

CHAPTER 2

MATERIALS AND METHODS

2.1 Samples preparation

A total of 60 green tourmaline samples from Madagascar, Mozambique and Tanzania used in this study were purchased from dealers at the Bangkok Gems and Jewelry Fair. The accurate source location of green tourmalines used in this study, however, is unknown. The samples show color range in green, bluish green, yellowish green to brownish green, greenish blue and blue. The samples are transparent with Fe-stained fractures. Before analysis, the samples were cleaned by soaking in 15% HCl 24 hours. Then, all samples were polished in perpendicular to C-axis (Figure 2.1).

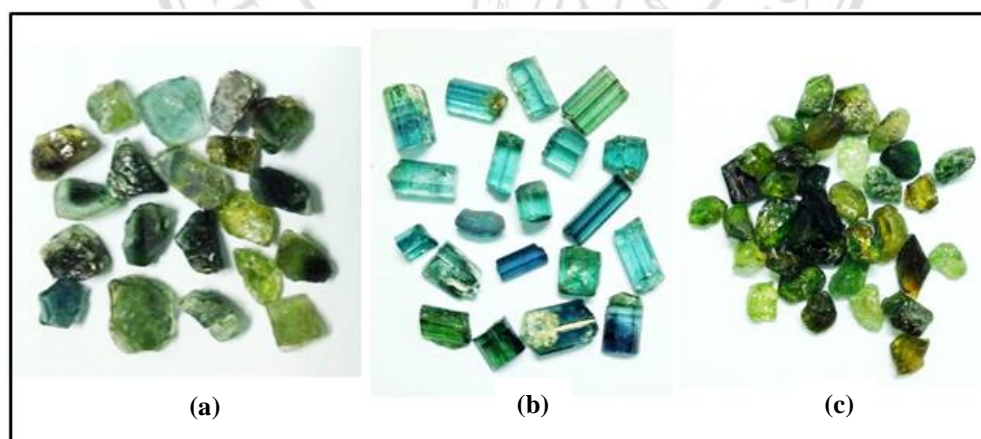


Figure 2.1 The samples used in this study from (a) Madagascar, (b) Mozambique and (c) Tanzania.

All samples from Madagascar, Mozambique and Tanzania were categorized into 3 groups, and are described in detail as follows:

2.1.1 Group I : The samples from Madagascar

Twenty samples from Madagascar were classified into 4 groups on the basis of their colors as green, bluish green, yellowish green and watermelon tourmaline (Figure 2.2).

