

# Effect of grain size and moisture content on major and minor elements concentrations using portable X-ray fluorescence

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**Abstract.** The elemental compositions measurements of the geological samples using portable X-ray fluorescence (pXRF) technique in the laboratory were studied. The influences of the grain size and the moisture content of the samples on major and minor elements concentrations were also investigated. The pXRF was used to determine the major (Al, Ca, Fe, K, Mg, Si and Ti) and minor (Mn, Nb, Pb, Rb, Sr, Th and Zr) elements in the geological samples with different depths collected from Phang-nga province, Thailand. Seven reference materials were utilized to calibrate the analytical method. The calibrated values were strongly correlated to that reference values ( $R^2 > 0.95$ ) for Al, Ca, Fe, K, Mg, Mn, Rb, Si, Sr, Th, Zr except for Cu, Nb, Ni, P, U, V, W, Y, Zn. The results showed that both grain size and moisture content had significant effect on the elemental concentrations measured by pXRF. The decreasing of grain size resulted in an increase the elements concentrations. While the moisture content in the sample increased with decreasing of the elements concentrations. The measured elements were Si (22.03 – 25.79 wt%), Al (17.39 – 21.38 wt%), Fe (4.39 -7.41 wt%), Ti (0.70 – 1.23 wt%), Nb (47 – 99 mg/kg), Rb (50 – 99 mg/kg) and Zr (499 – 900 mg/kg). These elements concentrations were measured by pXRF under the optimum conditions, the grain size of the sample of  $< 75 \mu\text{m}$  and the moisture content in the sample of less than 1 wt%, as well as were good agreement with that WDXRF results. For Ca, K, Mg and Mn, their concentrations were lower than detection limits of the pXRF.

## 1. Introduction

It has been reported that the southern of Thailand could be a source of rare earth elements (REEs). Kenzo S [1] studied REEs containing on the 12 m thick weathering profile of the Kata Beach granite in Phuket, Thailand. The REEs concentration of 592 ppm could be found in the parent rock of ilmenite-series biotite granite with transitional characteristics from I type to S type. In addition, REEs were contained in fluorocarbonate including allanite, titanite, apatite, and zircon. The upper part of soil profile from the surface to 4.5 m depth shown lower REEs contents ranging from 174 to 548 ppm. Previous work, we done to determine the REEs in various geological samples collected from the southern of Thailand.

However, major and minor elements concentrations vital to determine for further understanding the distribution and behavior of REEs formation.

X-ray fluorescence (XRF) spectroscopy is a well-established and commonly technique to obtain chemical composition in geological samples [2]. The XRF could be applied for eliminating the matrix effects and the sample heterogeneity but analytical precision and the ultimate accuracy of the results depend on several factors including; instrumental setting and stability, the calibration procedure, mineralogical and matrix effects, the reference materials used to calibrate the instrument, sample preparation and the strategy adopted to maintain the results within accepted limits [3]. The measurements can be costly, require intensive sample preparation and analysis time for providing the higher quality data possible [2].

The pXRF has precisions comparable to benchtop models. The technique can scan directly soil monoliths. It is cheaper than benchtop model [4-6]. The pXRF is considered with low root mean square errors [7]. The technique can be used for both qualitative and quantitative analysis of geological characterization. In the present, the pXRF has been applied to analyze major and minor elements in different materials (rocks, soil, sediment, wood and archaeological) [8]. Mechanism of pXRF analysis is explained following; (1) an inner shell vacancy in which an electron leaves the inner shell is created by an incident X-ray photon produced from a radioisotope source excitation device of the equipment, (2) an outer shell electron falls to make up for the inner shell vacancy, when the atom is relaxed to the ground state, (3) photons are given off with energy from the X-ray region of the electromagnetic spectrum that is equivalent to the different of energy between the two shells, (4) the elements and their concentrations are identified the energy level and intensity of these emitted X-rays [8]. However, the pXRF analysis has some limiting factors in the efficient application which constrain its reliable uses for optimal element analysis of different types of materials.

The quality and precision of pXRF measurement are normally affected by various physico-chemical parameters of soil and rock such as surface irregularity, mineralogy, moisture, chemical matrix effects, and spectral interferences [7]. Soil moisture and grain size have been considered as the main factors affecting pXRF measurement. Sahraoui and Hachicha [9] reported that moisture content in the soil sample caused a significant under-reporting of elemental concentrations compared to the scanning on dry sample.

