Effects of plastic film in a loosed powder form of sample preparation on elemental analysis by portable X-ray fluorescence spectrometer

S Nuchdang¹, W Patthaveekongka² and D Ratanaphra¹

¹ Research and development division, Thailand institute of nuclear technology (Public organization) Nakhon Nayok 26120, Thailand
² Department of chemical engineering, Faculty of engineering and industrial technology, Silpakorn university, Nakhon Pathom 7300, Thailand
E-mail: sasikarn@tint.or.th

Abstract. The aim of this research was to study the effects of plastic film types and film thickness on elemental analysis by portable X-ray fluorescence spectrometer (pXRF). Mylar polyester film with 3.6 µm and 6.0 µm thickness, and 4.0 µm Prolene thin film were used in this study. Five rock samples were prepared by loosed powder method. The pXRF analysis of each plastic films was calibrated and evaluated the method with seven reference materials. The calibrated curves of three films were strongly correlated to referenced values ($R^2 > 0.95$) for Al, Ca, Fe, K, Mn, Si, Sr, Th, Ti, V, Y, Zn and Zr, except for Cu, Nb, Ni, P, U, V and W. The results showed that the pXRF could be used to determine some elements in rock samples and the thickness and types of the analyzed film influenced on the analysis. The element determination using each film required the developed method by calibration curve construction (linear regression of measured values obtained by the pXRF instrument against their certified values). In addition, the results after the recalibration of each film (both Prolene thin film and Mylar polyester film) agreed well.

1. Introduction
A principal information for geochemical studies is chemical composition analysis in the samples [1]. Many types and a complex matrix composition in the geological samples especially in rock have been found to have significant effect on an accuracy and precision of the analysis using x-ray fluorescence (XRF) spectroscopy [2]. XRF is a well-established and most commonly technique to obtain chemical composition [3]. The XRF technique has been used to reduce matrix effects and heterogeneous sample problem but analytical precision and the ultimate accuracy of the results depend on several factors. For example, some rock type samples contained abundant sheet silicate minerals, quartz, and accessory minerals, caused in an increasing of particle size effects (grain size, inter-mineral, and mineralogical effects) [4]. In addition, instrumental setting and stability, the calibration procedure, mineralogical and matrix of the sample, the reference materials used to calibrate the instrument and sample preparation have also effect on the analysis [2]. However, the measurements can be costly, require intensive sample preparation and analysis time for providing the higher quality analysis [3]. Portable X-ray fluorescence (pXRF) spectroscopy is a new application for element analysis. It allows for direct substrate measurements or using special containers for the analyses. The mechanism of pXRF analysis is that an excited inner shall electron is replaced by an outer shell electron and release the excess...
energy in the form of X-ray photon. This energy is characteristic of each chemical element in a sample. The spectrum of the element is measured by the pXRF detector. However, only some elements of the periodic table can be determined because of low energy responses [5]. In recent years, the pXRF has been applied to analyze elements in many types of material such as rocks, soil, sediment, wood and archeological [6, 7, 8]. The limitations of pXRF analysis are calibration of a small amount of element analyses, measurement based on the instrument’s internal calibration, a priori measuring-time determination based on the relative deviation as a determinant factor and absence of criteria to establish the minimum amount of sample that can be measured and its container material [5, 9]. Previous studies found that grain size and the moisture content in the sample have significant effect on the elemental analysis. The geological samples should be prepared with the grain size less than 75 µm and the moisture content in the sample less than 1 wt% [10].

It is important to develop the suitable calibrated method for measuring elemental composition in some kind rock samples using the pXRF equipment. In this study, the pXRF was applied to determine chemical compositions in rock samples and aimed to study the effect of film types and film thickness on the analysis. The calibration of the methods was done by geological reference materials. The accuracy of the methods was done using known concentration rock samples.

2. Materials and methods

2.1. Sample locations and sample preparation

Five known concentration rock samples from department of Mineral Resources, Thailand were used for testing calibration method of the pXRF analysis. The sample locations are shown in table 1. The sample was crushed into small pieces using mechanical crusher and then were manually homogenized and passed through a 75 µm sieve. Then, the sample was dried to constant weight at 110°C (moisture content ≤ 1 wt%).

| NO. | Sample code | Sample location                      |
|-----|-------------|-------------------------------------|
| 1   | SR04        | Takuk Tai, King Amphoe Wiphawadi, Surat Thani |
| 2   | SR06        | Nam Hak, Khiri Rat Nikhom, Surat Thani |
| 3   | SR08        | Lamphun, Banna San, Surat Thani       |
| 4   | SR11        | Lamphun, Banna San, Surat Thani       |
| 5   | SR12        | Pak Chalui, Tha Chang, Surat Thani    |

