CHAPTER VI

CHEMICAL ANALYSIS

6.1 Introduction

Corundum is chemically composed of aluminium oxide (Al_2O_3) which is naturally colorless in its pure state. However most natural corundums not pure but contain trace concentration of other elements replacing in their crystal structures. Consequently, various colors of corundum can be generated by particular trace elements and perhaps crystal defect, called color center. For coloring elements in corundum, they are usually characterized by some transitional metals, particularly Cr, Fe and Ti. Chromium normally produces pink to deep red colors in corundum depending on its concentration. Iron, itself, can give color varieties (e.g. pale green, yellow and brownish color) to corundum; moreover, it can also combine with titanium which they are able to produce wide ranges of green, blue-green and blue colors (Nassau, 1994).

In the previous chapters, detailed information has been reported on the physical properties and absorption spectra of the Ilakaka-Sakaraha sapphire samples. This chapter will present and discuss chemical analyses which were analyzed using Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometer and Electron Probe Micro-Analysis (EPMA) techniques. In order to understand causes of color and color development after heat treatment of corundum, trace analyses would be investigated. Then, chemical analysis for trace elements contained in the studies sapphires were taken into account.

6.2 EDXRF Analysis

Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometer is a non-destructive analysis method; therefore, it has been conventionally used to investigate chemical compositions of gemstones in most gemological laboratories over the world. This technique is an application on energy emission of electrons in atoms. These electrons are excited by X-ray and then they move to the higher energy levels in their own atoms or may be ejected away from their atoms. Consequently, electrons in the

higher energy level will replace the lost electrons; this process must emit energy in particular range. Each element has different atomic weight that leads to dissimilar energy level. Therefore, those different energies can be utilized for determination of chemical constituent of material.

In this study, the trace analysis of sapphire samples was carried out using Oxford Energy Dispersive X-ray Fluorescence Spectrometer, model ED 2000 (Figure 6.1) at the Gem and Jewelry Institute of Thailand (GIT). The X-ray source used in the machine is silver (Ag) X-ray tube, while standardless calibration is applied for all analyses. Therefore, trace analyses yielded from this technique would be just semiquantitative level.

Trace elements of 45 unheated sapphires were analyzed and reported as weight % oxides (e.g. Fe_2O_3, TiO_2, Cr_2O_3, V_2O_3 and Ga_2O_3). The analytical results are summarized in Table 6.1 whereas the total numbers of analyses are listed in Table IV.1, Appendix IV. Each sample was analyzed at the center of both polished faces. These trace element contents are summarized as ranges of minimum and maximum values in Table 6.1. In addition, analytical data in Table 6.1 are graphically revealed as histogram in Figure 6.2. Variations of trace compositions in each sapphire group under this study are described below.

Figure 6.1 Oxford energy dispersive X-ray fluorescence spectrometer, model ED 2000, based at GIT.

Table 6.1 Ranges of EDXRF analyses of some trace elements contained in Ilakaka-Sakaraha sapphire samples. Minimum - maximum values are given along with the average ± standard deviation in parentheses below each range.

Group of samples	Number of samples	Concentration (wt%)				
		Fe_2O_3	TiO_2	Cr_2O_3	V_2O_3	Ga_2O_3
Dark blue	5	0.10 - 0.35 (0.20± 0.102)	0.05 - 0.13 (0.09± 0.028)	0.00 - 0.13 (0.01± 0.008)	0.00 - 0.01 (0.00± 0.004)	0.02 - 0.03 (0.02± 0.002)
	6*	0.28 - 0.44 (0.37± 0.065)	0.02 - 0.07 (0.04± 0.018)	0.03 - 0.13 (0.08± 0.031)	0.00 - 0.01 (0.01± 0.004)	0.01 - 0.01 (0.01± 0.002)
Medium blue	10	0.12 - 0.66 (0.29± 0.177)	0.01 - 0.04 (0.03± 0.010)	0.00 - 0.05 (0.01± 0.014)	0.00 - 0.01 (0.00± 0.002)	0.00 - 0.03 (0.02± 0.006)
Very light blue	11	0.14 - 0.49 (0.23± 0.107)	0.03 - 0.12 (0.06± 0.030)	0.00 - 0.01 (0.01± 0.003)	0.00 - 0.01 (0.00± 0.001)	0.01 - 0.04 (0.02± 0.007)
Milky, very light blue	5	0.10 - 0.23 (0.14± 0.029)	0.04 - 0.27 (0.11± 0.095)	0.00 - 0.01 (0.00± 0.002)	0.00 - 0.01 (0.00± 0.002)	0.01 - 0.02 (0.01± 0.004)
Dark violet	3*	0.27 - 0.39 (0.31± 0.062)	0.01 - 0.04 (0.03± 0.016)	0.11 - 0.14 (0.13± 0.014)	0.00 - 0.01 (0.01± 0.004)	0.01 - 0.02 (0.02± 0.002)
Medium violet	2*	0.33 - 0.33 (0.33± 0.001)	0.04 - 0.03 (0.04± 0.010)	0.05 - 0.05 (0.05± 0.003)	0.00 - 0.01 (0.01± 0.002)	0.01 - 0.02 (0.01± 0.008)
Light violet	3	0.15 - 0.50 (0.29± 0.189)	0.04 - 0.06 (0.05± 0.011)	0.01 - 0.03 (0.02± 0.006)	0.00 - 0.01 (0.05± 0.004)	0.02 - 0.02 (0.02± 0.001)

* Samples with color-change effect.

