

CHAPTER 3

EXPERIMENTAL PROCEDURES

This chapter explains the methodology and overall working process as shown in the Figure 3.1. All investigated natural corundum, as shown in Table 3.1, were supplied by the Division of Material Science (Gems and Jewelry), Department of General Science, Faculty of Science, Srinakharinwirot University and Mr. Sommai Srisupawattana. These corundum are also shown in Figure. 3.2.

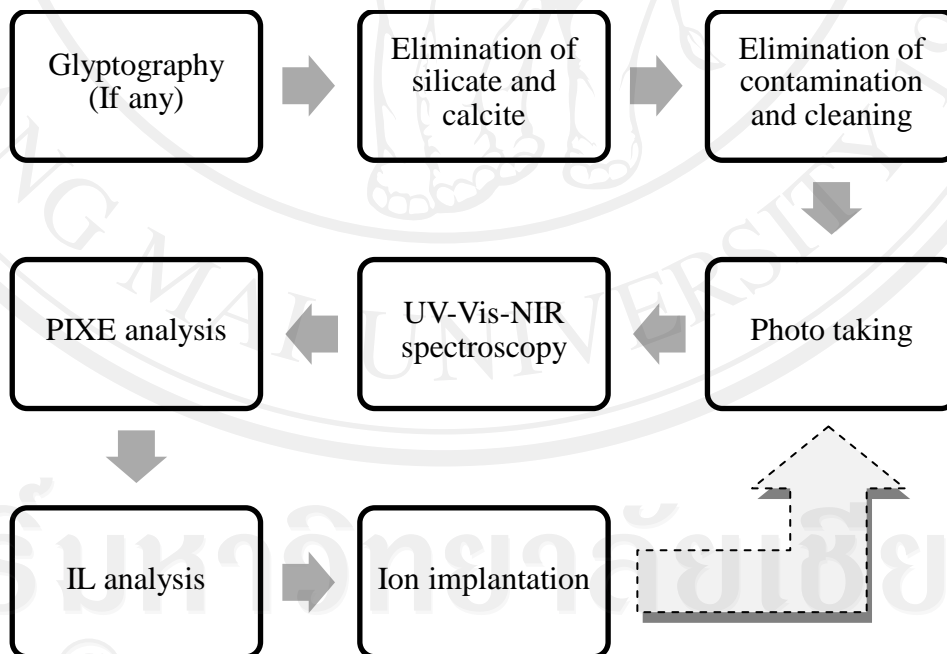


Figure 3.1. The overall process diagram.

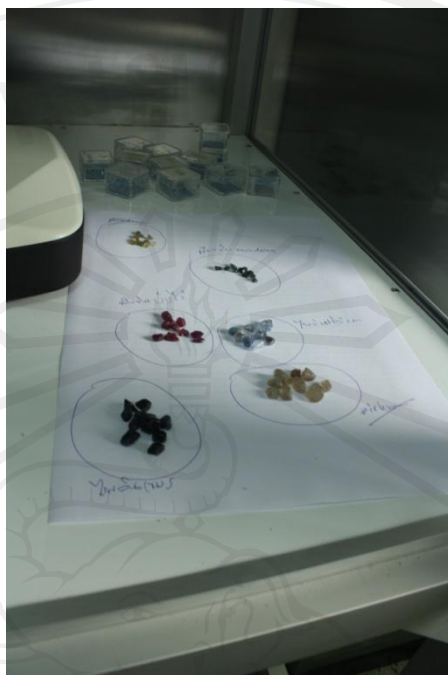


Figure 3.2. A photo of corundum used in this study.

Table 3.1. Details of natural corundum being investigated by the PIXE technique.