green color



bluish green color

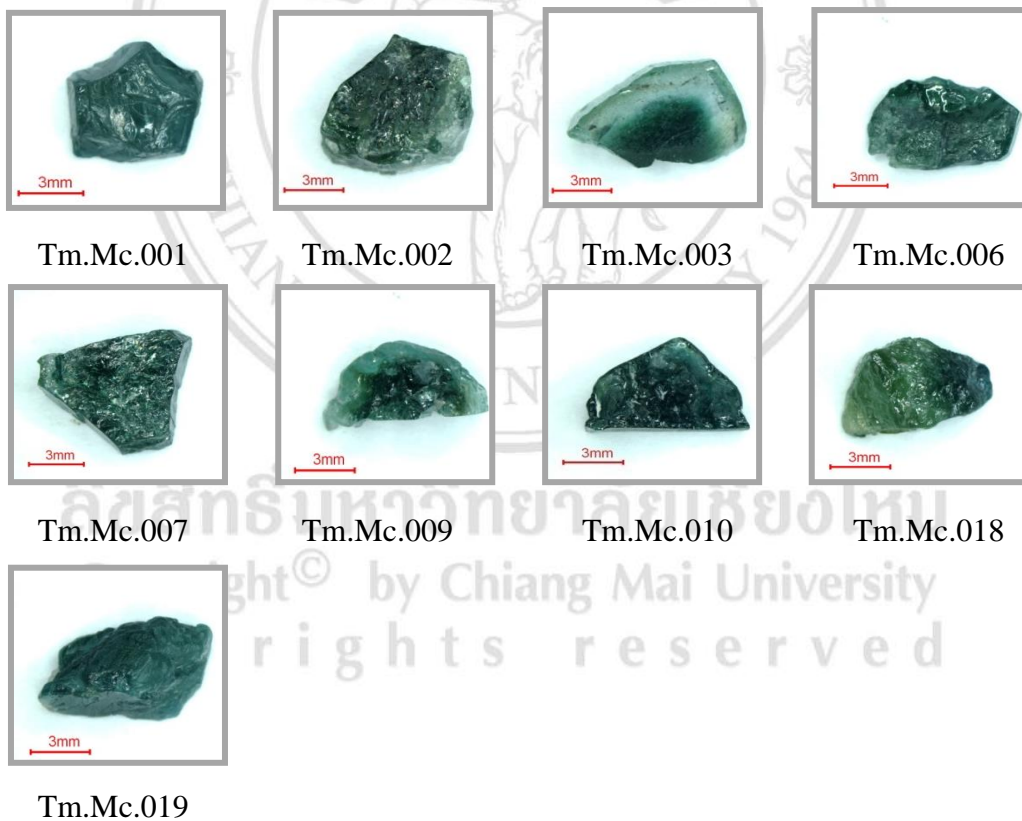


Figure 2.2 Group I: The samples from Madagascar, with their abbreviations from Tm.Mc.001 to Tm.Mc.020

yellowish green color



watermelon tourmaline

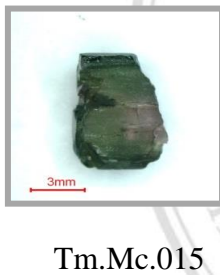


Figure 2.2 Group I (continued)

2.1.2 Group II : The samples from Mozambique

Twenty samples from Mozambique were classified into 4 groups based on their coloration as greenish blue, blue, green and bi-color tourmaline (Figure 2.3).

greenish blue color

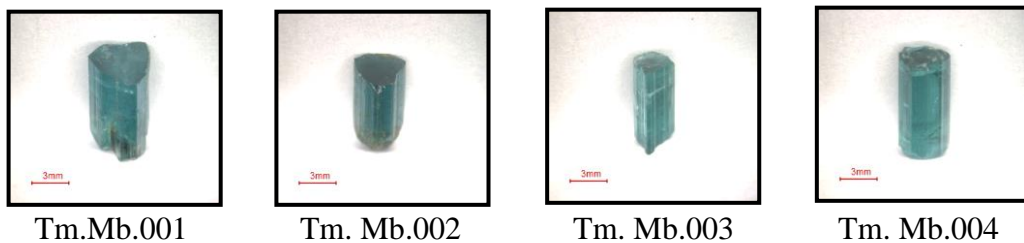


Figure 2.3 Group II: The samples from Mozambique, with their abbreviations from Tm.Mb.001 to Tm.Mb.020



Tm.Mb.005



Tm. Mb.006



Tm. Mb.007



Tm. Mb.008



Tm.Mb.009



Tm. Mb.010



Tm. Mb.011



Tm. Mb.012

blue color



Tm.Mb.013



Tm. Mb.014

green color



Tm. Mb.015



Tm. Mb.016



Tm.Mb.017



Tm. Mb.018

bi-color tourmaline



Tm. Mb.019



Tm. Mb.020

Figure 2.3 Group II (continued)

2.1.3 Group III : The samples from Tanzania

Twenty samples from Tanzania were classified into 3 groups based on their coloration as yellowish green, yellow-green and green (Figure 2.4).

yellowish green color



Figure 2.4 Group III: The samples from Tanzania, with their abbreviations from Tm.Tz.001 to Tm.Tz.020

yellow-green color



green color



Figure 2.4 Group III (continued)

2.2 Analytical techniques

The analyses used in this study consist of basic analytical methods, color grading, and advanced analytical techniques.

2.2.1 Basic analytical techniques

The basic analytical instruments were applied to determine gemological properties of the samples including specific gravity, refractive index, birefringence, fluorescence and inclusions. All techniques were carried out at the Gemological Laboratory of the Department of Geological Sciences, Faculty of Science, Chiang Mai University, Thailand.

- (1) hydrostatic balance (Figure 2.5 a): to determine weights and specific gravity (S.G.) of the samples.
- (2) refractometer (Figure 2.5 b): to determine refractive index (R.I.) of the samples.

- (3) ultraviolet lamp (Figure 2.5 c): using both long-wave (365.4 nm) and short-wave (253.7 nm) ultraviolet radiation: to observe fluorescence of the samples.
- (4) gemological microscope (Figure 2.5 d): to examine inclusions in the samples.