In this study, the major and minor elements in geological samples were determined by the portable XRF (pXRF). Effects of the grain size and moisture content of the geological samples on the major and minor elements concentrations were investigated. The accuracy and precision of the pXRF results were also compared with the usual WDXRF techniques.

## **2. Materials and methods**

### *2.1. Materials*

Seven geological reference materials were used in this study including: JA-1, JG-1a, JG-2, JSy-1 (andesite, granodiorite, granite, syenite, GSJ, Japan); BCR-2, COQ-1, GSP-2 (basalt, carbonatite, granodiorite, USGS, Virginia).

Four samples were taken at different depth with topsoil 0 – 1 m, 1 – 2 m, 2 – 3 m and 3 -5 m. The sample location was Tambon Thai Mueang, Amphoe Thai Mueang, Phang-nga province, Thailand (Latitude 8°24'37.81"N, longitude 98°15'30.74"E).

### *2.2. Sample preparation*

The samples were dried to constant weight at 110°C and manually homogenized before the element analyses. The sample was prepared by 2 methods following;

*Loose powder method:* The sample was sieved into 5 different grain sizes of 2 mm - 300 µm, 300 - 250 µm, 250 - 150 µm, 150 - 75 µm and < 75 µm. Prolene® thin film with thickness of 4 µm was used in this study. Each cup was covered with thin film. The fine powder sample was then filled into the cup.

*Pressed pellet method:* After drying and homogenizing, each sample was passed through a 250 µm sieve. The sample (8.00 g) was mixed with boric acid (2.00 g) by an automatic mortar for 2-3 min. The

mixture was pressed under 150 kN of pressure into 40 mm diameter, 7.5 mm thick pellet XRF standards. The pressure was held for 20-30 s and then the pressure was quickly dropped to zero. The sample pellet was removed from the mold.

### 2.3. Moisture content effect

The effect of moisture content in the sample on the pXRF analysis (signal absorption) was studied for the sample at the depth of 3 to 5 m. The samples were saturated with ultrapure water (18.2 mΩ/cm) by different moisture contents of 1, 5, 10, 20, 30 and 50 wt%.

### 2.4. Wavelength dispersive X-ray fluorescence spectrometry (WDXRF) analysis

The geological sample was prepared by pressed pellet technique. A Bruker S8 Tiger wavelength dispersive X-ray fluorescence (WDXRF) spectrometer was used in this study. This spectrometer is based on end-window Rh-anode tube equipped with 1 kW intensity X-ray generator at 50 kV operating voltage and 50 mA currents.

The concentrations of major and minor elements in the reference materials were measured by the WDXRF with pressed pellet technique. Some elements including Al, Ca, Fe, K, Mg, Mn, Nb, Rb, Si, and Zr were reliable when compared to referenced values ( $\leq 30\%$  error). Some minor elements such as Sc, Sr, Th and U could be not detected. The detectable range of Al, Ca, Fe, K, Mg, Mn, Nb, Rb, Si, Ti, and Zr were 6.60 – 12.26%, 1.50 – 5.09%, 1.40 – 9.65%, 0.64 – 4.48%, 0.42 – 0.95%, 120 - 1520 g/kg, 27 – 390 g/kg, 48 – 178 g/kg, 1.62 – 35.91%, 0.09 – 1.35%, and 188 – 550 g/kg, respectively.

### 2.5. Portable X-ray fluorescence spectrometry (pXRF) analysis

The sample in this study was prepared by the loose powder method with different grain sizes and moisture contents. The elements were analyzed by a Delta Professional pXRF Analyzer, DPO 2000 (Olympus Scientific Solutions Americas, Inc.) equipped with an instrument's prolene window of 8 mm<sup>2</sup>, a 4 W miniature X-ray tube (200 μA maximum current), and silicon drift detector (SDD) using Geochem mode with two beams. The first beam (40 kV) measured the elements V, Cr, Fe, Co, Ni, Cu, Zn, W, Hg, As, Se, Pb, Bi, Rb, U, Sr, Y, Zr, Th, Nb, Mo, Ag, Cd, Sn and Sb, also Ti and Mn. The second (10 kV) was used to determine the light elements Mg, Al, Si, P, S, Cl, K, Ca, Ti and Mn. The measuring time for an individual beam was set at 120 s. The internal pXRF stability was monitored by measuring Fe K- $\alpha$  count on a 316-stainless steel coin every day of use. Each sample was analysed three times.