Abbreviation	Sample	Origin	Description
R	Ruby	Bo rai (Thailand)	Tone: Dark Saturation: Bright Primary color: Red (Pigeon blood) Intermediate color: Violet
B	Blue sapphire	Sri Lanka	Tone: Light Saturation: Pale Primary color: Blue
BG	Blue green sapphire	Bang Kha Cha (Thailand)	Tone: Medium Saturation: Moderate Primary color: Green Intermediate color: Blue
Y	Yellow sapphire	Montana (USA.)	Tone: Light Saturation: Bright Primary color: Yellow
DB	Dark-blue sapphire	Pailin (Cambodia)	Tone: Very dark Saturation: Bright Primary color: Blue Intermediate color: Brown

Table 3.1. Details of natural corundum being investigated by the PIXE technique

(Continued).

G	Dull white sapphire	Sri Lanka	Tone: Dark Saturation: Dull Primary color: Colorless
RM	Ruby	Mogok (Myanmar)	Tone: Dark Saturation: Bright Primary color: Red (Tomato sauce) Intermediate color: Violet
WS	White sapphire	Unknown	Tone: Light Saturation: Moderate Primary color: Colorless
BS	Blue sapphire	Unknown	Tone: Light Saturation: Pale Primary color: Blue
PS	Pink sapphire	Unknown	Tone: Medium Saturation: Moderate Primary color: Pink Secondary color: Violet
YS	Pale yellow sapphire	Unknown	Tone: Medium Saturation: Moderate Primary color: Yellow Secondary color: Violet
BGL	Green blue sapphire	Unknown	Tone: light Saturation: bright Primary color: blue Secondary color: green
BGX	Light-blue green sapphire	Bang Kha Cha (Thailand)	Tone: light Saturation: moderate Primary color: blue Secondary color: green
BGD	Dark-blue green sapphire	Unknown	Tone: dark Saturation: bright Primary color: blue Secondary color: green
Moz	Pink sapphire	Madagascar	Tone: medium Saturation: bright Primary color: red
LGAF	Light-green sapphire	Africa	Tone: light Saturation: moderate Primary color: green
DBAF	Dark-blue	Africa	Tone: dark Saturation: vivid Primary color: blue

Table 3.1. Details of natural corundum being investigated by the PIXE technique
(Continued).

GAF	Green sapphire	Africa	Tone: medium Saturation: bright Primary color: blue Secondary color: green
GBAF	Green blue sapphire	Africa	Tone: medium Saturation: moderate Primary color: green Secondary color: blue
YGAF	Yellow green sapphire	Africa	Tone: light Saturation: moderate Primary color: green Secondary color: yellow

3.1 Sample preparation

3.1.1 Glyptography

In case of necessary, corundum sample was faceted in the same way as normally do in the jewelry business. Each of corundum was fixed to the stick called “Tuan” in Thai by the self-made glue generally called on shellac. Next, corundum at the end of the Tuan was pressed on the grinding machine in the parallel direction with the C-axis. In general, the C-axis is supposed to be the longest crystalline axis in a hexagonal structure. Therefore, the light can be more transparent in this axis than another. The traditional method for finding the C-axis direction is by looking at the gemstone through the light. Any direction of maximum transmission is parallel to the C-axis. After this, corundum was pulled out of the Tuan with tweezers by melting the glue with flame. All of corundum were soaked in ethanol for about 15 minutes. Lastly, it was cleaned in water which labeled by the code, as shown in Table 3.1, and kept in the plastic box.

3.1.2 Elimination of silicate and calcite

In some cases, silicate and calcite have to be removed prior to the above process. The process could be done by filling the hydrofluoric acid into the plastic bottle which submerged the corundum, as follows.

- All corundum are put in the Low Density Polyethylene (LDPE) bottle which has the lid covering.
- The experimenter should carefully pour the 48% hydrofluoric acid where corundum totally submerge in the acid.
- The experimenter must always wear the latex glove and the face mask.
- Leave corundum in the acid for about 24 hours in a fume hood of good ventilation and after this return the acid to other bottle.
- Fill clean water over corundum and shaking well.
- Repeat the above procedure about three to five times.