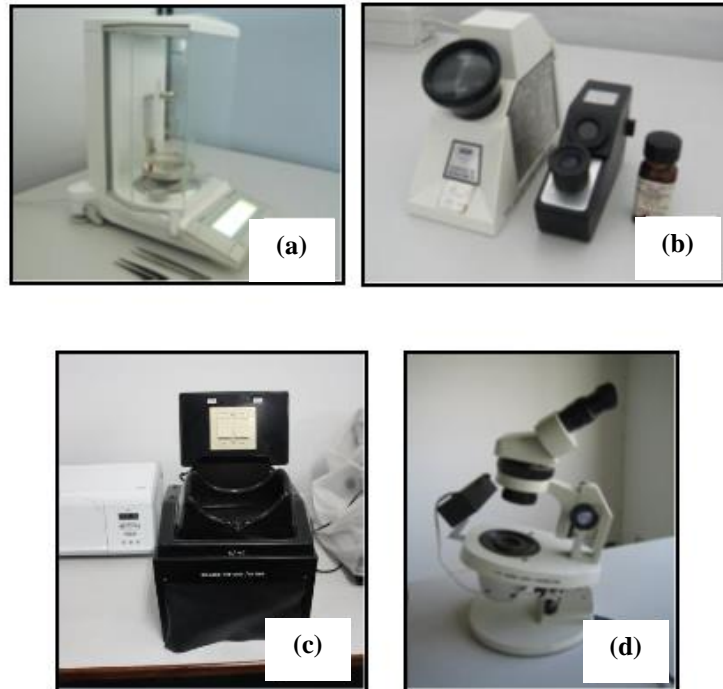


Figure 2.5 Basic analytical instruments used in this study

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2.2.2 Color grading

The color of the samples using GIA Gemset from Gemological Institute of America (Figure 2.6) and description in terms of hue, tone and saturation are as follows;

Hue	Abbreviation	Hue	Abbreviation
Purple	P	Green	G
Reddish Purple	rP	very slightly bluish Green	vslbG
Purple-Red or Red-Purple	PR/RP	slightly bluish Green	slbG
strongly purplish Red	stpR	strongly bluish Green	stbG
slightly purplish Red	slpR	Green-Blue or Blue-Green	GB/BG
Red	R	very strongly bluish Green	vstgB
orangy Red	oR	greenish Blue	gB
Red/Orange, Orange/Red	RO/OR	very slightly greenish Blue	vslgB
reddish Orange	rO	Blue	B
Orange	O	violetish Blue	vB
yellowish Orange	yO	bluish Violet	bV
orangy Yellow	oY	Violet	V
Yellow	Y	bluish Purple	bP
greenish Yellow	gY		
Yellow/Green, Green/Yellow	YG/GY	Exception:	
strongly yellowish Green	styG	Pink	Pk
yellowish Green	yG	Brown	Brn
slightly yellowish Green	slyG		

Tone	Description	Abbreviation	Saturation	Description
2	very light	vl	1	grayish (brownish)
3	light	l	2	slightly grayish (brownish)
4	medium light	ml	3	very slightly grayish (brownish)
5	medium	m	4	moderately strong
6	medium dark	mdk	5	strong
7	dark	d	6	vivid
8	very dark	vdk		

The term of color are presented by abbreviations; the hue abbreviation followed (after space) by just the tone and saturation numbers, separated by slash. Such as styG 7/3; The styG explain the hue (strongly yellowish Green in this case), 7 stand for the tone and 3 indicate the level of saturation.



Figure 2.6 The GIA Gemset from Gemological Institute of America

2.2.3 Advanced analytical techniques

(1) Ultraviolet-Visible-Near Infrared (UV-Vis-NIR) absorption spectroscopy

UV-Vis-NIR absorption spectroscopy used to determine the causes of coloration by analyzing the metal ion site occupancy, oxidation states and concentrations in term of the coloration effect in the samples.

The UV-Vis-NIR spectrophotometer comprises beam condenser and polarizing filter for polarized spectroscopy and scan over the ultraviolet (UV), the visible (Vis) and the near infrared (NIR) regions (250-2000 nm range). Absorption spectra obtained by measuring the transmission of light through the samples. The radiation passes through the sample and is absorbed by the electrons, some are scattered and reflected. The detector detects and measures the transmitted radiation. The resulting transmission or absorption spectral is detected and presented results as a graph. The light sources used for ionization are generated from deuterium (D₂) discharge tube for ultraviolet region, and a 50 W iodide tungsten (W) lamp for visible-near infrared region. Photomultiplier (for ultraviolet-visible region), and cooled-type PbS cell (for near infrared region) detectors were used to determine the spectral with wavelength accuracies of ± 0.2 nm in ultraviolet-visible region, and ± 0.1 nm in near infrared region joined with automatic wavelength calibration function.