2.2. Portable X-ray fluorescence spectrometry (pXRF) analysis

The sample was prepared by the loose powder technique with three film types including (1) 4 µm Prolene® thin film, (2) 3.6 µm Mylar® polyester film and (3) 6.0 µm Mylar® polyester film. Each cup was covered with the film. Then, the fine powder sample was filled into cup with sample thickness of 1.0 cm. A Delta Professional pXRF Analyzer, DPO 2000 (Olympus Scientific Solutions Americas, Inc.) equipped with an instrument’s prolene window of 8 mm², a 4W miniature X-ray tube (200 µA maximum current), and silicon drift detector (SDD), was used for elemental measurement using Geochem mode with two beams. The elements including 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, Ti and Mn were measured with first beam (40 kV). The light elements including Mg, Al, Si, P, S, Cl, K, Ca, Ti and Mn were determined by second beam (10 kV). Each measuring time for an individual beam was set at 60 s (Total time = 120 s). The internal pXRF stability was monitored by measuring Fe K-α count on a 316-stainless steel coin every day of use. Each sample was analyzed three times.

For pXRF calibration, eight geological reference materials: JA-1, JB-2, JG-1a, JG-2, JSy-1 (andesite, basalt, granodiorite, granite, syenite, GSJ, Japan); BCR-2, COQ-1, GSP-2 (basalt, carbonatite, granodiorite, USGS, Reston) were used. Each reference material was analyzed ten times to provide standard curve.
2.3. Data analysis
For calibration method of the pXRF, linear curve of each element was plotted between analyzed value (x) and recommended value (y). Slope and intercept of the graph was used for recalibration of the pXRF measurement, if coefficient of determination ($R^2$) was greater than 90. In the case of recalibration requirement, different value between the measured and the recommended values was higher than 30 percentages.

3. Results and discussion
3.1. Calibration curves
The calibrations of each films were constructed by linear regression analyses with an the intercept in the independent variable axis. The obtained data of the reference materials were constructed linear calibration curve with the reported values for each element. The slope, intercept with the ordinate axis and detection limit of the resulting curves (DL$_{met}$) for 4 µm Prolene® thin film, 3.6 µm Mylar® polyester film and 6.0 µm Mylar® polyester film are reported in Table 2, 3 and 4, respectively. In this study, DL$_{met}$ was calculated using the approach promulgated by the EPA (40 CFR 136) as shown in equation (1).

$$DL_{met} = \sigma$$

(1)

when $t$ is the rounded Student’s t-factor and $\sigma$ is the standard deviation of non-consecutive replicate measurements.

In this study, each geological reference material was repeatedly analyzed 10 times. The DL$_{met}$ was then calculated based on the average of standard deviation of the replicate analyses and the Student’s t statistic with n-1 degrees of freedom and alpha of 0.01 [11,12].

For all plastic film, it was found that the calibration curves of Ag, As, Cd, Co, Cr, Hg, Mg, Mo, Nb, Ni, S, Sb, Se, Sn, U and W were poor because of the most concentrations in the standard materials were the restricted range (The results did not show). The calibration curves of P and V were non-linear curves due to their very low concentrations containing in the samples. In case of Na, it could not be detected by the pXRF spectrometer because of it was too light to be detected by the pXRF [3]. Hunt and Speakman [13] suggested that Na-X rays were extremely low energy, K$_a$ line at 1.041 keV, and re-absorbed into the sample matrix and scattered as Bremsstrahlung radiation. There was a much higher degree of scatter between the analysis and the results at low concentration [14]. Whereas those of Al, Ca, Fe, K, Si, Ti, Cu, Mn, Pb, Rh, Sr, Th, Y, Zn and Zr were acceptable with $R^2 \geq 0.90$. The slopes of the regression lines for the elements with $R^2 \geq 0.90$ were directly inputted into the pXRF analyzer software for automatic correction of sample data. Some elements analysis was required for recalibration method because there was a difference between the measured and the recommended values over 30 percentages.

At least for our particular pXRF analyzer, the values obtained from the analysis in this study could be a good approximation for Ca, Fe, K, Si, Cu, Sr, Th, Y and Zr. The DL$_{met}$ for Ag, As, Bi, Cd, Co, Cr, Hg, Mg, Mo, Nb, Ni, P, S, Sb, Se, Sn, U, V and W were not reported since their linear regressions were not statistically significant for the analysis.