Certainly, the glass container is forbidden in this process because the acid would corrode the glass.

3.1.3 Elimination of contamination and cleaning

Prior to ion beam analysis and modification, stains and small particles on the gems' surfaces were cleaned by dispersing with ethyl alcohol in an ultrasonic bath as shown in Figure 3.3. First, corundum was put into the beaker, followed by pouring the ethyl alcohol until the samples were totally submerged. Furthermore, the beaker was placed at the bottom of the ultrasonic bath which filled to one-third of the bath by water and loaded them by the metal weight. The cleaning time was 15 minutes, then,

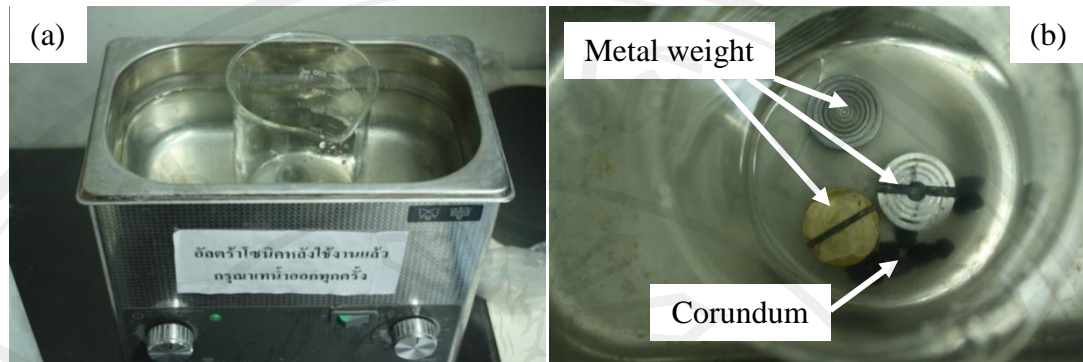


Figure 3.3. The ultrasonic bath (a) used for cleaning the particle on the sample surface, and the sample is soaked in the ethyl alcohol (b).

washed by pure water. This method is vital for the analysis of actual element concentration in corundum and further investigation.

3.2 Photo taking

All corundum samples were recorded by the optical microscope for 10x magnification. The Motic SMZ-168 Series of stereomicroscopes was used for closely observing the samples, as shown in Figure 3.4, together with a magnification ratio of 1:6.7. Note that the standard eyepieces present a field of view 30.7 mm to cover more of sample in short time. There are either overall or selective point photos which noted the taking condition. The camera also captured the image by a various white balance mode, in other words, the terms of shade related to a light source including auto, day light, fluorescence, and tungsten. The focusing mode of camera was selected for an evaluative, macro, and used the sensitivity of the image sensor (ISO) for 100. The samples were posited on the white circular plate when using the top light source as



Figure 3.4. Motic SMZ-168 Series of stereomicroscopes (Motic., n.d.) used in this study.

tungsten bulb. On the other hand, the samples were posited on the opaque glass when using the beneath light source as a white bulb. Moreover, a focus knob of microscope also coarsely adjusted with a camera focusing. Each of the photos was recorded by the 10.0 Mega Pixel Canon PowerShot A495 camera and written down the condition in the log book for repeating after the modification.

3.3 UV-Vis-NIR spectroscopy

The standard technique of UV-Vis-NIR spectroscopy is used for comparison purposes. This measurement was performed by using the Hitachi UV

spectrophotometer U-4100 at the Gemology program, Department of Geological Science, Faculty of Science, Chiang Mai University, as shown in Figure 3.5, which has specific details as follows (Hitachi High Technologies America, Inc., 2012):