In this study, the absorption spectra were recorded over the range of 250-1500 nm in transmission mode, and were saved as absorbance. Scan speed is 300 nm/min, with 2.00 mm slit width. The samples were measured of the ordinary and extraordinary rays. The data from this experiment were collected and stored by Hitachi spectrophotometer UV solution program. The samples were obtained from Hitachi U4001 spectrophotometer (Figure 2.7) at the Gemological Laboratory of the Department of Geological Sciences, Faculty of Science, Chiang Mai University.



Figure 2.7 The Hitachi U4001 UV-Vis-NIR Absorption Spectrophotometer

(2) Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy is a technique non-destructive analysis used to determine vibrational absorption features of materials. FTIR identifies chemical bonds in a molecule by producing an infrared absorption spectrum. The infrared spectrum of the sample is recorded by passing a beam of infrared light through the sample and determining what fraction of the incident radiation is absorbed at a particular energy. The energy of the peak in an absorption spectrum appears depended on the frequency of a vibration (bond stretching vibration or bond bending vibration) of a part of sample molecule. The records of the intensity of infrared are wavelength (μm) or wave number (cm^{-1}). The gemstones have different infrared spectrums because different chemical composition, molecular structure, packing atom and molecular bonds.

Infrared radiation or infrared light are electromagnetic spectrum which has a longer wavelength and lower frequency than visible light. The infrared region is usually divided on the experimental technique and applications into three portions as follows: (1) Near Infrared (NIR) = 750 nm – 2500 nm ($13300 - 4000 \text{ cm}^{-1}$), (2) Mid Infrared (Mid-IR) = 2500 nm – 25000 nm ($4000 - 400 \text{ cm}^{-1}$) and, (3) Far Infrared (Far-IR) = 25000 nm – 300000 nm ($400 - 33 \text{ cm}^{-1}$).

In this study, infrared absorption spectrum obtained in the range 4000-500 cm^{-1} due to the stretching vibration of Si-O, BO_3 and hydroxyl groups using Bruker Tensor 27 FTIR spectrometer (Figure 2.8) equipped with a transmittance attachment, using a standard resolution of 4 cm^{-1} with 120 scans per second. Measurements were at room temperature, and liquid nitrogen was purge during measurement. This work was analyzed at the Gemological laboratory of Department of Geological Sciences, Faculty of Science, Chiang Mai University.

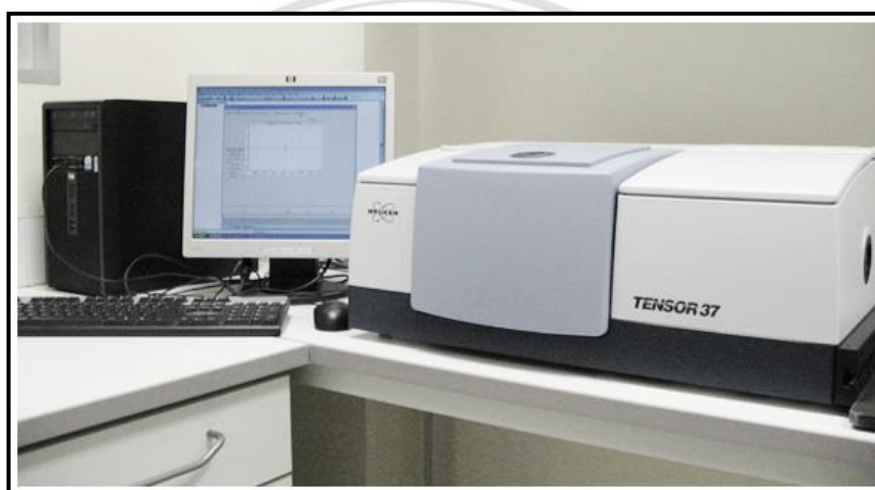


Figure 2.8 The Bruker Tensor 27 FTIR Spectrometer

(3) Electron Probe Micro-Analyser (EPMA)

