulae are to be recalculated using stoichiometric rules.
4) Probe analysis cannot distinguish between different valence states of the Fe so it is evaluated by other techniques.

Fig 1. Instrumentation of Electron Probe Micro Analyzer



CONCLUSION

At the present time, the instrumentation available for electron probe microanalysis had reached a very high standard of performance and its handling is as straightforward as its likely to be achieved. The method offers very great possibilities to analytical chemistry both alone and in combination with other methods indeed there are few branches of science to which the application of electron probes can bring new and valuable results that could not be achieved by other means. There is a considerable discrepancy between the very rapid production of signals and their very slow evaluations, but as electron probe systems became fitted with on-line computers this problem will disappear. The technique is adaptable for the automatation and work on these lines is proceeding rapidly in many places.

REFERENCES

1. Micro beam analysis-Electron micro beam analysis. Method for elemental mapping analysis using wavelength dispersive spectroscopy. 2012, ISO 11932.
2. Reed SJB. Electron microprobe analysis and scanning electron microscope in geology. Cambridge University press. 2nd ed, 2009.
3. Goldstein, New bury, Echlin DE, Jou P, Lyman DC, Sawyer E and Michael. Scanning electron microscopy and X-ray microanalysis: A text book for material scientist and geologist, 3rd ed, 2008.
4. Kaegi R and Holzer L. Transfer of single particle for combined SEM and TEM analysis. 2005, 82-95.
5. Neilsen C. Micro Raman analyzer: European microscopic analysis, 2003, 51-83.
6. Heinrich KFG, Van Nostrand Reinhold: Electron beam X-ray microanalysis, 2000, 34-56.
7. Birks LS, Willey. Inerscience: Electron Probe Microanalysis, 1998, 20-61.
8. Nielsen CH and Sigurdsson H. Quantitative methods for electron micro probe analysis of sodium in natural and synthetic glasses: A mineral, 1996, 66, 547-552.
9. Scott VD and Love G. Quantitative electron probe microanalysis: Wiley and Sons, 1995.
10. Bastin GF and Heijilers HJM. Quantitative electron probe microanalysis of carbon in binary carbides: Parts I and Part II X-ray Spectra. 1994, 135-150.
11. Donovan JJ and Tingle TN. An improved mean atomic number correction for quantitative microanalysis. *In Journal of Microscopy*, 1992, V2-1, 1-7.
12. Quire MC, Francis AV and Dyar CA. Mineral standards for electron probe microanalysis of oxygen. *Am mineral*, 1989, 1087-1095.
13. Donavan JJ, Snyder DA and Rivers ML. An improved interference correlation for trace element analysis. *Micro beam analysis*, 1985, 23-28.
14. Duncumb P and Melford PA. X-ray optics and microanalysis, 1982, 240.
15. Anderson CA, Mickinely TD. The electron microprobe, 1980, 58.
16. Castaing R, Guinier A. Proceedings on a conference on electron microscopy, 1980.
17. Armstrong JT. Micro beam analysis San Fransico, 1982, 239.
18. Goodhew PJ, Gulley. The Determination of alkali metals in glasses by electron probe microanalysis. *Glass technology*, 1974, 123-126.
19. Hunt JB, Hill PG. An inter-laboratory comparison of electron probe microanalysis of glass geochemistry. *Proceedings of the Ocean Drilling Program, Scientific Results*, 1972, 34-36, 229-241.
20. Morgan GB, London D. Optimizing the Electron microprobe analysis of hydrous alkali aluminosilicate glasses. *American mineralogist*, 1970, 1176-1185.
21. Spray JG, Rae DA. Quantitative electron microprobe analysis of alkali silicate glasses: A review and user guide. 1970, 323-332.
22. Shuman H, Somlyo AV. Quantitative electron microprobe analysis of biological thin sections. *Ultra microscopy*, 1976, 317-339.
23. Hall TA, Gupta BL. The localization and assay of chemical elements by microprobe methods. *Quarterly Reviews of Biophysics*, 1975, 279-339.