- Wavelength range 175 to 2,600 nm Band pass NIR Region
- Switching in 0.2 nm steps from 0.24 to 8.0 nm
- Scan speed 0.3 (0.75), 3 (7.5), 15 (37.5), 30 (75), 60 (150), 120 (300), 300 (750), 600 (1,500), 1200 (3,000), and 2400 (6,000) nm/min. Speeds in parenthesis are speeds for NIR region.
- Detectors are Photomultiplier (UV-Vis region) and Cooled PBs (NIR region)

For this measurement, the samples were attached to the aluminium plate with 1 mm-diameter hole for allowing the light transmission. A piece of Blu-Tack held corundum on the plate as shown in Figure 3.6. The scanning of light is over the range of 250 – 800 nm. In each measurement the absorbance parameter and the wavelength of incident light were recorded simultaneously.



Figure 3.5. Hitachi spectrophotometer U-4100: outside (a) and inside (b).

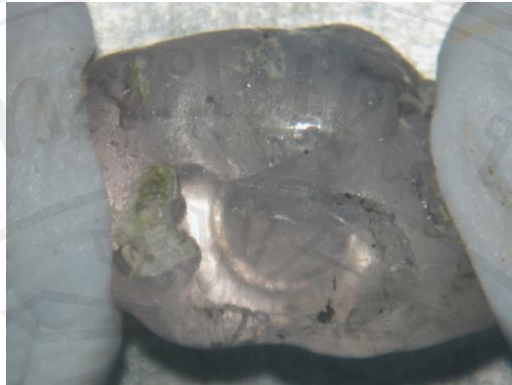


Figure 3.6. The holding of sample for UV-Vis-NIR spectroscopic measurement.

3.4 Ion beam analysis

One of the main objectives of this investigation is to establish a standard technique for classifying the origin of corundum in the Thai market which related to the price setting. Additionally, the fingerprint of corundum could reveal the characteristic of them for further investigation, accompanied by comparing them with the conventional gemology analysis techniques. Furthermore, these data are used to compare between before and after the corundum treatment.

3.4.1 Particle-induced X-ray emission (PIXE) analysis

Samples were attached on a small bolt with a piece of carbon tape and then skewed onto the sample holder. Certainly, samples had been polished and cleaned before analysis in the same way as Osipowicz *et al.* (1995). All samples need to be adjusted till the level were all equally, then, inserted into the control system which placed in the analysis chamber. Prior to the PIXE experiment, the high-voltage supply of detector is adjusted slowly to -500 V, and wait at least 30 minutes to let the system stable. The other associated systems such as preamplifier supply and amplifier supply

also turn on the same way as was mentioned. Subsequently, the vacuum pressure was generated by the turbo molecular pump with rotary backing pump until the vacuum pressure is below 1×10^{-5} torr. The analysis chamber has an aperture of 1 mm-diameter for collimating the ion beam at the entrance of the chamber and can be opened or closed by a switch in the control room as shown in Figure 3.7. At first, the zero-coordinate was set up at the center of the scintillation plate which is made of alumina. The ion beam current was approximately measured at the small bolt placed nearby the scintillator plate and verified the matching of channel number and X-ray energy. If it is mismatch, adjusting at the amplifier gain is required. Afterward, the sample holder is moved up by the stepping motor to the required position. The measurement time depend on the ion current, density of sample, and the distance to detector, however, it consumes normally about 600 – 900 seconds. The data was saved as the labeled name by the Maestro software separately in each day for convenient of later searching. Subsequently, the data was evaluated by GUPIXWIN software and reported element concentration as parts per million by weight (ppm).



Figure 3.7. Control system of the 1.7 MV tandem accelerator (a) and the data accumulation and acquisition system (b).

Prior to PIXE measurement on corundum, the detecting was checked and calibrated by observing a PIXE spectrum of a standard sample NISM SRM610. The calibration was done by adjusting the amplifier's gain to the suitable position. The result is shown in Figure 3.8, which the trace element concentration is also reported in Table 3.2.

