

CHAPTER 3

CHARACTERIZATION TECHNIQUES

This chapter contains the description of techniques used to characterize the fabric surface. The contact angle and absorption time measurements are main techniques that fundamentally identify the ability to repel water and resist permeation of water on fabric, respectively. X-ray photoelectron spectroscopy (XPS) used to study the chemical bounds on fabric surface will be described. Scanning electron spectroscopy (SEM) and atomic force spectroscopy (AFM) are the techniques used to characterize the surface morphology and surface roughness, respectively. In addition, the atomic species analysis in SF₆ plasma using optical emission spectroscopy (OES) technique will also be mentioned briefly.

3.1 Contact Angle and Surface Tension/Energy

The contact angle (θ) is an angle between the solid surface and liquid droplet at the contact point, measured within the body of liquid, opposed to the ability to repel water. Fig. 3.1 shows the schematic diagram of the contact angle and the surface tension forces of water droplet, due to the balance of surface tension forces at interfaces between solid/liquid (γ_{SL}), solid/vapor (γ_{SV}), and liquid/vapor (γ_{LV}) at equilibrium.

The relation between contact angle and surface tension can be expressed via

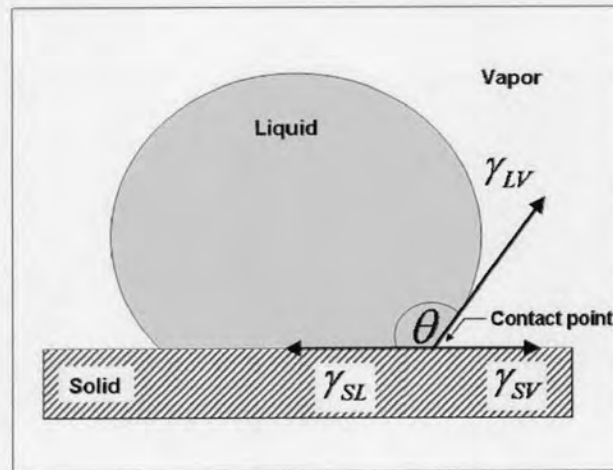


Figure 3.1: Schematic diagram of contact angle, showing the balance of surface tension force, applied from [27].

the Young equation, as defined by [27],

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL}. \quad (3.1)$$

In addition, surface energy or work of adhesion (W_a) is defined as work required to separate a unit area of interface between liquid and solid that the surface wettability. The work of adhesion is given by,

$$W_a = \gamma_{LV} + \gamma_{SV} - \gamma_{SL}. \quad (3.2)$$

Substituting equation (3.1) into equation (3.2), the relation between contact angle and surface energy is

$$W_a = \gamma_{LV}(1 + \cos \theta), \quad (3.3)$$

where surface tension of water in air (γ_{LV}) equal to 73 dynes/cm (0.073 N/m)[27]. According to equation (3.3), a higher contact angle represents a lower surface energy or more ability to repel water, as exhibited in Fig. 3.2.

In this thesis, the droplets contact angles of treated fabrics were measured by the Tantac CAM-PLUS contact angle meter, as shown in Fig. 3.3. However because the contact angle meter of CAM-PLUS can only measure only hydrophobic

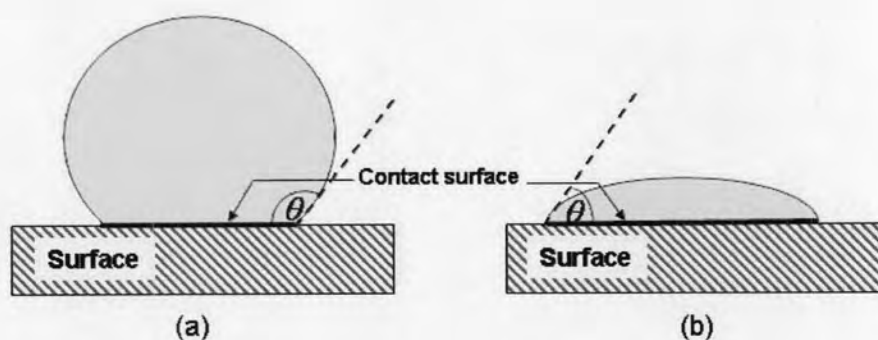


Figure 3.2: Two extremes of adsorptive wettability; (a) showing a higher contact angle that means the water droplet can hold bulk and less absorb by surface (b) showing a lower contact angle that means surface absorbs water.