The pXRF was calibrated with seven geological reference materials. Then, each linear calibration curve was constructed. The slope of the regression line for each element was inputted into the pXRF analyzer software for automatic correction of sample data, if the difference between the pXRF analyzed value and the CRM recommend value was more than 10%. The recalibration factors for Al, Fe, K, Si, Ti, Rb and Th were 1.0649, 0.8487, 0.9140, 0.9615, 0.9810, 0.9892 and 0.9167, respectively.

Comparison between the pXRF results and the WDXRF was also done. The errors were calculated as follows equation (1).

$$\% \text{Error} = (C_{\text{pXRF}} - C_{\text{WDXRF}}) / C_{\text{WDXRF}} \times 100 \quad (1)$$

where  $C_{\text{pXRF}}$  and  $C_{\text{WDXRF}}$  are mean concentrations of measured results for pXRF and WDXRF, respectively.

## 3. Results

### 3.1. Effect of the grain size of sample on the major and minor elements concentrations

The concentrations of major and minor elements in geological samples measured by the pXRF technique with the use of recalibration method are shown in Table 1. The samples at different five grain sizes; (2 mm - 300 μm, 300 - 250 μm, 250 - 150 μm, 150 - 75 μm and < 75 μm) were experimented. The measured results obtained from the pXRF were compared to that WDXRF results. It was found that the grain size of the samples influenced on the major and minor elements concentrations. The elemental concentrations of all samples increased significantly with the decreasing of grain size for almost all elements except for

Si. The concentrations of Al, Fe, Nb, Rb, Ti and Zr with grain size less than 250  $\mu\text{m}$  were reliable when compared to WDXRF.

The concentrations of other elements such as Ca, K, Mg and Mn were significantly underestimated by the pXRF. However, these elements could be detected by WDXRF. It can be also noted that the WDXRF with pressed pellet technique was not sensitive enough to measure the concentration of Th. However, Th could be detected by pXRF. There are several factors such as particle size, uniformity, heterogeneity, and surface condition, resulted in the accuracy and reliability of the pXRF result. The pXRF efficiency decreased for the larger grain sizes of sample because the surface area and density of soils in the XRF cup was decreased.

**Table 1.** Elemental concentrations in the geological samples at various depths measured by pXRF with the different of grain sizes and WDXRF techniques.