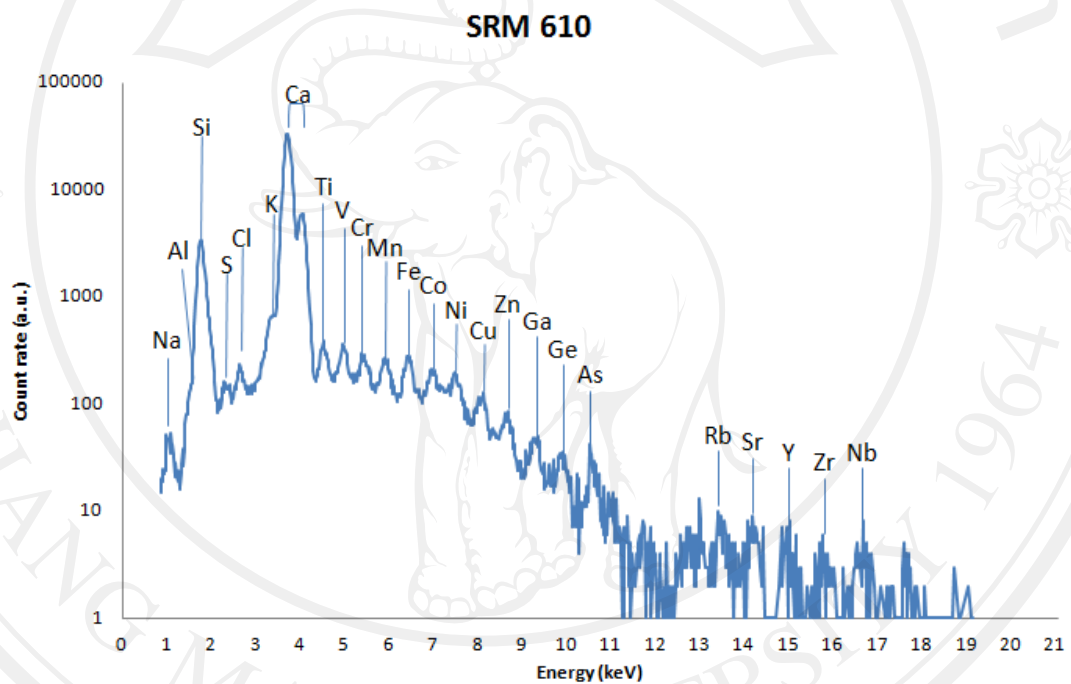


Figure 3.8. The PIXE spectrum of a standard sample: NISM SRM610.

Afterward, all of PIXE spectra could be quantified, by the GUPIXWIN software, which are concluded in Table 3.2. Furthermore, the relations of the element concentration or the relations of the ratio of element concentration in various relation would be plotted for identifying the deposit type. This is described in details in section 4.4.

Table 3.2. Comparison between the measured values and the preferred average values by Pearce *et al.* (1997) of element concentration in the standard sample (SRM610).

Matrix	Preferred value	Analysis value	Trace elements	Preferred value	Analysis value
Na ₂ O	14	0.99	Ti	434	448.4
Al ₂ O ₃	2	2.61	V	441.7	409.4
SiO ₂	72	82.80	Cu	430.3	425.5
CaO	12	11.06	Zn	456.3	446.4
			Tm	420.1	459.4
			Re	103.7	103.4

3.4.2 Ionoluminescence (IL) analysis

IL experiment was performed inside the analysis chamber in which samples were placed in front of the beam exit. In the similar way as PIXE experiment, 2 MeV proton beams are used as a probe. The preparation and conditions of experiment is quite the same as the PIXE analysis except that the detector is fiber optic light guide and the analyzer is an Ocean Optic spectrometer in this case. The luminescent light from corundum inside the chamber was collected and guided through the optical fiber to the spectrometer outside the chamber. The spectrometer and personal computer were located close to the analysis chamber as shown in Figure 3.9. The data accumulation time was about 500 – 3,000 ms. The analysis of these data reveals the luminescence mechanism which was the qualitative data by fitting with the OriginPro