sample (contact angle in the rang of 90° - 180°), our untreated fabrics contact angles were obtained measured directly from the photograph of droplets which were recorded by digital camera in macro mode. Then, the images of the droplets were transferred to computer and the droplets contact angle was graphically extracted and calculated with AutoCAD 2005 program. For contact angle measurement contact angle meter, a water droplet ($4\mu\text{l}$ in volume) was placed using microsyring onto the surface fabric. While using Tantac CAM-PLUS, the image of droplet as it rests on the fabric is projected on screen, where contact angle can be measured with HALF-ANGLE technique [28], by drawing a line from the interface point between the liquid and solid surface through the apex of droplet that is perpendicular to a half distance of contact surface. The HALF-ANGLE technique is demonstrated in Fig. 3.4.

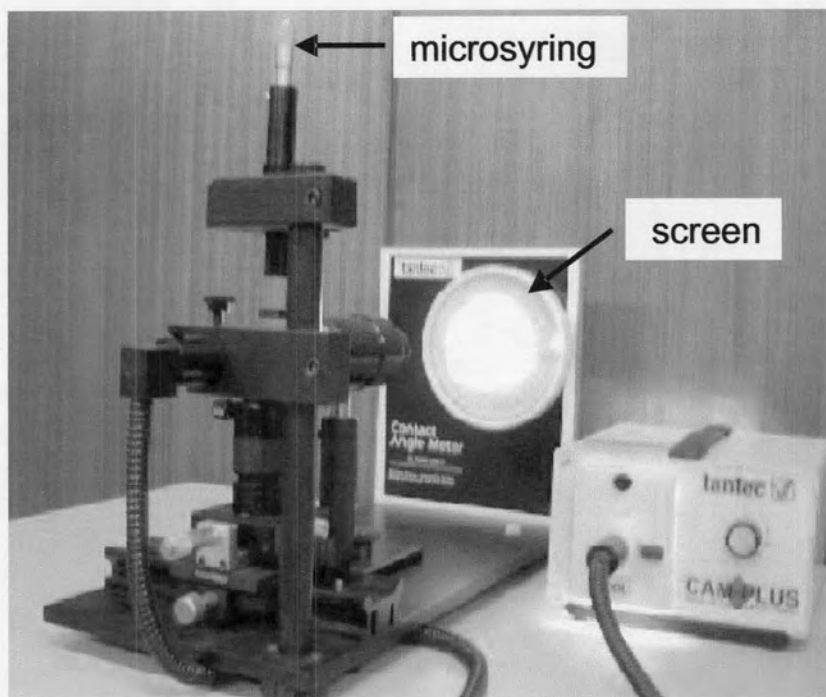


Figure 3.3: Photograph of the Tantac CAM-PLUS contact angle meter.