Electron probe micro-analysis with wavelength dispersive X-ray fluorescent spectrometry (EPMA-WDS) is a technique non-destructive used to determine a quantitative chemical analysis of solid minerals on a minute volume and can be obtained the in situ. This is executed by focusing a beam of electrons as energy source, which is in the range of 5 to 30 keV, on the surface of the minerals. X-rays are generated by the atom within mineral and have wavelength or energies that are characteristics of elements present within mineral. The intensity of characteristics X-ray was measured and investigated. The analytical spot is approximately 2 μm . The samples were prepared as polish section. Analysis of the sample mounts required carbon coated on polish section. Carbon coating provides a conduction path of the probe current and protects electron charging. Qualitative and

quantitative determination of elements can be obtained on elements with an atomic number greater than five (boron) to detectable limits in the order of 0.01 percent (Reed, 1996; Reed and Romanenko, 1995). The EPMA analyses are reported as oxides of elements. Therefore, cation proportions and mineral formulae must be recalculated following stoichiometric rules.

In this study, three random locations on eleven samples of all color groups from other localities (Figure 2.9) were analyzed using a JEOL Electron Probe Micro-Analyzer (EPMA), Model JXA-8100 super probe (Figure 2.10), at the Department of Geology, Faculty of Science, Chulalongkorn University, Bangkok, Thailand. The chemical elements selected for analysis are Al, Si, V, Mn, Ti, F, B, Cr, Fe, Ca, Mg, Na, Cu and K. The certified standards of minerals and metal standards are used in EPMA to calibrate the measurement of X-ray intensities for comparison with the sample of interest. The analyses were carried out at acceleration voltage of 15 kV, probe current of 2.184×10^{-8} and beam diameter of 1-5 micrometer. The results were automatically corrected by the JEOL quantitative analysis with ZAF method (Atomic Number Absorption Fluorescence Correction). Mineral and oxide standards are wollastonite (Ca), quartz (Si), corundum (Al), jadeite (Na), periclase (Mg), manganosite (Mn), fayalite (Fe), potassium titanium phossonate (K), lead vanadium germanium oxide (V), eskolaite (Cr), copper pure metal (Cu), and internal standard for Ti, F and Na. The detection limit of the standards is 0.05 percent.

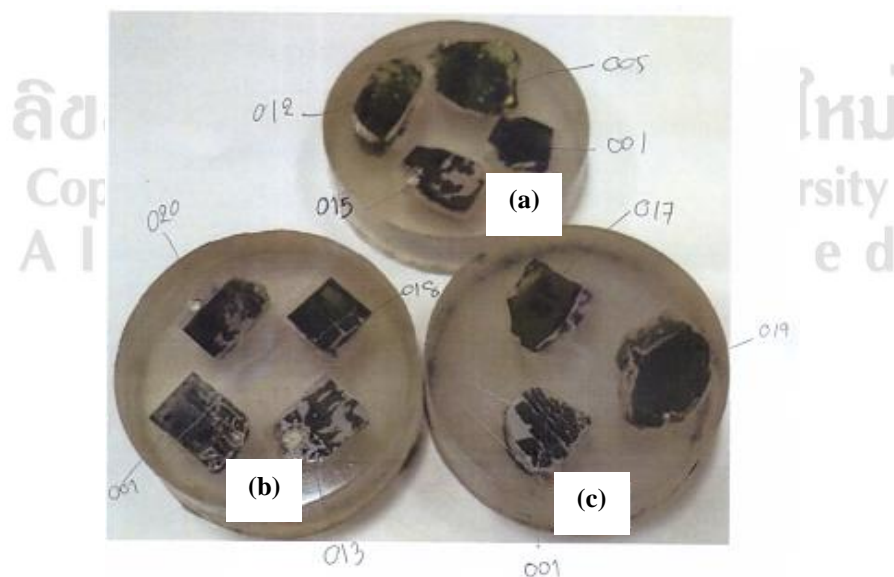


Figure 2.9 Carbon coated on polish section of green tourmalines from (a) Madagascar, (b) Mozambique and (c) Tanzania



Figure 2.10 Electron Probe Micro Analyzer (JEOL Model JXA 8100)

(4) Laser Ablation-Inductively coupled plasma-mass Spectroscopy (LA-ICP-MS)