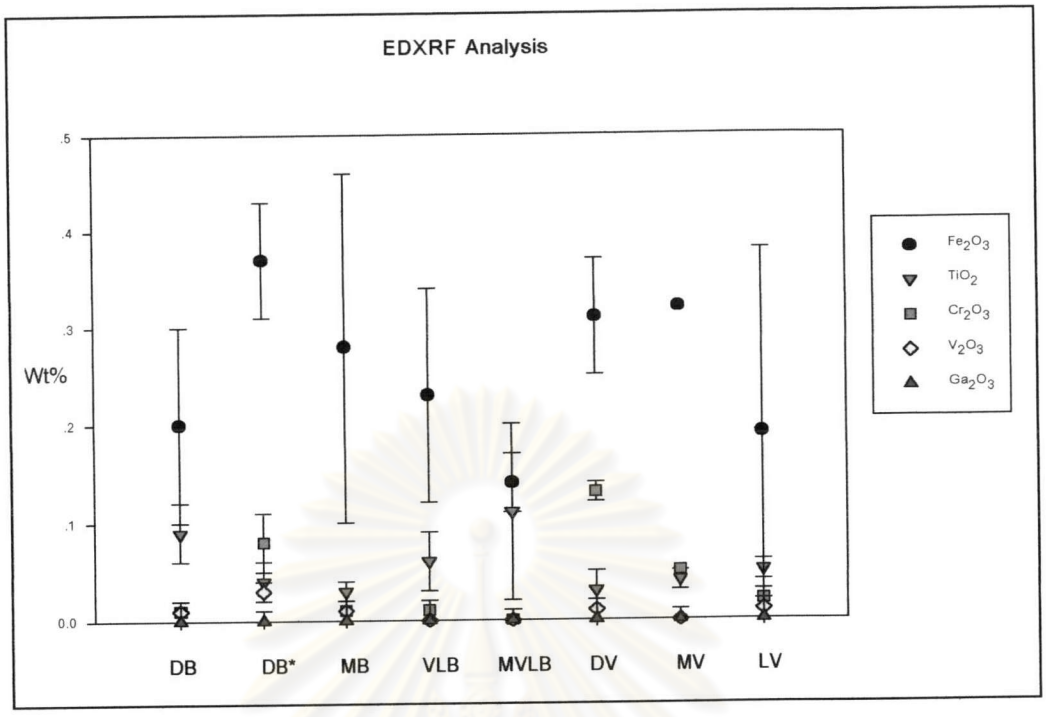


Figure 6.2 Histogram showing averages and standard deviation values of trace element analyses using EDXRF from most groups of sapphire samples before heating experiments; data are plotted from Table 6.1.

DB, DB*: Dark blue sapphire; MB: Medium blue sapphires;

VLB: Very light blue sapphires; MVLB: Milky, very light blue sapphires;

DV*: Dark violet; MV*: Medium violet; LV: Light violet.

* Samples with color – change effect.

Dark blue sapphire samples contains about 0.10 – 0.35% Fe_2O_3, 0.05 – 0.13% TiO_2, <0.15% Cr_2O_3, ≤0.01% V_2O_3 and 0.02 – 0.03% Ga_2O_3. For dark blue sapphires with color change effect, they compare relatively higher contents of Fe_2O_3, Cr_2O_3, V_2O_3 but lower TiO_2 and Ga_2O_3 content than those of the normal samples.

Medium blue sapphires have trace compositions ranging from 0.12 – 0.66% Fe_2O_3, 0.01 – 0.04% TiO_2, ≤0.05% Cr_2O_3, <0.01% V_2O_3 and <0.03% Ga_2O_3.

Very light blue sapphires possess wide ranges of trace elements 0.14 – 0.49% Fe_2O_3, 0.03 – 0.12% TiO_2, ≤0.01% Cr_2O_3, <0.01% V_2O_3 and 0.01 – 0.04% Ga_2O_3.

Milky, very light blue sapphires contain 0.10 – 0.23% Fe_2O_3, 0.04 – 0.27% TiO_2, <0.01% Cr_2O_3, <0.01% V_2O_3 and 0.01 – 0.02% Ga_2O_3.

Dark violet sapphires which usually show color change effect, comprise approximately 0.27 – 0.39% Fe_2O_3, 0.01 – 0.04% TiO_2, 0.11 – 0.14% Cr_2O_3, <0.01% V_2O_3 and 0.01 – 0.02% Ga_2O_3.

Two medium violet sapphires which mostly possess color change effect; yield about 0.3% Fe_2O_3, 0.03 – 0.04% TiO_2, 0.05% Cr_2O_3, <0.01% V_2O_3 and 0.01 – 0.02% Ga_2O_3.

Light violet sapphires contain about 0.15 – 0.50% Fe_2O_3, 0.04 – 0.06% TiO_2, 0.01 – 0.03% Cr_2O_3, ≤0.01% V_2O_3 and <0.02% Ga_2O_3.

In conclusion, iron is the most dominant trace element in all sapphire groups. The milky, very light blue sapphire contain relatively higher than titanium contents those of the others groups (see Figure 6.2). This sapphire group can be heated to develop a blue coloration depending on the sufficient amounts and proper ratios of titanium and iron that will be described in detail in the next chapter. Concentration ranges of chromium contents of blue and violet sapphires with color - change effect are higher than those of the others (Figure 6.2). On the contary, blue sapphires without color - change effect contain very small amount of chromium that is usually lower than detection limit. Generally, chromium in corundum can produce red to pink colors; however, combination between Cr and intervalence charge transfer (IVCT) of Fe^{2+}/Ti^{4+} (cause of blue shade) will therefore create violet color with respect to sapphires with color – change effect, they are mostly characterized by such combination, besides their Cr contents are likely to be higher than Ti contents. However, the other possible causes, particularly V, should still be taken into consideration. Vanadium and gallium contents are fairly uniform in all sapphire types. They are mostly very low concentrations that are below or close to the detection limit of the machine.

EDXRF analyses with standardless calibration most likely yield semi-quantitative results. All trace analyses and major Al contents measured from this

technique are automatically recalculated to make up total values as 100%. Hence the concentration of trace elements analyzed from this technique seem to be estimate value should be regarded as an approximation value only. Electron Probe Micro-Analyzer (EPMA) is an advanced technique that would yield analytical results with more accuracy. Then it was engaged for quantitative trace analyses in the final stage of this study.

6.3 EPMA Analysis

Twenty-five samples of heat-treated sapphire samples were selected for quantitative analysis using a JEOL Electron Probe Micro-Analyzer (EPMA) model JXA 8900 equiped with EDXRF system at Center of Gemstone Research, Institute of Geosciences, University of Mainz, Germany. Conditions for analysis were set at 20 kV and 20 nA with different counting times for each element. The TAP crystal in spectrometer 1 was selected to analyze for Al, Si and Mg with counting times of 40, 40 and 100 seconds, respectively. Standards used for each element were synthetic corundum for Al, wollastonite for Si and pure metal MgO for Mg. The PET crystal in spectrometer 2 was used for Ti and Cr with equally counting times of 100 seconds, pure metal $MnTiO_3$ and metallic chromium were used as standards for Ti and Cr, respectively. The LiF crystals in spectrometers 3 and 4 were engaged for V and Ga with counting times of 200 seconds; standard for Ga was pure GaAs, whereas pure vanadium was calibrated for V. The LiFH crystal in spectrometer 5 was then applied for Mn and Fe with counting times of 100 seconds; pure metal Fe_2O_3 was Fe standard and pure metal $MnTiO_3$ was Mn standard. The detection limit of EPMA analysis for most trace elements is about 0.01 weight %.

The major element (Al_2O_3) and some trace elements (TiO_2, V_2O_3, Ga_2O_3, $Fe_2O_{3(total)}$, SiO_2, Cr_2O_3, MnO and MgO) of selected sapphires after heating up to 1650 °C were analyzed. Each sample was analyzed about 6 - 12 points depending on homogeneity of the samples. At least three analytical points were made for each color zone. Generally, trace analyses from the homogeneous zone are quite similar. On the contrary, trace elements, particularly TiO_2 and $Fe_2O_{3(total)}$ of different color zones in the

same sample appear to be somewhat different values. These oxide contents were converted into atomic proportions on the basis of 3 oxygen atoms as in the typical formula of corundum (Al_2O_3); they are displayed in Table IV.2, Appendix IV. Table 6.2 shows statistically EPMA analyses in different color zones of each sapphire group (see Figures 6.3, 6.5, 6.7, 6.9, 6.11 and 6.13); in addition, these data are also presented as histograms (Figures 6.4, 6.6, 6.8, 6.10, 6.12 and 6.14).

