Application of handheld X-ray fluorescence spectrometer for major element analysis and characterization of geological samples in Southern Thailand

S Nuchdang¹, J Channuie², O Leelanupat³ and D Rattanaphra¹,*

1 Research and Development Division, Thailand Institute of Nuclear Technology, Phathumtani, Thailand
2 Reactor Center, Thailand Institute of Nuclear Technology, Bangkok, Thailand
3 Nuclear Technology Service Center, Thailand Institute of Nuclear Technology, Nakhon Nayok, Thailand
E-mail: sasikarn@tint.or.th

Abstract. The handheld X-ray fluorescence spectrometer (hXRF) was applied to major element analysis in the geological samples and the results were compared with the results of the wavelength dispersive X-ray fluorescence spectrometer (WDXRF). In addition, the analytical compositions were confirmed by X-ray diffractometer (XRD) and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX). In the case of pXRF analysis, eight geological reference materials were used to calibrate the analytical method and four known concentration samples were used to prove the method. In research, ten geological samples from Phuket province, Thailand were collected with different depths corresponding to O horizon (0-0.1 m), A horizon (0.1-0.3 m), B1 horizon (0.3-1.0 m), B2 horizon (1.0-2.0 m), C1 horizon (2.0-3.0 m), C2A horizon (3.0-5.0 m), C2B horizon (5.0-8.0 m), C3 horizon (8.0-12.0 m), D horizon (12.0-20.0 m) and RK horizon (> 20.0 m). The elemental analysis results showed that the pXRF results were matched well with that WDXRF results. The concentration range in ten samples were Si (18-22 wt%), Al (12-15 wt%), Fe (1-4 wt%), K (0.4-3.2 wt%) and Ti (0.2-0.4 wt%). The concentration of some elements such as Ca and Mg on those ten samples are low and they are unable to analysed by hXRF. The XRD patterns revealed that all samples consisted of quartz, kaolinite, halloysite, illite, vermiculite and biotite.

1. Introduction
Parent material, topography, biology and climate interacting over time effect on soil properties. The parent material is a key determinant for soil formation. Soil texture, permeability and a range of chemical properties (major elements such as aluminum (Al), iron (Fe), calcium (Ca), potassium (K), sodium (Na), and magnesium (Mg)) are resulted from the rock or sediment composition [1]. Behaviors of elements during weathering are interesting [2]. Climate is an important factor for weathering, plant growth and microbial activities. It influences the soil hydrothermal condition, the migration and transformation of minerals and organic matter. Most soil properties indicate the quality of environment [1]. According to the increasing of environmental catastrophe, there are requires rapid and reliable multi-element analysis techniques for better understanding the causes in order to prepare further remedy plan. The variation of matrix composition and the concentration ranges of the elements in the particular...
samples are complicated and need to be considered. Although no single analytical technique is suitable for all applications, the most common techniques for major elemental analysis and characterization of environmental samples are inductively coupled plasma optical emission spectrometry (ICP-OES), X-ray diffractometer (XRD), X-ray fluorescence spectrometry (XRF) and scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM-EDX). However, it is necessary to develop methods or to modify existing procedures for enhancing capacity and results [3]. The ICP-OES offers excellent multi-element capacities but the analysis requires lot of time and skill for extremely accurate and precise in the processing [4,5]. Energy dispersive X-ray fluorescence (EDXRF) can simultaneously determine a large number of elements in solid samples in a wide range of concentrations [3]. EDXRF analysis comprises of 2 main parts; irradiating a sample with X- or γ -rays and of detecting the secondary fluorescent X-ray spectrum emitted by the sample itself. Each element emits a typical set of X-ray lines and is characterized by their energies. Thus, many lines as the elements composing in the sample compose of form specific the X-ray spectrum. The intensity of each line is relative in corresponds to the concentration of the elements. Portable system of EDXRF is handy and suits can be active for on-site analysis in various fields applications [6].

The objectives of this research are to study the potential of handheld XRF (hXRF) for major elemental analysis of geological samples in comparison to WDXRF. X-ray diffractometer (XRD) and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) were also used to analyze these elements for confirming their analysis results. In addition, the mineral forms of these samples were characterized using the XRD pattern.