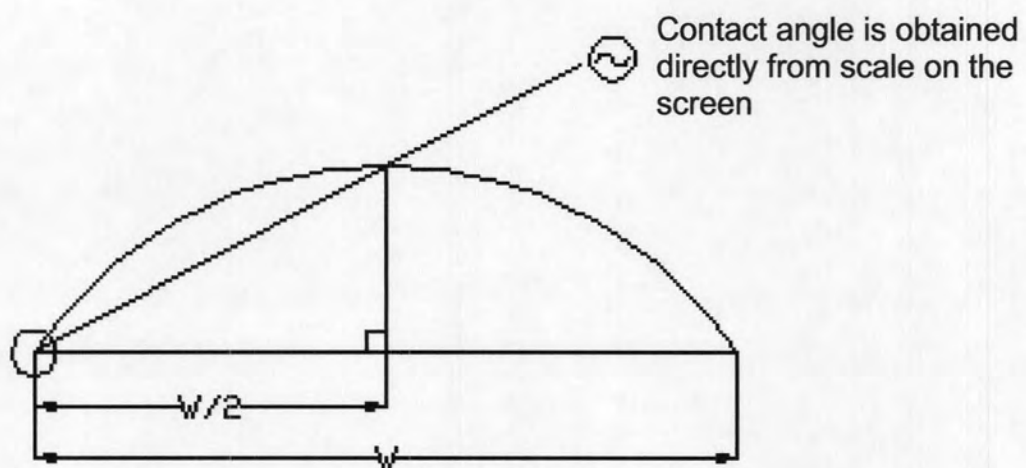


Figure 3.4: HALF-ANGLE technique for measurement contact angle of water droplet by Tantac CAM-PLUS contact angle meter.

3.2 Absorption Time Measurement

Absorption time is defined as a time in which the fabric totally adsorbs water. The absorption time was measured in order to observe the ability to resist permeation of water on fabric. The water droplet $40 \mu\text{l}$ in volume was released using micropipet at three different positions at the radial distance of 3 cm from the center of each sample fabric as showed in Fig. 3.5. The data of absorption time and contact angle are obtained as average time from these three droplets. The absorption time was limited at 210 minutes according to dripped water volume. After this, the water volume lost is considered mostly due to evaporation.

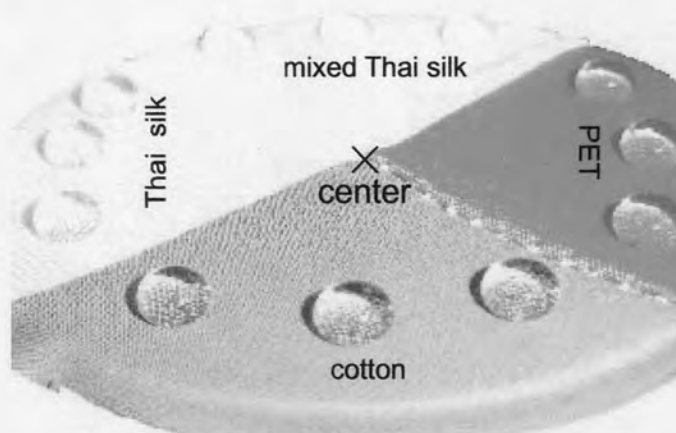


Figure 3.5: The photograph of water droplets placed onto three positions of each sample fabrics (polyethylene terephthalate (PET), mixed Thai silk, Thai silk, cotton) and radial distance from center.

3.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA) is a surface analytical technique which provides the chemical state information of outer layer surface [1, 35]. This technique is based on the photoelectric effect. Commonly, X-ray photon of MgK_{α} (1253.6 eV) or AlK_{α} (1486.6 eV) is an energy source to create the photoelectron.

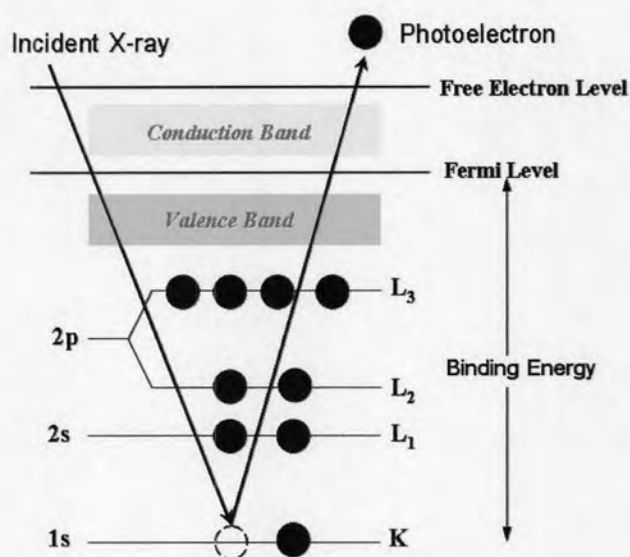


Figure 3.6: Schematic diagram of XPS process [35].