Table 6.2 Ranges of trace element analyses using Electron Probe Micro-Analyzer of most sapphire groups except light violet group. All 24 samples were heated up to 1650 °C before analysis. Minimum – maximum values and their averages ± standard deviation values in parentheses are summarized from different color zones of each group. Numbers in parentheses below color zones in the first column represent numbers of analytical points.

Color Zones	Concentration (weight %)								
	Al_2O_3	TiO_2	V_2O_3	Ga_2O_3	FeO	SiO_2	Cr_2O_3	MnO	MgO
Dark Blue Sapphires									
Dark blue (24)	98.23-100.29 (99.27±0.679)	0.05-0.40 (0.11±0.081)	0.01-0.02 (0.01±0.005)	0.00-0.03 (0.02±0.008)	0.10-0.31 (0.19±0.067)	0.01-0.04 (0.03±0.007)	0.00-0.04 (0.01±0.017)	0.00-0.01 (0.00±0.004)	0.00-0.02 (0.01±0.006)
Blue (24)	98.54-100.07 (99.23±0.480)	0.02-0.10 (0.05±0.025)	0.00-0.01 (0.00±0.004)	0.00-0.03 (0.01±0.009)	0.04-0.27 (0.17±0.088)	0.02-0.06 (0.03±0.009)	0.00-0.08 (0.03±0.035)	0.00-0.01 (0.00±0.004)	0.00-0.01 (0.01±0.006)
Light blue (30)	98.25-100.42 (99.31±0.694)	0.00-0.06 (0.03±0.016)	0.00-0.02 (0.01±0.005)	0.00-0.03 (0.02±0.006)	0.04-0.37 (0.17±0.123)	0.01-0.04 (0.02±0.004)	0.00-0.05 (0.02±0.021)	0.00-0.01 (0.00±0.004)	0.00-0.01 (0.00±0.004)
Pink (6)	98.56-99.75 (99.21±0.490)	0.01-0.03 (0.02±0.006)	0.01-0.02 (0.01±0.003)	0.01-0.02 (0.01±0.003)	0.28-0.30 (0.29±0.006)	0.02 (0.02±0.002)	0.10-0.11 (0.11±0.002)	0.00-0.01 (0.00±0.004)	0.00-0.01 (0.01±0.005)

Table 6.2 (cont.)

Color Zones	Concentration (weight %)								
	Al_2O_3	TiO_2	V_2O_3	Ga_2O_3	FeO	SiO_2	Cr_2O_3	MnO	MgO
Medium Blue Sapphires									
Dark blue (6)	98.44-99.07 (98.76±0.257)	0.01-0.03 (0.02±0.007)	0.00-0.01 (0.00±0.004)	0.00-0.01 (0.00±0.004)	0.14-0.18 (0.15±0.015)	0.02-0.03 (0.02±0.005)	0.00-0.01 (0.01±0.004)	0.00-0.01 (0.01±0.004)	0.00-0.01 (0.00±0.005)
Blue (12)	98.97-99.75 (99.39±0.220)	0.03-0.10 (0.06±0.028)	0.00-0.01 (0.00±0.004)	0.01-0.02 (0.01±0.005)	0.10-0.17 (0.14±0.030)	0.01-0.04 (0.02±0.007)	0.00-0.01 (0.00±0.002)	0.00-0.01 (0.00±0.004)	0.00-0.01 (0.00±0.003)
Very light Blue (12)	98.66-99.64 (99.16±0.336)	0.02-0.06 (0.04±0.011)	0.00-0.01 (0.00±0.004)	0.01-0.03 (0.02±0.007)	0.08-0.27 (0.17±0.109)	0.02-0.05 (0.02±0.009)	0.00-0.01 (0.00±0.003)	0.00-0.01 (0.00±0.004)	0.00-0.03 (0.01±0.003)
Light pink (8)	99.09-100.02 (99.61±0.319)	0.00-0.02 (0.01±0.007)	0.00-0.01 (0.00±0.004)	0.00-0.01 (0.00±0.005)	0.14-0.19 (0.16±0.023)	0.02-0.03 (0.03±0.004)	0.01-0.03 (0.02±0.005)	0.00-0.01 (0.00±0.004)	0.00 (0.00±0.000)
Colorless (12)	97.78-100.04 (99.37±0.649)	0.00-0.02 (0.01±0.006)	0.00-0.01 (0.00±0.003)	0.01-0.03 (0.02±0.005)	0.12-0.34 (0.22±0.112)	0.02-0.05 (0.03±0.008)	0.00-0.01 (0.00±0.003)	0.00-0.01 (0.00±0.004)	0.00-0.01 (0.00±0.005)
Very Light Blue Sapphires									
Dark blue (6)	99.56-100.15 (99.77±0.223)	0.05-0.09 (0.06±0.014)	0.00-0.01 (0.01±0.005)	0.01-0.02 (0.01±0.005)	0.09-0.11 (0.10±0.009)	0.02-0.09 (0.03±0.025)	0.00-0.01 (0.00±0.004)	0.00-0.01 (0.00±0.004)	0.01-0.03 (0.02±0.006)

Table 6.2 (cont.)

Color Zones	Concentration (weight %)								
	Al_2O_3	TiO_2	V_2O_3	Ga_2O_3	FeO	SiO_2	Cr_2O_3	MnO	MgO
Very Light Blue Sapphires									
Blue (24)	98.29-100.23 (99.40±0.633)	0.03-0.17 (0.07±0.034)	0.00-0.01 (0.00±0.004)	0.00-0.02 (0.01±0.005)	0.08-0.23 (0.13±0.055)	0.01-0.09 (0.03±0.021)	0.00-0.01 (0.00±0.004)	0.00-0.01 (0.00±0.004)	0.00-0.03 (0.02±0.012)
Light blue (18)	98.64-100.44 (99.72±0.540)	0.01-0.04 (0.03±0.008)	0.00-0.01 (0.00±0.004)	0.00-0.02 (0.01±0.007)	0.08-0.22 (0.12±0.057)	0.02-0.03 (0.02±0.004)	0.00-0.01 (0.00±0.002)	0.00-0.01 (0.00±0.004)	0.00-0.01 (0.00±0.005)
Very light blue (6)	99.35-99.63 (99.47±0.103)	0.01-0.04 (0.02±0.011)	0.00 (0.00±0.000)	0.00-0.03 (0.01±0.008)	0.07-0.12 (0.09±0.015)	0.02-0.05 (0.03±0.009)	0.00 (0.00±0.000)	0.00-0.01 (0.01±0.003)	0.00 (0.00±0.000)
Colorless (18)	98.44-100.55 (99.74±0.639)	0.01-0.05 (0.02±0.012)	0.00-0.01 (0.00±0.003)	0.00-0.03 (0.01±0.007)	0.12-0.32 (0.21±0.070)	0.02-0.03 (0.02±0.005)	0.00-0.01 (0.00±0.001)	0.00-0.01 (0.01±0.004)	0.00-0.03 (0.01±0.008)
Milky, Very Light Blue Sapphires									
Milky, blue (12)	99.20-100.44 (99.77±0.559)	0.16-0.52 (0.27±0.098)	0.00-0.01 (0.00±0.005)	0.00-0.02 (0.01±0.006)	0.05-0.07 (0.06±0.008)	0.01-0.05 (0.03±0.007)	0.00-0.01 (0.00±0.004)	0.00-0.01 (0.01±0.004)	0.03-0.05 (0.03±0.007)
Blue (6)	99.16-100.95 (100.15±0.774)	0.03-0.05 (0.04±0.008)	0.00-0.01 (0.01±0.005)	0.01-0.02 (0.01±0.003)	0.11-0.13 (0.12±0.008)	0.02-0.03 (0.02±0.002)	0.00-0.01 (0.00±0.004)	0.00-0.01 (0.01±0.005)	0.01 (0.01±0.001)

Table 6.2 (cont.)