2. Materials and method

2.1. Sample preparation

Ten mineral samples were taken per horizon which varied in depth of sample collecting zone according to the profile characteristics, O horizon (0-0.1 m), A horizon (0.1-0.3 m), B1 horizon (0.3-1.0 m), B2 horizon (1.0-2.0 m), C1 horizon (2.0-3.0 m), C2A horizon (3.0-5.0 m), C2B horizon (5.0-8.0 m), C3 horizon (8.0-12.0 m), D horizon (12.0-20.0 m) and RK horizon (> 20.0 m). The sample location was Tambon Chalong, Amphoe Meuang, Phuket province, Thailand (Latitude 7°51’24.22”N, longitude 98°19’19.49”E).

Each sample was dried at room temperature. After that, it was manually homogenized, quartered, and sieved for removing plant matters and its sizes become smaller than 75 µm. Finally, a portion of the sample was dried to constant weight at 110°C and kept in a desiccator for a day.

2.2. X-ray diffraction (XRD) analysis

The powdered sample was put in the sample holder, and then XRD was performed. XRD study was analyzed using a Bruker D8 ADVANCE powder diffractometer with Cu-Kα radiation (λ = 1.5406 Å). Each XRD pattern was recorded in the 2θ interval of 10-100° with increment angle of 0.04°.

2.3. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) analysis

Major element analysis of mineral sample was supplemented by examination of the polished sections using a scanning electron microscope (SEM) TESCAN VEGA3LM in conjunction with an energy dispersive X-ray spectrometer (EDX); X-MaxN Silicon Drift Detector (Oxford). The samples were not coated for low vacuum SEM working conditions. The beam voltage was 20.0 kV. Images were captured by a retractable solid state back scattered electron detector and map scan mode was used to study the major elements content. In this study, we did not mention on the images from the instrument.

2.4. Handheld X-ray fluorescence spectrometry (hXRF) analysis

A Delta Professional hXRF Analyzer, DPO 2000 (Olympus Scientific Solutions Americas, Inc.) equipped with an instrument’s prolene thin film support window of 8 mm², a 4W miniature X-ray tube (200 µA maximum current), and silicon drift detector (SDD) was used to measure all samples 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 beam (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 hXRF stability was monitored by measuring Fe-Kα count on a 316-stainless steel coin every day of use. Each sample was analysed three times.

The sample was prepared by the loose powder method with 4 µm Prolene® thin film. Then, the hXRF instrument was fixed with a laboratory case designed by the instrument manufacturers. The sample holder was placed on top of compartment and radiation containment.

The hXRF was calibrated after measuring intensities in the following eight geological reference materials: JA-1, JB2, JG-1a, JG-2, JSy-1, BCR-2, COQ-1 and GSP-2 which are andesite, basalt, granodiorite, granite, syenite from GSJ, Japan; basalt, carbonatite, granodiorite from USGS, Reston. Each reference material was analysed ten times. The calibration method was confirmed by four known concentration samples from Department of Mineral Resources, Thailand. The horizon and location of the sample are shown in table 1. This study accepted for scientifically element determinations in the geological samples with different value ≤ 30%.

Table 1. Sample horizon and locations of the known concentration samples used in this study.

| Code  | Horizon | Location                  |
|-------|---------|---------------------------|
| CP15(1) | O-A     | Thung Kha Wat, Lamae, Chumphon |
| CP15(2) | A-B     |                           |
| CP15(3) | B-C     |                           |
| SR12rk | RK      | Pak Chalui, Tha Chang, Surat Thani |

2.5. **Wavelength Dispersive X-ray Fluorescence (WDXRF) analysis**

The sample was prepared by the fused bead method with optimized condition for major element determination (based on our previous study). The sample (0.62 g) was mixed with 0.08 g ammonium iodide, 1.24 g of lithium metaborate and 4.96 g of lithium tetraborate. Then, the mixed sample-flux was transferred to a platinum crucible. The fusion was performed at 1000°C for 2.30 min in a furnace. The fused disc sample was analysis for major element contents using a Bruker S8 Tiger WDXRF spectrometer.