If the incident X-ray has sufficient energy which can hit electron in the core level, the escaped electron is called photoelectron. Fig. 3.6 shows the schematic of XPS process.

The photoelectron with its kinetic energy (E_k^F) is detected by spectrometer which is placed within hemispherical analyzer. By detecting kinetic energy of photoelectron, we can determine the binding energy (E_b^F) by equation (3.4)[35],

$$E_k^F = h\nu - E_b^F - \phi_{sp}, \quad (3.4)$$

where, $h\nu$ is energy of the incident x-ray and ϕ_{sp} is the work function of the

spectrometer. Since the binding energy is the characteristic energies of each atom or molecule, this information can demonstrate the chemical composition. There are two types of spectrums obtained from XPS analysis, (a) survey spectrum (scan in range of 1000 eV), and (b) high-resolution spectrum (scan in range of 10-20 eV).

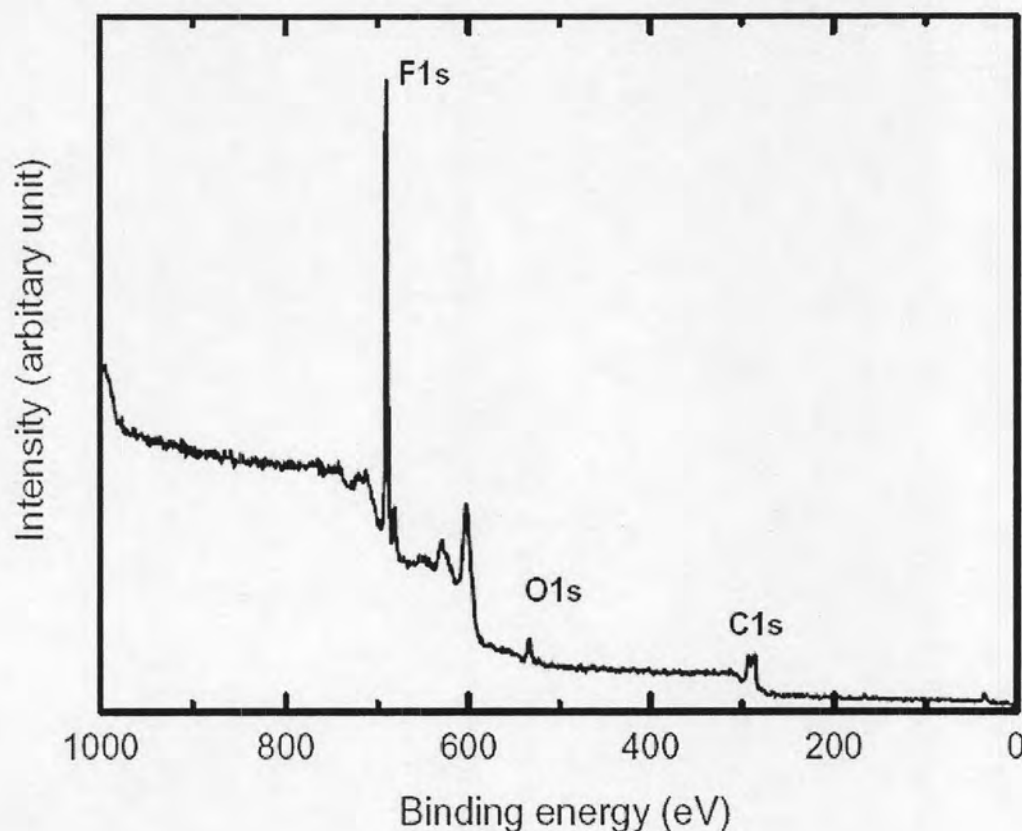


Figure 3.7: XPS spectrum obtained from polyethylene terephthalate fabric sample treated by SF_6 plasma using $\text{MgK}\alpha$ radiation.

Fig. 3.7 shows a survey spectrum of polyethylene terephthalate fabric treated by SF_6 plasma. Three peaks correspond with F1s, O1s, and C1s core level which give information of elements composition while high resolution spectrum (see Fig. 5.19) gives the details of chemical state and atomic concentration.