Color Zones	Concentration (weight %)								
	Al_2O_3	TiO_2	V_2O_3	Ga_2O_3	FeO	SiO_2	Cr_2O_3	MnO	MgO
Very Light Blue Sapphires									
Light blue	99.19-100.69 (99.97±0.775)	0.02-0.03 (0.02±0.004)	0.00-0.01 (0.00±0.004)	0.01-0.02 (0.01±0.004)	0.10-0.12 (0.10±0.004)	0.02-0.03 (0.02±0.004)	0.00 (0.00±0.00)	0.00-0.01 (0.00±0.004)	0.00-0.01 (0.01±0.004)
Milky, Very Light Blue Sapphires									
Very light blue	99.30-100.84 (100.81±0.681)	0.03-0.07 (0.05±0.015)	0.00-0.01 (0.01±0.005)	0.00-0.02 (0.01±0.005)	0.05-0.06 (0.06±0.003)	0.02-0.03 (0.02±0.005)	0.00-0.01 (0.00 ±0.003)	0.00-0.01 (0.00 ±0.002)	0.02-0.03 (0.02 ±0.002)
Colorless	99.56-100.68 (100.08±0.511)	0.01-0.03 (0.02±0.005)	0.00-0.01 (0.00±0.004)	0.01 (0.01±0.001)	0.05-0.06 (0.05±0.004)	0.02-0.03 (0.02±0.002)	0.00-0.01 (0.00±0.002)	0.00-0.01 (0.00±0.004)	0.01-0.02 (0.01±0.003)
Dark violet									
Violetish blue	99.05-100.99 (100.08±0.804)	0.00-0.01 (0.01±0.004)	0.00-0.01 (0.01±0.005)	0.01-0.02 (0.01±0.006)	0.21-0.25 (0.23±0.015)	0.02-0.09 (0.04±0.026)	0.09-0.11 (0.10±0.006)	0.00-0.01 (0.00±0.005)	0.00-0.02 (0.01±0.007)
Pink	98.16-99.96 (98.88±0.418)	0.00-0.01 (0.00±0.005)	0.00-0.01 (0.01±0.005)	0.01-0.02 (0.01±0.005)	0.21-0.26 (0.24±0.021)	0.02-0.04 (0.03±0.007)	0.10-0.12 (0.10±0.006)	0.00-0.01 (0.01±0.003)	0.00-0.01 (0.00±0.004)
Medium Violet Sapphires									
Light pink	97.88-99.45 (98.75±0.657)	0.01-0.03 (0.02±0.008)	0.00-0.01 (0.01±0.004)	0.00-0.01 (0.01±0.005)	0.16-0.19 (0.18±0.011)	0.02-0.03 (0.03±0.004)	0.02-0.04 (0.03±0.009)	0.00-0.01 (0.01±0.004)	0.00-0.01 (0.01±0.005)

Dark blue sapphire samples were separated into 4 zones including dark blue, blue, light blue and pink (Figure 6.3). Averages and standard deviation values of EPMA analyses of each zone are presented as in Figure 6.4. In general, iron contents are quite high in all color zones, whereas the other elements are lower than iron. Dark blue zone contains high titanium contents, which may correspond to Fe^{2+}/Ti^{4+} IVCT, caused of blue color. Pink zone in dark blue sapphire sample has significant chromium contents that are higher than titanium.

Medium blue sapphire samples were separated into 5 zones (e.g. dark blue, blue, very light blue, light pink and colorless) (see Figure 6.5). Averages and standard deviation values of EPMA analyses of each color zone are presented as in Figure 6.6. High contents of iron are still present in all zones. It should note that colorless zone contains highest iron content but its titanium is quite low. Chromium contents are obviously revealed in light pink zone; minor amount is also detected in dark blue zone.

Very light blue sapphire samples were separated into 5 color zones, such as dark blue, blue, light blue, very light blue and colorless zones (Figures 6.7). Averages and standard deviation values of each zone are graphically plotted in Figure 6.8. Iron contents are still higher than other elements. However, these iron contents are relatively lower than those of dark blue and medium blue sapphires. Iron is quite significant in colorless zone but its titanium content is very low which may not be enough to generate blue component. On the contrary, iron contents in dark blue and blue zones are lower but their titanium contents are much higher than those of colorless zone.

Milky, very light blue sapphire samples were separated into 5 color zones, such as blue with milky appearance, blue, light blue, very light blue and colorless zones (Figures 6.9). Averages and standard deviation values of each zone are plotted in Figure 6.10. Milky, blue color zone shows obviously high titanium content, which may be caused by milky appearance of rutile (TiO_2) dust. Magnesium contents are obviously high while chromium mostly disappears in all color zones. In addition, iron is still a significant constitute, although it is relatively lower than those of the previous groups.

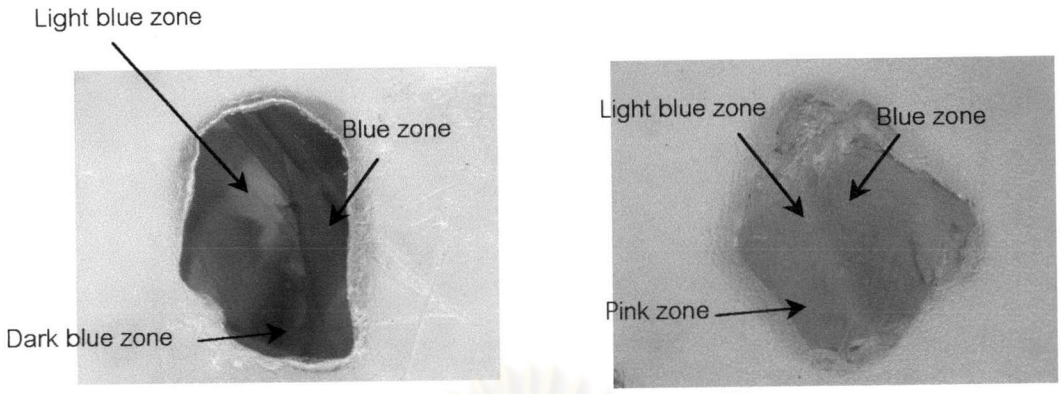
Dark violet sapphire samples were separated into 2 color zones (e.g. violetish blue and pink zones) (Figure 6.11). Averages and standard deviation values of each zone are graphically shown in Figure 6.12. High contents of iron and chromium are clearly present in both zones, whereas titanium is quite low in this sapphire group. However, titanium in violetish zone is slightly higher than those in pink zone.