3. **Results and discussion**

3.1. **Calibration curves of hXRF analysis**

The linear calibration curves for major elements were plotted by certified value and measured values of the 8 reference materials (Figure 1). The results show strong linear relationships between the measured and certified values with R² > 0.95 for Al, Ca, Fe, K, Si and Ti. However, P at the concentrations typically found in the geological reference materials could not be measured by this pXRF spectrometers. In the case of Na, its Kα line is about at 1.041 keV which is too low to be detected by the pXRF [7]. Besides, the Na- Kα line was simple self-absorbed and simple self-absorbed and scattered into the sample matrix as Bremsstrahlung radiation [8]. There was a much higher degree of scattering between the pXRF analysis and the results at low concentration [9]. The major element measurements were most likely related to the fact that their detections were at the currently available pXRF instrument capabilities. For the calibration curves of Mg, it was poor because the most concentrations in the standard materials were very low and it could not be determined accurately by this pXRF (The results did not show). The detected ranges of each major elements in this study were 7.1-12%, 1.5-35%, 0.06-9.6%, 1.5-4.5%, 1.6-36% and 0.15-1.4% for Al, Ca, Fe, K, Si and Ti measurement, respectively. The results from recalibration method of the known concentration samples are shown in table 2. The data comparison between results obtained by measured and referenced values was showed in figure 1. The percentage of different values (Diff.) in table 2 were calculated as follows:
where $C_{\text{ref}}$ and $C_{\text{pXRF}}$ are the reference and the measured values obtained from pXRF, respectively. It can be noted from table 2 that the concentration values of 6 elements obtained by pXRF showed good agreement with those reference values ($\leq 30\%$ difference).

$$\text{Diff.} (%) = \frac{(C_{\text{pXRF}} - C_{\text{ref}})}{C_{\text{ref}}} \times 100$$  \hfill (1)

3.2. Characterization of soil samples by XRD

The X-ray diffractometer spectrometry (XRD) is usually used for identifications of minerals in the soil and rock samples. In this research, XRD was used for studying the mineral profiles and estimating the major element content. In Thailand, there are found that the granite area can be divided into four regions: Eastern, Northern, Main Range, and Western. Granite plutons are dispersed from northern of Thailand to western of Indonesia through eastern of Myanmar and Peninsular Malaysia. Phuket is in a Western region of Thailand. There are higher rare earth elements contents compared with the other granites in Thailand [10]. The profile of weathering is divided into O, A, B, C, D and RK horizons from the surface to the bottom. The O and A horizon is top soil with dark brown color. It contains high organic matters, clay minerals, quartz and small amounts of rock-forming minerals [10]. The XRD results (Figure 2) show that the main minerals were quartz and kaolinite. The B horizon is clay-rich weathered granite with organic matters. This horizon shows yellowish- and reddish-brown color. Clay minerals contain mainly of kaolinite and halloysite [10] that could be confirmed by the results from XRD analysis. The C horizon is a friable weathering shell of the parent granite with yellowish or gray color and XRD result informed that this horizon mainly comprised of quartz, kaolinite, halloysite and illite with small amounts of vermiculite. Some significant difference in the mineral accumulation of the C horizon was found when compared to that of the B horizon. The C horizon slowly changes to the B horizon without clear boundary [10]. For D and RK horizon, it had white-gray color with a main component of quartz and small amounts of kaolinite, halloysite, illite, vermiculite and biotite. Kaolinite and halloysite were the common clay minerals for all horizons. In addition, vermiculite and biotite

---

**Figure 1.** Calibration curves of the pXRF analysis; (a) Al, (b) Ca, (c) Fe, (d) K, (e) Si and (f) Ti.
were scarce in the upper part of the horizon (horizon A to B) but were found commonly in the lower part of the profile (horizon C to D).