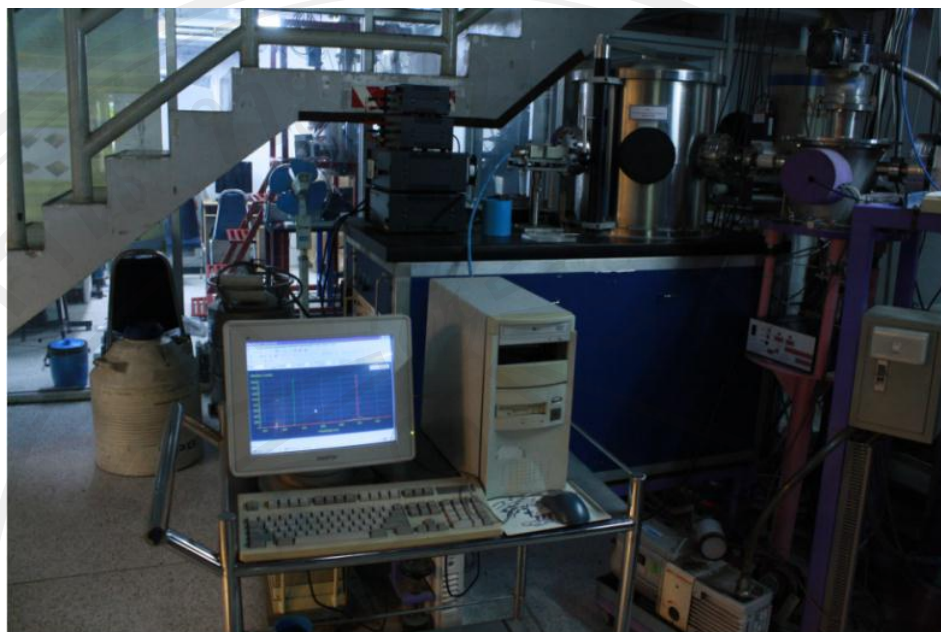


Figure 3.9. Data accumulation system of the IL technique.

8 software (OriginLab, 2007). Each of the luminescence spectra was normalized by averaging the accumulation time prior to analysis.

The emission spectra acquired by the IL technique will be collected and some of them will be analyzed in relating to the Cr^{3+} concentration which can be preliminary observed by the color appearance. Furthermore, the results can directly compare with the absorption spectra from the UV-Vis-NIR spectroscopy technique.

3.5 Ion beam enhancement

According to the conventional method of heat treatment, there are two main processes for modification, i.e. reducing condition and oxidizing condition. This seems resemble to the negative ion and positive ion irradiation.

3.5.1 Nitrogen and argon ions beam modification

The samples were prepared in the same way as the ion beam analysis, and recorded the figure in every view point. Next, the samples were attached to the square-aluminium sample holder with a piece of carbon tape as shown in Figure 3.10. In fact, the sample holder was also covered by the aluminium foil which described a reason in section 3.5.2. Eventually, inserted the sample holder to the irradiation chamber and pumping down until the pressure is below 1×10^{-5} torr.

Nitrogen and argon positive ions are generated by a Freeman type ion source of the 200 kV Varian ion implanter as mentioned earlier. The ion beam is scanned both on horizontal and vertical direction to be a rectangular cross section beam with



Figure 3.10. The sample holder used for Ar^+ and N_2^+ ion beam irradiations.

10×10 cm²-size. Subsequently, the ion beam distribution is adjusted by monitoring the four Faraday cups at the corner of the ion beam cross section. Consequently, the remaining ion beam is chopped to circular cross section with radius about 10 inch.-diameter to the target section. The 0.502655 cm²-area hole which is at the center of the platform behind the sample holder is used for ion beam fluence monitoring by a Faraday cup.