Medium violet sapphire sample was analyzed only in light pink area (Figure 6.13). Average and standard deviation of analyses are plotted in Figure 6.14 which shows obvious high iron and chromium contents.

The other trace elements analyzed by EPMA are V_2O_3, Ga_2O_3, SiO_2, MnO and MgO, which their average content are mostly very low (<0.05 wt%) in all color zones of all sample groups. Even though they present with very little amount some of these elements may strongly effect colors of the corundum. These elements are not regularly found in all color zones and all sapphire groups. Among these elements, silica is most likely found in all sample groups and its concentration is slightly higher than those of the rest. Manganese is the least element or absent in all sapphire group (they are mostly below the detection limit of 0.01%). Vanadium and gallium contents are irregularly present with very low concentrations.

Although the data from EDXRF and EPMA analyses could not be compared directly to one another, the correlation may be however useful for a few aspects, such as composition changed during heat treatment and estimating accuracy of EDXRF analysis. In general, trend of analytical results, both EDXRF and EPMA, are quite similar, although absolute concentrations are somewhat different. Iron is the most common trace elements in all sapphire groups, whereas gallium and vanadium are present with very minor amounts or perhaps absent in some samples. Titanium concentration appear to be related to blue shade while chromium contents are more likely compatible to violet sapphire groups. These similar trends may imply that qualitative analyses yielded by EDXRF are good enough for routine analysis in gemological laboratory. However, they could not be used for advanced scientific research. For chemical change during heating experiment, there is still no strong

evidence to prove this aspect; however, similar trends of average analyses of each element in most sapphire groups may potentially indicate that proportions of trace elements in the whole stone are not much changed during heating. However, composition transfer between different zone may be taken place in proper condition. The best example would be shown by milky very light blue sapphires that appear to turn intense after heating at high temperature (above 1400 ^{o}C). EPMA analyses show clearly that titanium contents in these stones are different in each color zone (Figure 6.10).



IDB 1 IDB 3

Figure 6.3 Dark blue sapphire samples after heated at 1650 °C; IDB 1 shows dark blue, blue and light blue zones; IDB 3 shows blue, light blue and pink zones.

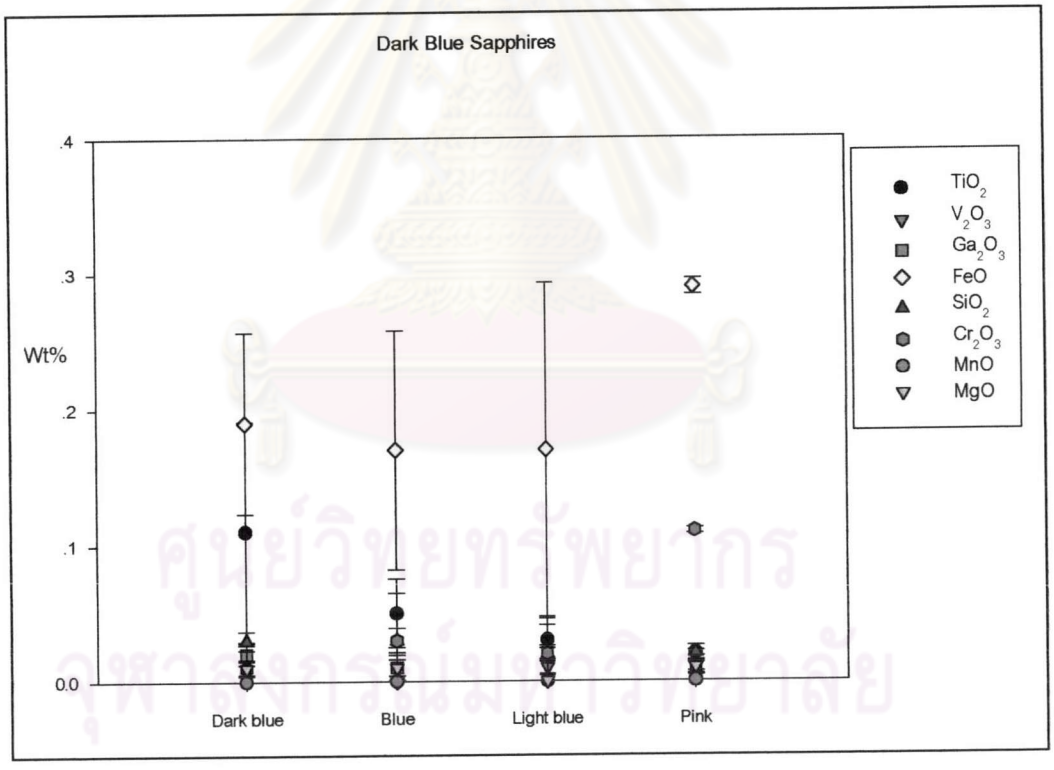
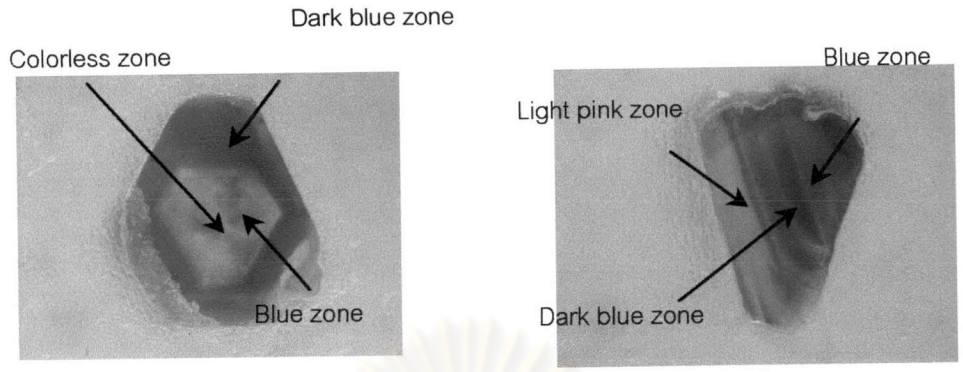


Figure 6.4 Histogram showing averages and standard deviation values of trace element analyses using EPMA in different color zones of dark blue sapphire samples after heated at 1650 °C.



MB 4 MB 9

Figure 6.5 Medium blue sapphire samples after heated at 1650 °C; MB 4 shows dark blue, blue and colorless zones; MB 9 shows dark blue, blue and light pink zones.