Laser ablation-inductively coupled plasma-mass spectroscopy (LA-ICP-MS) is a technique non-destructive used to determine quantitative data for major, minor, and trace elements of samples, which variation diagrams and chemical element fingerprint. The fingerprint can display differences between samples of each geographic origin. This method can be measured a wide range of element from helium to uranium, which in the range of parts per million (ppm) to even parts per billion (ppb). LA-ICP-MS instruments consist of three components as follows (Abduriyim and Kitawaki, 2006): the association of laser ablation with ICP-MS (Figure 2.11a) used to determine elements and in situ analysis of solid materials. In the process, the sample is located in the ablation cell (which does not need to be under vacuum) and a minute portion of sample is vaporized by a high-energy laser beam that is directed through the objective lens. The surface of the sample is viewed with a charge-coupled device (CCD) camera mounted on the microscope. The ablated aerosols are transported in argon or helium gas to the plasma of the ICP-MS. Helium is used as the carrier gas in the sample cell, and is combined with argon in the tubing that leads to the ICP. The sample is brought in a flow of argon gas into a torch that is inductively heated to approximately 10,000 °C. At this temperature all matter in the sample is atomized and ionized, forming plasma that

furnished a rich source of both excited and ionized atoms. The combination of ICP and MS is speedy quantitative analysis with high correctness and low detection limits (Figure 2.11b). Mass spectrometer used in ICP-MS is the quadrupole mass analyzer (Figure 2.11c), which comprise four parallel metal rods arranged in a square. Each pair of opposite rods has a combined AC and DC electrical potential. When the DC and AC voltages are set to confident values, only ions with a specific mass-to-charge ratio (m/z ratio) are able to continue on a path between the rods and can detect an array of different ions. The determination of the mass spectrum or isotope ratios is obtained by measuring the intensities of the ions passing through the quadrupole mass analyzer as the voltages on the rods are changed.

The three random locations on 11 samples of all color groups from three different localities were measured quantitatively at the Gem and Jewelry Institute of Thailand (Public Organization), Bangkok, Thailand using an Agilent 7500a (inductively coupled plasma-mass spectrometer) joined to the New Wave UP-213 laser-ablation adjustment (Figure 2.12). The laser operated at a wavelength of 213 nm with helium as the carrier gas (flow rate of 0.85 liter/minute). Laser-ablation parameters were as flow: 55 μm spot diameter approximately 12-13 J/cm^2 laser energy density (fluence), 10 Hz repetition rate, and 30 seconds laser dwell time. For calibration, NIST SRM610 glass reference materials were used as external standard and tourmaline % Al_2O_3 was used as an internal standard.

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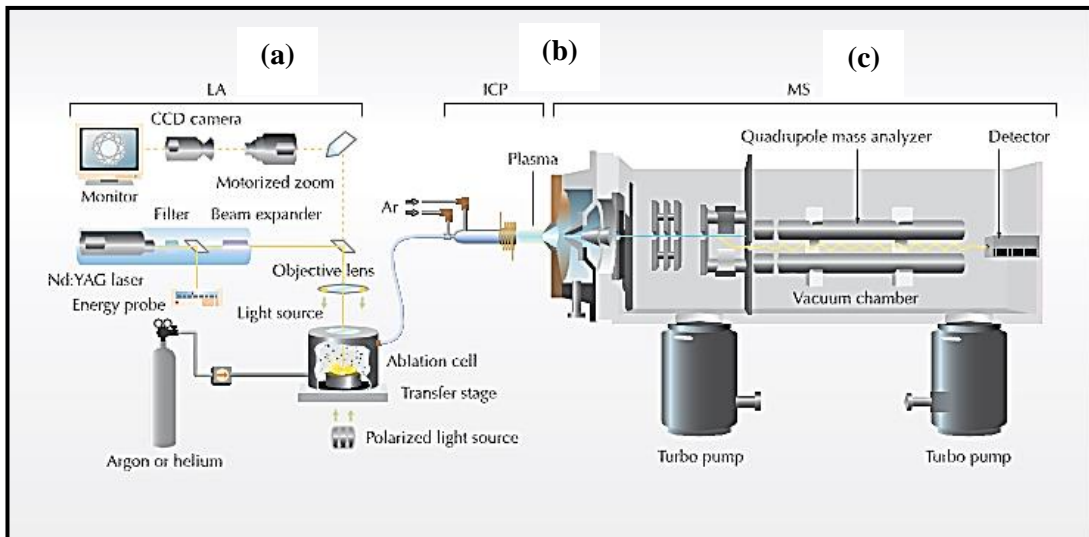


Figure 2.11 The schematic diagram presents the component of Laser ablation-Inductively Coupled Plasma-Mass Spectroscopy (LA-ICP-MS) (Abduriyim and Kitawaki, 2006).



Figure 2.12 Laser Ablation-Inductively Coupled Plasma-Mass Spectrometer (LA-ICP-MS)