3.5.2 Oxygen ion beam modification

The oxygen ion beam is generated by the Cs-sputter source of the tandem accelerator. The MnO₂ powder was used to generate the O⁻ ions at a 23 keV kinetic energy ion. The ion beam is sent through the 2 cm-diameter aperture which is placed in front of the irradiation chamber. Corundum were attached to the fan-like sample holder by a piece of double-sided carbon tape. The sample holder was also covered by the aluminium foil for gradually attenuating an energy loss of the incident ion as shown in Figure 3.11. Additionally, the holder can be rotated for each blade to meet with the ion beam each time. Prior to ion irradiation, the vacuum pressure must be kept below the 1×10⁶ torr, and checked the ion beam position by observing the luminescence from scintillation plate on the sample holder which can be seen through the window on the side of the chamber. Unfortunately, the video camera is not set up inside the irradiation chamber, so the observation can be done by seeing through the mirror beside the irradiation chamber. Furthermore, the Faraday cup in front of the sample holder is used to measure ion beam current normally about 10 – 20 μA.

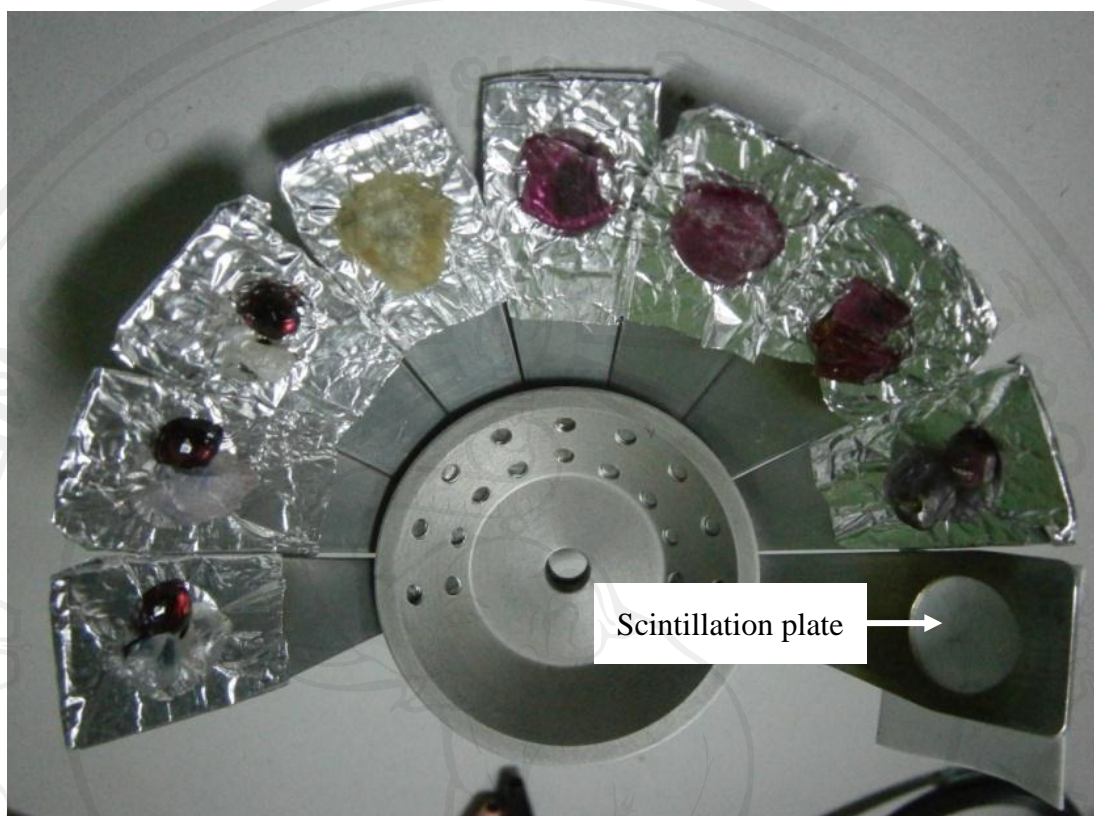


Figure 3.11. The fan-like sample holder for oxygen ion modification.