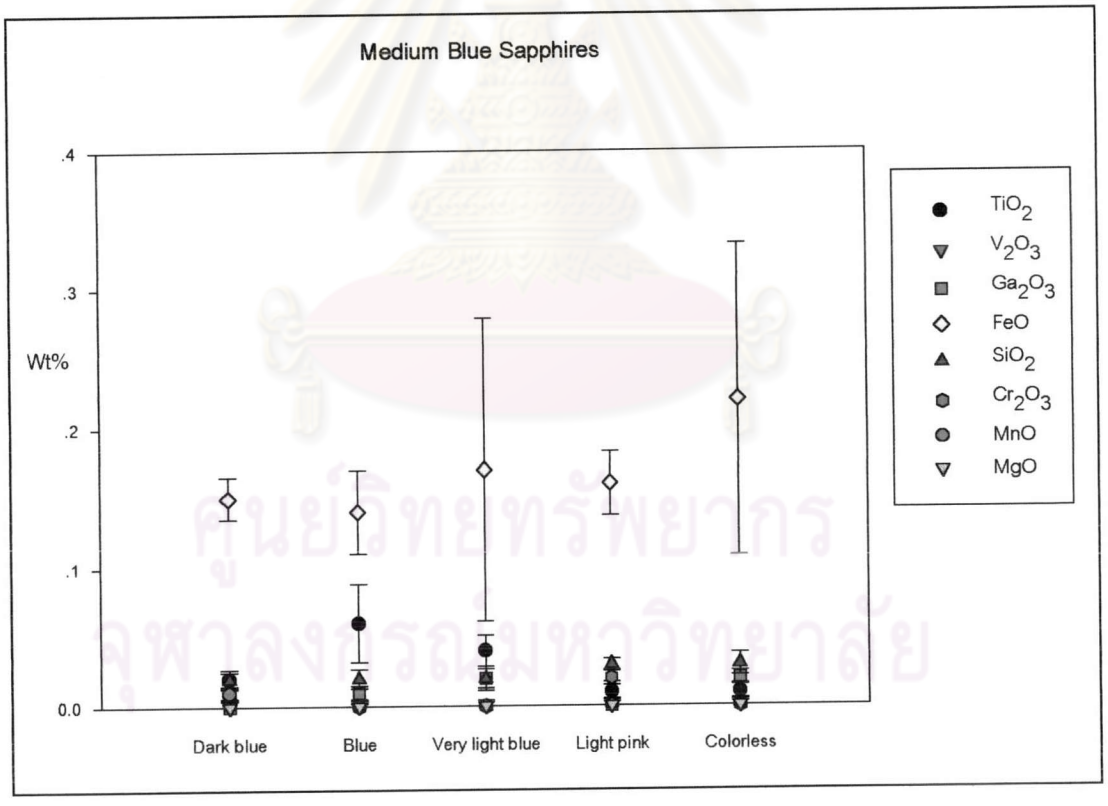
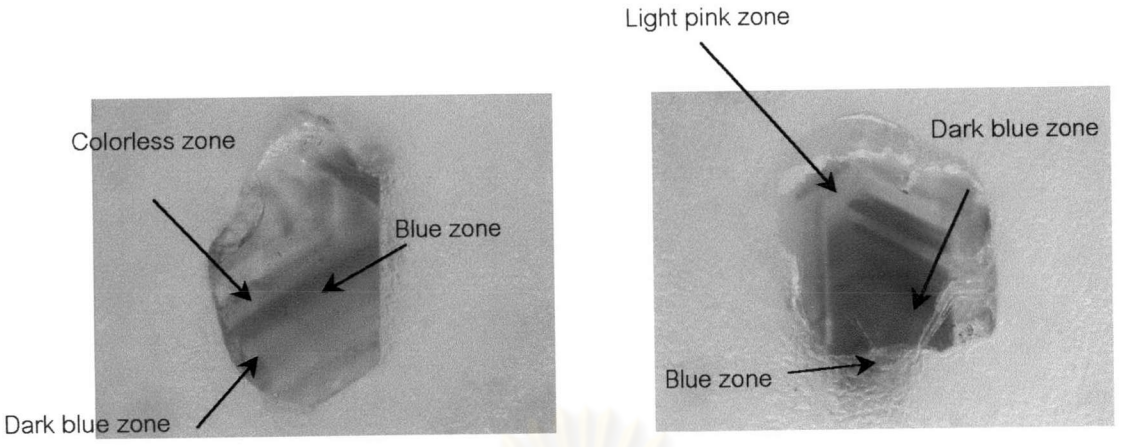


Figure 6.6 Histogram showing averages and standard deviation values of trace element analyses using EPMA in different color zones of medium blue sapphire samples after heated at 1650 °C.



VLB 1 VLB 4

Figure 6.7 Very light blue sapphire samples after heated at 1650 °C; VLB 1 shows dark blue, blue and colorless zones; VLB 4 shows dark blue, blue and light pink zones.

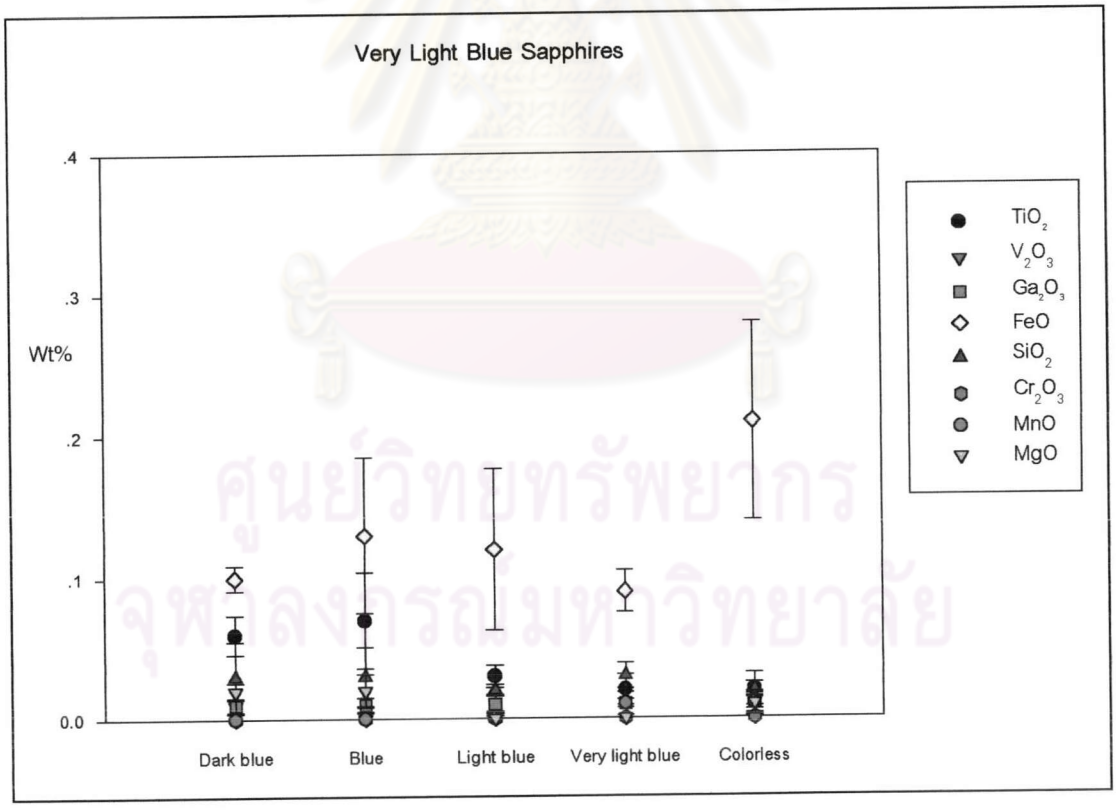


Figure 6.8 Histogram showing averages and standard deviation values of trace element analyses using EPMA in different color zones of very light blue sapphire samples after heated at 1650 °C.