Element	Unit	depth (m)	pXRF with recalibration					
			WD-XRF	loosed powder				
			pressed pellet	$\Phi 300 \mu\text{m} - 2 \text{ mm}$	$\Phi 250 - 300 \mu\text{m}$	$\Phi 150 - 250 \mu\text{m}$	$\Phi 75 - 150 \mu\text{m}$	$\Phi < 75 \mu\text{m}$
Al	wt%	0 - 1	17.39 - 17.89	10.2 - 10.31	9.88 - 10.25	10.66 - 11.04	11.98 - 12.01	13.30 - 13.61
		1 - 2	18.60 - 19.50	12.90 - 13.24	12.74 - 12.82	14.58 - 14.59	13.54 - 13.63	12.97 - 13.13
		2 - 3	20.40 - 21.10	12.83 - 13.00	13.24 - 13.44	13.81 - 13.93	13.82 - 13.86	14.99 - 15.06
		3 - 5	21.10 - 21.38	13.68 - 14.17	14.87 - 15.03	14.71 - 14.86	15.31 - 15.56	16.88 - 16.98
Fe	wt%	0 - 1	5.61 - 5.80	2.45 - 2.53	2.58 - 2.64	2.72 - 2.75	3.48 - 3.50	4.06 - 4.11
		1 - 2	4.69 - 4.97	3.12 - 3.16	3.26 - 3.27	4.25 - 4.27	3.82 - 3.86	3.50 - 3.55
		2 - 3	4.39 - 4.46	2.73 - 2.77	2.94 - 3.03	2.93 - 2.95	3.14 - 3.17	3.38 - 3.42
		3 - 5	7.10 - 7.41	3.68 - 4.22	4.59 - 4.68	4.57 - 4.61	5.29 - 5.39	6.39 - 6.47
K	wt%	0 - 1	0.61 - 0.63	na.	na.	na.	na.	na.
		1 - 2	0.48 - 0.50	0.05 - 0.06	0.04 - 0.05	0.18 - 0.19	0.08 - 0.09	0.04 - 0.06
		2 - 3	0.52 - 0.53	na.	0.01 - 0.02	0.01 - 0.02	0.03 - 0.04	0.04 - 0.05
		3 - 5	0.39 - 0.42	na.	na.	na.	na.	na.
Si	wt%	0 - 1	25.11 - 25.79	20.26 - 20.41	21.17 - 21.22	20.72 - 20.87	18.52 - 18.71	17.90 - 18.06
		1 - 2	24.67 - 25.67	16.36 - 16.78	17.04 - 17.23	15.66 - 15.85	16.75 - 16.92	17.02 - 17.11
		2 - 3	23.58 - 24.24	17.37 - 17.86	17.36 - 17.45	17.42 - 17.57	17.68 - 17.69	18.50 - 18.70
		3 - 5	22.03 - 22.83	15.49 - 16.40	15.96 - 16.25	16.08 - 16.25	16.39 - 16.58	15.86 - 15.90
Ti	wt%	0 - 1	1.15 - 1.23	0.50 - 0.54	0.52 - 0.54	0.57 - 0.61	0.73 - 0.77	0.79 - 0.81
		1 - 2	0.91 - 0.96	0.53 - 0.55	0.57 - 0.58	0.65 - 0.67	0.65 - 0.68	0.62 - 0.63
		2 - 3	1.04 - 1.08	0.57 - 0.58	0.61 - 0.64	0.69 - 0.71	0.66 - 0.67	0.66 - 0.69
		3 - 5	0.70 - 0.80	0.45 - 0.47	0.46 - 0.56	0.44 - 0.45	0.49 - 0.51	0.55 - 0.56
Nb	mg/kg	0 - 1	82 - 99	55 - 61	66 - 67	73 - 76	107 - 110	126 - 127
		1 - 2	47 - 62	56 - 60	75 - 78	101 - 103	94 - 97	86 - 87
		2 - 3	51 - 70	72 - 75	87 - 91	89 - 93	101 - 102	105 - 106
		3 - 5	53 - 67	57 - 64	69 - 70	80 - 81	88 - 92	93 - 97
Mn	mg/kg	0 - 1	400 - 500	141 - 193	172 - 180	159 - 182	237 - 245	270 - 280
		1 - 2	200 - 300	98 - 114	67 - 96	120 - 145	113 - 127	91 - 110
		2 - 3	300 - 500	227 - 265	200 - 218	218 - 243	181 - 211	215 - 235
		3 - 5	na.	na.	na.	na.	na.	na.
Rb	mg/kg	0 - 1	86 - 99	36 - 37	40 - 43	46 - 47	66 - 67	78 - 81
		1 - 2	63 - 67	42 - 46	52 - 53	88 - 91	67 - 68	57 - 58
		2 - 3	64 - 76	44 - 47	53 - 56	52 - 54	59 - 60	64 - 65
		3 - 5	50 - 66	39 - 45	40 - 42	47 - 49	49 - 52	56 - 57
Th	mg/kg	0 - 1	na.	59 - 62	62 - 74	70 - 79	99 - 101	119 - 122
		1 - 2	na.	65 - 70	81 - 90	123 - 125	103 - 107	92 - 104
		2 - 3	na.	92 - 93	109 - 113	112 - 113	120 - 121	135 - 135
		3 - 5	100 - 200	107 - 115	122 - 123	145 - 146	186 - 187	206 - 207
Zr	mg/kg	0 - 1	800 - 900	330 - 352	384 - 412	447 - 461	924 - 1002	1528 - 1609
		1 - 2	700 - 702	327 - 342	447 - 461	918 - 928	796 - 803	498 - 527
		2 - 3	700 - 701	416 - 431	497 - 563	461 - 477	640 - 678	745 - 750
		3 - 5	499 - 500	260 - 268	278 - 285	269 - 312	385 - 435	491 - 532

na. not available

Jang, M. [10] suggested that soil sample should be dried and sieved to obtain homogeneous sample with particle size less than 125  $\mu\text{m}$  for pXRF analysis. Imanishi, Y. et al. [11] reported that the particle size was strongly effect on the XRF intensity, especially the element with low energy X-rays such as Al ( $K\alpha = 1.486$ ) and Fe ( $K\alpha = 6.405$ ) due to the high energy X-rays generated in deep soils layer were

detected without serious absorption. However, the low concentration of trace elements could be not detected by WD-XRF. Thus, the trace elements should be studied by other techniques such NAA, ICP-MS.