In this thesis, XPS experiments with Kratos Analytical model, AMICUS were performed on freshly-treated fabrics using $\text{MgK}\alpha$ radiation to verify the changes in surface chemical composition of treated fabrics.

3.4 Scanning Electron Microscope

Scanning electron microscope (SEM) is one of the most widely used instruments for investigating surface morphology of samples. The technique uses secondary electron to create an image of sample. Fig. 3.8 illustrates the schematic diagram of a SEM. The main component can be divided into three main parts.

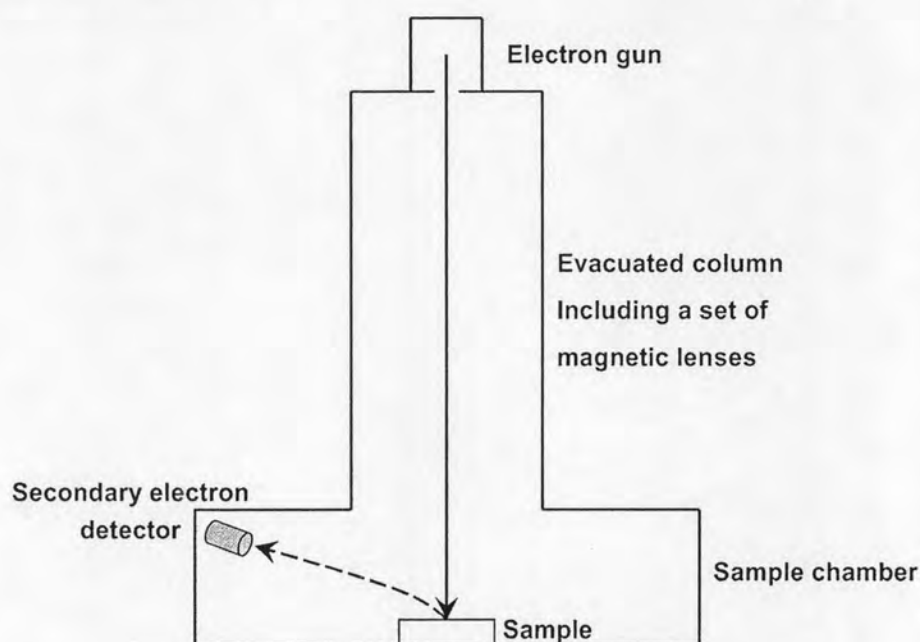


Figure 3.8: Schematic diagram of basic element of SEM.

The first part is electron gun which generates primary electrons by thermionic emission. The second part is an evacuated column including a set of magnetic lenses, which are used to focus and scan electron beam on the surface of sample. The third part is a sample chamber, consisting of sample holder and secondary electron detector. When the energetic electrons encounter the sample surface, the interaction between electron and sample produce several signals such as secondary electron, backscattered electron, characteristic x-ray, and auger electron etc. Fig. 3.9 illustrates the interaction of primary electron beam on the sample surface, showing the excitation volumes for several signals. The size of excitation volume is determined by scattering of the electron beam in the solid which depends on energy