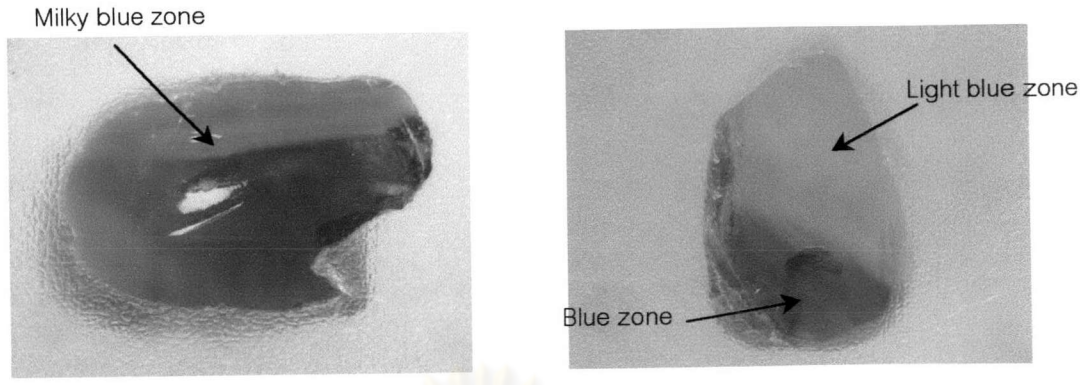


Figure 6.9 Milky, very light blue sapphire samples after heated at 1650 °C; MVLB 3 shows milky blue zones; MVLB 5 shows blue, light blue and colorless zones.

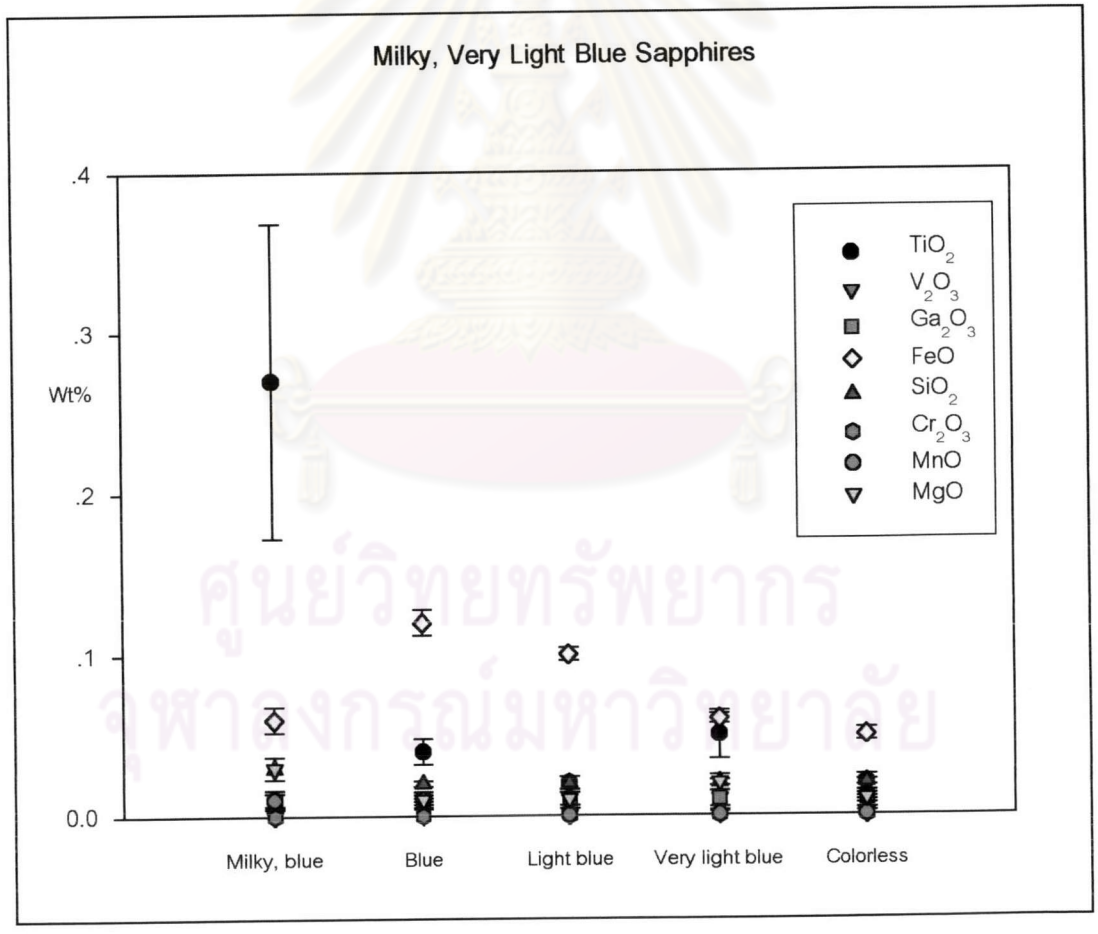


Figure 6.10 Histogram showing averages and standard deviation values of trace element analyses using EPMA in different color zones of milky, very light blue sapphire samples after heated at 1650 °C.

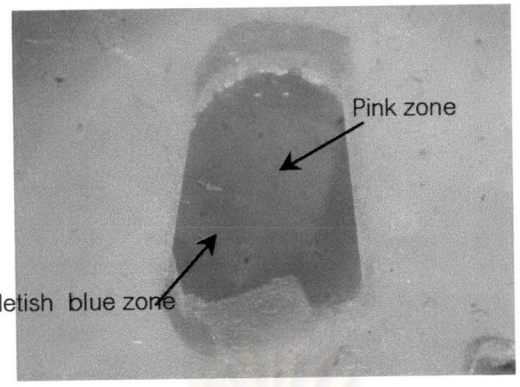


Figure 6.11 Dark violet sapphire sample after heated at 1650 °C (DV 1) showed violetish blue and pink zones.