### 3.2 Effect of the moisture content of sample on pXRF analysis

The effect of moisture content on pXRF measurement was studied by adding water into the dried and sieved sample at different amounts such as 1 wt%, 5 wt%, 10 wt%, 20 wt% and 50 wt%. The results as shown in Table 2 indicated that the moisture content had an obvious effect on the pXRF analysis. With increasing of moisture content in the sample, the elemental concentrations decreased dramatically for all elements. The moisture in the sample affected the matrix and the penetration depth of the radiation [12].

The presence of moisture repressed the strength of fluorescent X-rays reaching the detector window of the pXRF through absorption and scattering. The elements with low energy X-rays were easily absorbed by water [13]. The characteristic X-rays from the elements were absorbed and the scatter of the primary radiation from the excitation source was enhanced by the water in sample [14]. The deviations of pXRF scanning on the dry surface of the sample led to decrease the intensity of characteristic x-rays. While, the interstitial water of the sample increased because the stronger x-ray absorption by water than by air in fractures and macropores in the samples. Two types of water may be present in soils including (1) interstitial water which occurs in the pore between soil structural components and (2) water trapped during formation of constituent minerals [15]. When the moisture content of the sample exceeded its field capacity, the pressure inserted by the contact of pXRF during the scanning process could lead the release of interstitial water from macropores, which might then form a layer of water between the soil and the scanning window of the pXRF. When water content in soil sample was high, a noticeable layer of water covering the window was observed after the scanning was completed which caused a lower precision, poorer detection limit and lower accuracy [9].

**Table 2.** Elemental concentrations in the geological samples at the depth of 3-5 m and using the grain size of < 75  $\mu\text{m}$  measured by pXRF with the different of moisture contents and WDXRF techniques.

Element	Unit	WDXRF	Moisture content (wt%)						
			0	1	5	10	20	30	50
Al	wt%	21.10 - 21.38	16.88 - 16.98	15.43 - 15.59	13.60 - 14.11	13.45 - 13.75	12.38 - 12.46	11.82 - 11.87	4.35 - 4.53
Fe	wt%	7.10 - 7.41	6.39 - 6.47	5.88 - 6.22	5.13 - 5.37	5.08 - 5.26	4.76 - 4.77	4.61 - 4.67	3.80 - 3.86
Si	wt%	22.03 - 22.83	15.86 - 15.90	14.46 - 14.80	13.11 - 13.50	12.80 - 12.97	11.78 - 11.81	11.20 - 11.33	3.72 - 3.82
Ti	wt%	0.70 - 0.80	0.55 - 0.56	0.51 - 0.54	0.45 - 0.48	0.44 - 0.46	0.41 - 0.42	0.39 - 0.41	0.30 - 0.31
Nb	mg/kg	53 - 67	93 - 97	92 - 97	79 - 80	78 - 79	67 - 76	86 - 72	64 - 65
Rb	mg/kg	50 - 66	56 - 57	50 - 53	43 - 46	43 - 44	31 - 41	37 - 40	35 - 38
Th	mg/kg	100 - 200	206 - 207	196 - 201	158 - 165	156 - 159	148 - 191	144 - 146	132 - 134
Zr	mg/kg	499 - 500	491 - 532	525 - 564	473 - 502	464 - 505	357 - 480	437 - 465	406 - 443

## 4. Conclusion

The results shown that the pXRF could provide data consistent with laboratory reported values. Good agreement between the results obtained by pXRF and by WDXRF was found for some elements including Al, Fe, Si, Rb, Ti, Th and Zr. The study showed that the pXRF had significant potential as a geochemical tool. However, the factors such as the grain size and moisture contents significant effected on the major and minor elements concentrations. Large particle size and high moisture content of the soil sample led to less accurate results. In addition, the errors from sample preparation could be minimized by suitable techniques: sieving and drying methods. The results recommend that the samples should be dried until moisture less than 1 wt% and sieved into less than 75  $\mu\text{m}$  particle size.

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