Table 2. Comparison between the measured and recommended concentration values of known concentration samples obtained from pXRF.

| Element | Sample   | Recommended value (%) | pXRF with recalibration |
|---------|----------|-----------------------|-------------------------|
|         |          | AV | SD | Diff. (%) |
| Al      | CP15(1)  | 9.28 | 10.63 | 0.13 | 14.55 |
|         | CP15(2)  | 9.38 | 10.51 | 0.23 | 12.01 |
|         | CP15(3)  | 9.93 | 10.22 | 0.24 | 2.95  |
|         | SR12rk   | 7.25 | 6.28  | 0.03 | -13.43 |
| Ca      | CP15(1)  | 0.10 | n.a. | n.a. |
|         | CP15(2)  | 0.10 | n.a. | n.a. |
|         | CP15(3)  | 0.10 | n.a. | n.a. |
|         | SR12rk   | 1.70 | 1.56  | 0.02 | -8.24 |
| Fe      | CP15(1)  | 2.13 | 2.76  | 0.02 | 29.56 |
|         | CP15(2)  | 2.39 | 3.08  | 0.01 | 29.05 |
|         | CP15(3)  | 2.77 | 3.22  | 0.02 | 16.28 |
|         | SR12rk   | 1.89 | 2.21  | 0.03 | 16.95 |
| K       | CP15(1)  | 4.00 | 3.51  | 0.02 | -12.33 |
|         | CP15(2)  | 3.70 | 3.24  | 0.04 | -12.43 |
|         | CP15(3)  | 4.20 | 3.54  | 0.04 | -15.71 |
|         | SR12rk   | 3.70 | 4.04  | 0.02 | 9.28  |
| Si      | CP15(1)  | 29.22 | 25.64 | 0.54 | -12.25 |
|         | CP15(2)  | 24.44 | 25.09 | 0.32 | 2.67  |
|         | CP15(3)  | 28.89 | 25.42 | 0.37 | -12.00 |
|         | SR12rk   | 32.17 | 30.72 | 0.47 | -4.51 |
| Ti      | CP15(1)  | 0.28 | 0.30  | 0.01 | 7.29  |
|         | CP15(2)  | 0.26 | 0.27  | 0.01 | 2.88  |
|         | CP15(3)  | 0.27 | 0.26  | 0.02 | -3.53 |
|         | SR12rk   | 0.22 | 0.28  | 0.00 | 28.67 |

n.a. not available, AV average, SD standard deviation

Figure 2. Percentage of minerals in the samples with different soil horizons; quartz , kaolinite , halloysite , illite , vermiculite and biotite .

3.3. Comparison of pXRF, WDXRF, XRD and SEM-EDX performance for major element analysis

In this study, the results from recalibration method of the pXRF were compared with the routine WDXRF method. Normally, SEM-EDX and XRD techniques are applied for major mineral characterization. For this study, these two techniques were used to confirm these analytical results. The WDXRF analysis using fused bead technique could be used for major element measurements with the error of less than 10% when compared with the reference values (data not shown). According to
this reason, the results from WDXRF were high accuracy and used as control in this study. The fused bead method was used for eliminating matrix effects, but it was not suitable for minor and trace element analysis. A high dilution with the flux adding caused low fluorescent X-ray intensity resulting in difficulty of minor and trace element analysis [11]. For fused bead preparation, this study used the optimized condition of sample-flux ratio to major element analysis (base on our previous study). The results (Table 3) suggested that pXRF technique could be used for estimating the major elements content in geological samples. Four major elements including Al, Fe, Si and Ti, were reliable when compared to laboratory values (WDXRF results). The concentrations of K obtained by the pXRF tend to be significantly underestimated with high different value (> 30%). This was due to the particle size, mineralogical, the coexisting component effects (matrix effect) when the pXRF spectrometer was used for these geological samples even using the recalibration method. These effects were increased when the sample contains abundant sheet silicate minerals, quartz and accessory minerals [12]. The results from four techniques confirm that two main major elements in those samples were Si and Al, respectively.