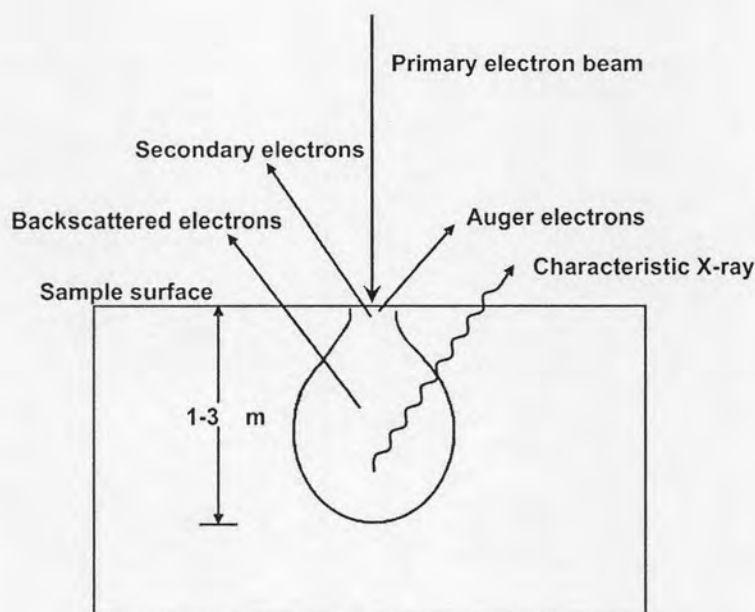


Figure 3.9: The interaction between primary electron beam on sample surface, showing the excitation volume generated secondary electrons, backscattered electrons, characteristic X-ray, and Auger electrons [29].

of electron beam and atomic number (Z) of the specimen [30]. This volume can extend down to a depth of $1-3 \mu\text{m}$ [29]. However, the secondary electron generated near surface of sample (a depth of $5-50 \text{ nm}$). Intensity of these electrons is detected to create the image of sample surface on a digital CCD array. The higher signal intensity is related to brighter on the image.

In this thesis, the sample is not electrically conducted, thus the thin gold layer ($\simeq 1 \text{ \AA}$) is deposited on fabric in order to avoid electrical charging during the analysis. The SEM images were recorded by a JEOL model JSM-6400 scanning electron microscope with voltage of 15 kV .

3.5 Atomic Force Microscope

The Atomic force microscope (AFM) is one type of scanning probe microscope (SPM), which is used for obtaining image of sample surface. AFM can be used to

investigate a variety of material surface, for example thin and thick films, ceramics, glass, biological membranes, metals, and polymers etc. This technique involves the force between atom of the probe tip and atom of sample surface (atomic force).

Fig. 3.10 shows the essential elements of AFM.

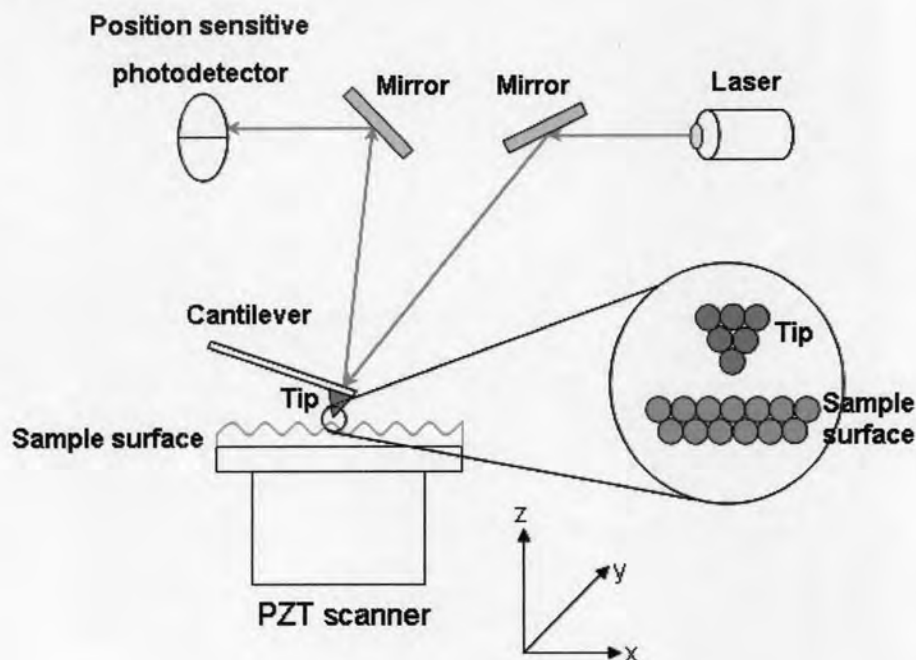


Figure 3.10: Schematic diagram of atomic force microscope.