The ion current was measured every 15 minutes for calculating the real-time fluence. During operation, the researcher guessed the ion beam fluence by using the area under the curve of the ion current and time relation which is shown in Figure 3.12 as an example. At the upper-left corner, the “a” and “b” represent the charge state and the number of atom per charge state in the ion beam, “e” is the electric charge of one electron, “A” is the ion beam cross section area, “I” is the ion current. The times in each row is the recording time at the instantaneous ion current, then, these data are plotted as a graph as shown on the right of the figure. The calculated fluence indicates the instant accumulation fluence at the sample.

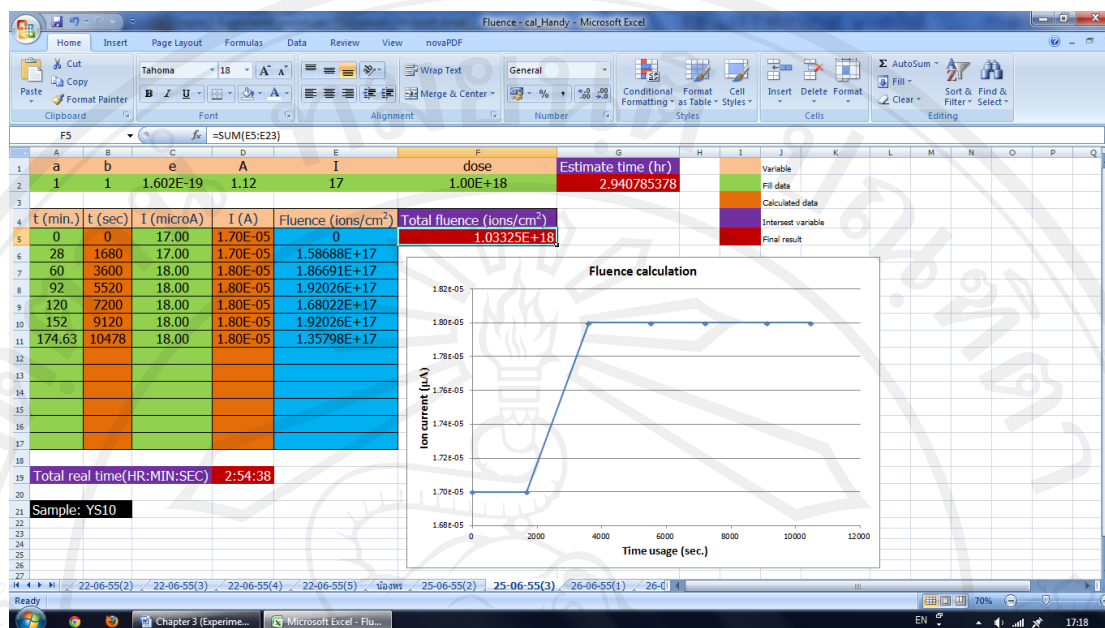


Figure 3.12. Ion beam fluence estimation.

Finally, all of the irradiated corundum were recorded by the optical microscope at the same magnification including other photo taking conditions. If there were some alterations such as clearer, more intense color, lighter color, etc., those samples would be analyzed by the following investigation. First, the standard technique of UV-Vis-NIR spectroscopy was used for comparison purposes by trying to measure at the same point at the before treatment. In the measurement the absorbance parameter and the wavelength of incident light were recorded at the same range, subsequently, the PIXE analysis was performed. This spectrum is directly compared with the previous investigation for considering the change of Fe/Ti ratio.

Note that this ratio is very important for the indication of the bluish tone or the violet tint in sapphire and ruby, respectively. For instance, if this ratio increases, the blue color is more intense.