3.4. Differentiating horizons
In this study, the pXRF analysis with recalibration method was applied to measure major element contents in soil and rock samples at different soil horizons. The results showed that the major elements consisted of Si (18-22 wt%), Al (12-15 wt%), Fe (1-4 wt%), K (0.4-3.2 wt%) and Ti (0.2-0.4 wt%). However, Ca and Mg could not be detected because there was below the limit of detection of the pXRF equipment. Figure 3 shows the major element concentration profile with different horizons of soil and rock. Silicon (Si) and aluminium (al) were accumulated in rock horizon (depth > 12 m). Iron (Fe) was accumulated in C horizon at a depth of 3 m to 12 m. In contrast, Ti was low and not significantly different with depth. In this study, the results suggested that the soil samples had high Si and Al content therefore this soil may be developed from high Al silicate rock. However, this assumption was still required more information to confirm the results. Wang et al. [1] suggested that climate has effect on the major soil elements. They found that soils with higher Al appeared in areas with silicate-rich and high-Al silicate clastic rocks and silicate-rich aluminosilicate loose sediments. The contents of Mg, Fe, Ca and Al in soil were more affected by precipitation and those elements decreased with increasing precipitation.

![Figure 3. Profile of major element concentrations with depth.](image-url)
Table 3. Major elements concentration in geological samples with different soil horizons measured by pXRF with recalibration using 4 μm Mylar film, WDXRF, SEM-EDX and XRD.

| Element (%) | Horizon | WDXRF | pXRF | SEM-EDX | XRD |
|-------------|---------|-------|-------|---------|-----|
|             | AV      | SD    | AV    | SD      | Diff. (%) |
| Al          | 13.92   | 0.26  | 11.93 | 0.13    | -14.25 |
|             | 14.51   | 0.82  | 4.24  | 12.80   | -8.02 |
|             | 15.40   | 0.11  | 19.18 | 15.90   | 6.02  |
| Fe          | 2.47    | 0.06  | 2.89  | 0.02    | 17.15 |
|             | 4.26    | 1.12  | 72.55 | 1.30    | -47.30 |
|             | 3.84    | 0.06  | 4.11  | 0.39    | 224.9 |
|             | 3.44    | 0.40  | -7.85 | 0.20    | -946.5 |
|             | 4.79    | 0.42  | 248.3 | n.a.    |       |
| K           | 4.35    | 0.05  | 3.08  | 0.05    | -2921 |
|             | 2.30    | 0.38  | -4708 | 0.40    | -98.80 |
|             | 1.77    | 0.40  | -4685 | n.a.    |       |
| Si          | 3.32    | 0.05  | 2.25  | 0.05    | -3223 |
|             | 1.77    | 0.40  | -4685 | n.a.    |       |
|             | 1.18    | 0.14  | -5735 | 0.10    | -9639 |
|             | 2.32    | 0.52  | -3577 | n.a.    |       |
|             | 1.44    | 0.13  | 1657  | 1.30    | -6341 |
|             | 2.09    | 0.42  | -4993 | 0.70    | -8326 |
|             | 2.31    | 0.39  | -3648 | 0.40    | -8899 |
|             | 0.85    | 0.48  | -5934 | 0.40    | -8094 |
|             | 3.34    | 1.18  | -2408 | 0.10    | -9773 |
|             | 2.53    | 0.14  | -4767 | 1.50    | -6893 |
|             | 20.27   | 1.09  | -3211 | 31.60   | 5.86  |
|             | 19.58   | 1.63  | -2923 | 28.50   | 3.03  |
|             | 18.34   | 4.24  | -3216 | 32.80   | 21.31 |
|             | 18.30   | 0.16  | -31.91| 29.20   | 8.65  |
|             | 26.72   | 0.06  | 1848  | 28.70   | 27.24 |
|             | 17.45   | 0.77  | -3471 | 29.10   | 8.86  |
|             | 18.29   | 5.16  | -3152 | 26.60   | -0.41 |
|             | 17.76   | 1.68  | -3573 | 25.40   | -8.06 |
|             | 20.82   | 0.36  | -2803 | 35.50   | 22.70 |
|             | 16.83   | 0.63  | -3999 | 38.30   | 36.56 |
Acknowledgements

Authors would like to acknowledge the Office of Atoms for Peace, Thailand for supporting Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) equipment and the Department of Mineral Resources, Thailand for supporting the rock samples.