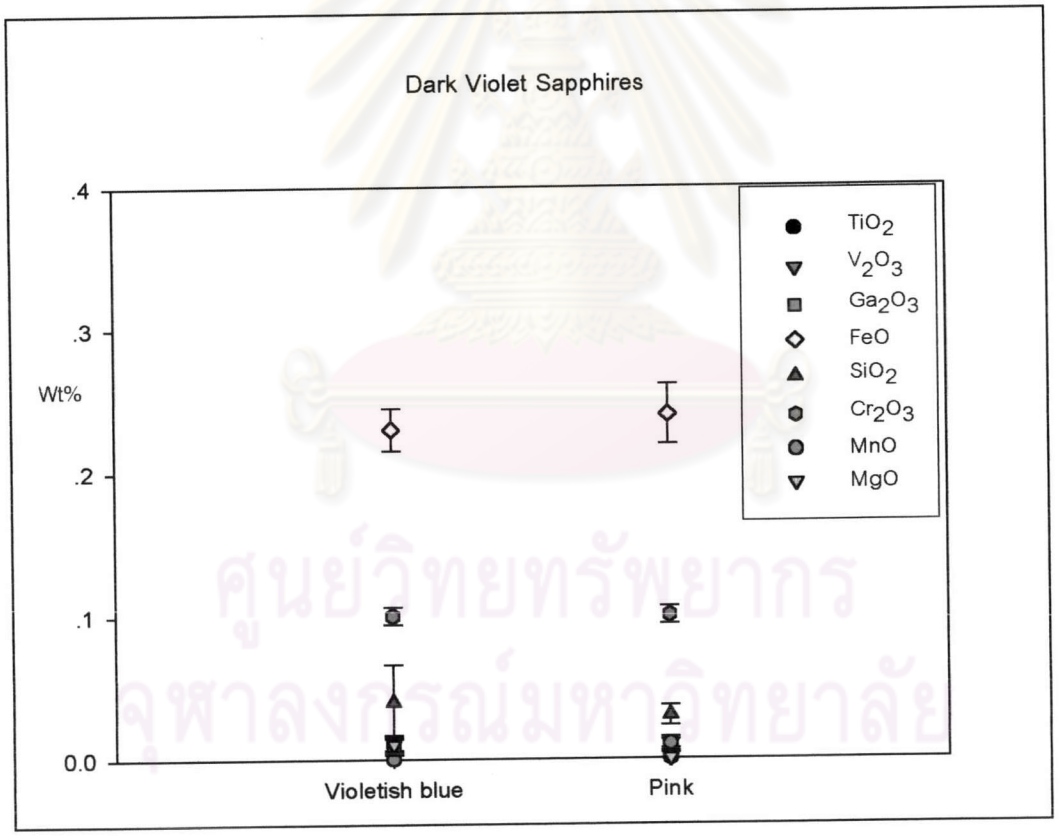


Figure 6.12 Histogram showing averages and standard deviation values of trace element analyses using EPMA in different color zones of dark violet sapphire samples after heated at 1650 °C.

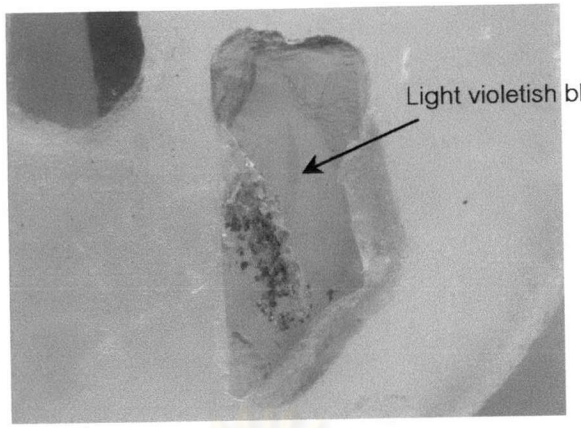


Figure 6.13 Medium violet sapphire sample (MV 3) after heated at 1650 °C shows light violetish blue zones.

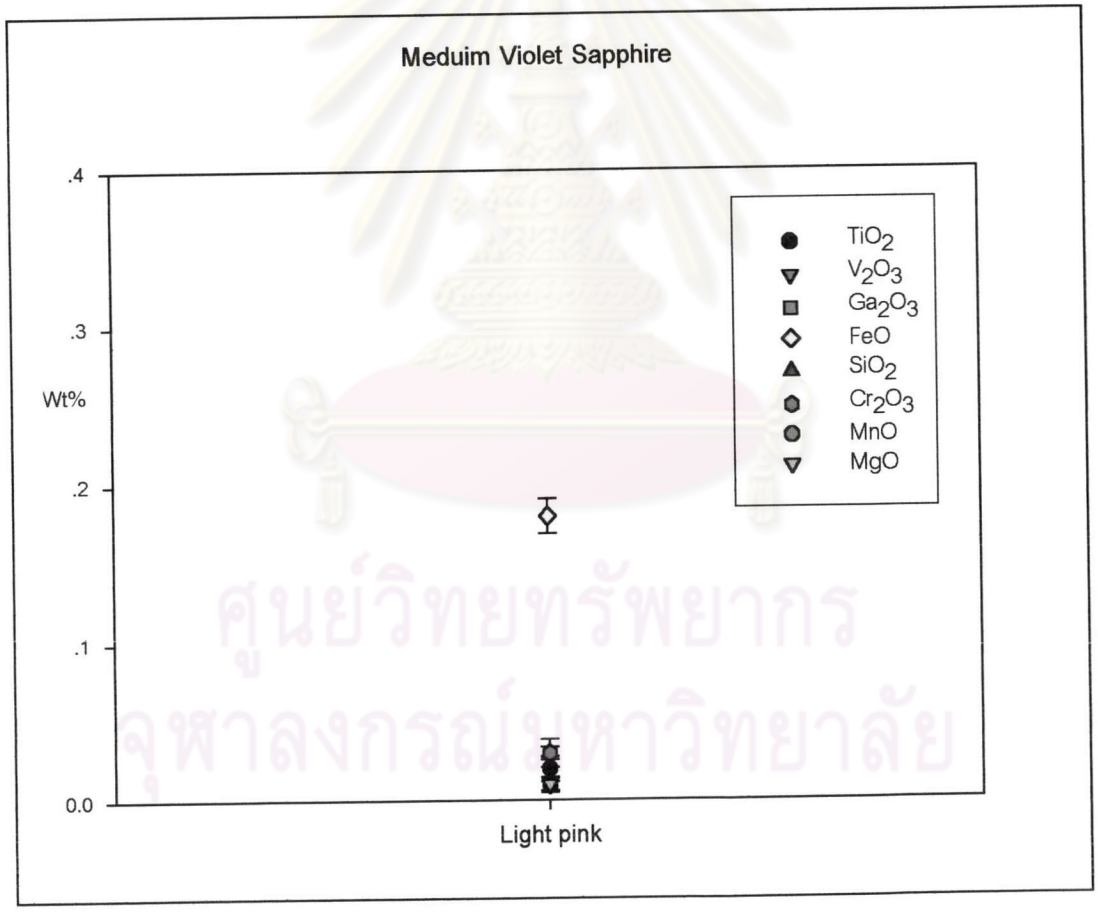


Figure 6.14 Histogram showing averages and standard deviation values of trace element analyses using EPMA in different color zones of medium violet sapphire samples after heated at 1650 °C.