The laser beam is focused onto the top of cantilever. The probe tip is mounted on another side of the cantilever. The reflected laser beam is detected by photodetector. The atomic force between the tip and sample is varied depending on the probe tip distance from sample. Thus, for probing the surface with roughness, the photodetector measures the vertical deflection of the cantilever, Here, topographic features of the surface can be displayed. There are three modes obtained by AFM including contact mode, Tapping mode and non-contact mode which can be described by Lennard-Jones potential [31]. However, in this thesis the sample surface is the fabrics, therefore the Tapping mode of AFM model Nanoscope IV is used. The AFM technique is used to obtain surface information such as the surface roughness which are quantified by root-mean-square (RMS)

value. The RMS surface roughness is standard deviation of the distribution of all height values within the surface area of interest, defined as

$$RMS = \sqrt{\frac{\sum_{i=1}^N (Z_i - \bar{Z})^2}{N}}, \quad (3.5)$$

where \bar{Z} is the average surface height within the interested surface area,

Z_i is the surface height of each particular point,

N is the number of data point.

3.6 Optical Emission Spectroscopy

The optical emission spectroscopy (OES) is a technique for the monitoring and the diagnostic of the light emitting from a plasma [21]. The advantage of this technique is that it is performed outside of the vacuum system with the real-time capability, so it does not perturb the plasma. In this work, the ocean optics HR4000 with OOIBase 32 software program is used to identify the atomic species in SF₆ plasma. The experimental setup of OES technique for SF₆ plasma is shown in Fig. 3.11.

The light emission from SF₆ plasma is guided through the fiber optic cable and dispersed by a grating. Only the selected wavelengths passed into the photodetector and recorded into the computer. The conventional data is showed as the intensities of emission spectra lines versus a wavelength. In order to identify the energetic levels or atomic species, the wavelength of spectrum lines are compared with atomic spectra database of National institute of standard and technology (NIST) [32].

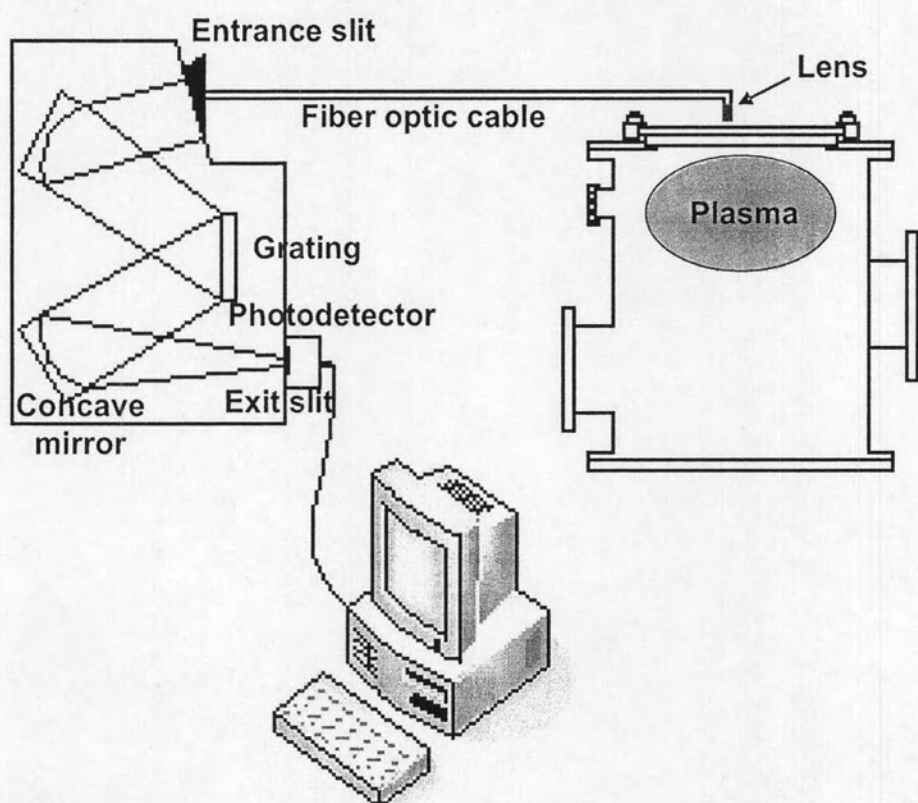


Figure 3.11: Experimental setup for optical emission spectroscopy of plasma.