The elemental concentration values for all film types and thicknesses compared to those values after recalibration and the recommend values are shown in figure 1. It can be seen that the analysis results could be improved significantly by the using of recalibration method for some samples. Some elements i.e. Al, Ca, K, Si, Rb, Sr, Th and Y after recalibration were reliable compared to those recommended values. An overestimation of Fe, Ti, Mn, Pb and Zn concentrations were observed whereas the Zr concentration was underestimation, when these results were compared with those recommended data (different > 30%). The recommended concentrations of chemical elements in the rock samples at different locations were in the range of Al 6.50-7.25 wt%, Ca 0.20-1.70 wt%, Fe 0.79-2.27 wt%, K 3.70-4.30 wt%, Si 30.73-33.90 wt%, Ti 0.07-0.30 wt%, Cu 10 mg/kg, Mn 130-470 mg/kg, Pb 34-89 mg/kg, Rb 258-558 mg/kg, Sr 30-220 mg/kg, Th 17.30-50.60 mg/kg, Y 26.50-35.30 mg/kg, Zn 19-127 mg/kg and Zr 963-1860 mg/kg. It can be also noted that the concentrations of Pb, Rb and Zr found in the studied samples were very high and over the calibrated range (Table 2, 3 and 4). The instrument was unable to use for Cu detection. This was due to the particle size, mineralogical, the coexisting component effects
(matrix effect) when the pXRF spectrometer was used for these rock samples even using the recalibration method. These effects were increased when the sample contains abundant sheet silicate minerals, quartz and accessory minerals [4]. For Pb analysis, the measured values were more large errors because of the overlapping of the (As) Kα (10.5 keV) and (Pb) Lα (10.5 keV) as well as Lβ (12.6 keV) lines [15, 16]. In addition, elements with low atomic number such as P may be a significant problem on the pXRF measurements [17, 18].

Table 2. Concentration interval (wt% or mg.kg⁻¹), detection limit, slope, intercept and correlation coefficients for the analysed geological reference materials using 4 µm Prolene® thin film.

| Element | Concentration (%) | Slope | Intercept | R² | DL_met | Recalibration |
|---------|------------------|-------|-----------|----|--------|---------------|
| Al      | 0.20 - 12.26     | 1.2986| -0.8133   | 0.9248 | 0.1357 |               |
| Ca      | 0.18 – 34.52     | 0.9945| -0.0820   | 0.9994 | 0.0334 |               |
| Fe      | 0.06 - 9.97      | 0.8540| -0.0357   | 0.9971 | 0.0606 | ✓             |
| K       | 0.13 - 4.48      | 0.8838| 0.3701    | 0.9948 | 0.0312 |               |
| Si      | 1.62 - 35.91     | 1.1027| 0.2697    | 0.9741 | 0.0660 |               |
| Ti      | 0.001 - 1.35     | 1.0657| -0.0139   | 0.9923 | 0.0229 |               |

(4 µm Prolene® thin film)

| Element | Concentration (ppm) | Slope | Intercept | R² | DL_met | Recalibration |
|---------|---------------------|-------|-----------|----|--------|---------------|
| Cu      | 0 - 225             | 0.8194| -0.0001   | 0.9974 | 16.782 | ✓             |
| Mn      | 18.59 - 3330        | 1.0852| -0.0086   | 0.9976 | 23.896 |               |
| Pb      | 0 - 42              | 0.9182|           | 0.9826 | 3.8662 |               |
| Rb      | 0 - 301             | 0.9860|           | 0.9996 | 1.4570 |               |
| Sr      | 17.9 - 12,000       | 1.2422| -0.0047   | 0.9998 | 2.3978 | ✓             |
| Th      | 0.23 - 105          | 0.9351| -0.0006   | 0.9883 | 11.364 | ✓             |
| Y       | 2.6 – 86.5          | 0.9924|           | 0.9846 | 3.0475 |               |
| Zn      | 3.2 - 127           | 0.8575| 0.0010    | 0.9204 | 5.8658 |               |
| Zr      | 51.2 - 550          | 1.0480| -0.0009   | 0.9792 | 4.7585 |               |

Table 3. Concentration interval (wt% or mg.kg⁻¹), detection limit, slope, intercept and correlation coefficients for the analysed geological reference materials using 3.6 µm Mylar® polyester film.

| Element | Concentration (%) | Slope | Intercept | R² | DL_met | Recalibration |
|---------|------------------|-------|-----------|----|--------|---------------|
| Al      | 0.20 - 12.26     | 1.4700| 0.1006    | 0.9625 | 0.2083 | ✓             |
| Ca      | 0.18 – 34.52     | 0.9990| -0.0287   | 0.9997 | 0.0267 | ✓             |
| Fe      | 0.06 - 9.97      | 0.8804| -0.0471   | 0.9979 | 0.0042 | ✓             |
| K       | 0.13 - 4.48      | 0.9511| 0.2573    | 0.9978 | 0.0046 | ✓             |
| Si      | 1.62 - 35.91     | 1.3158| 0.4040    | 0.9941 | 0.0475 | ✓             |
| Ti      | 0.001 - 1.35     | 1.1767| -0.0613   | 0.9877 | 0.0223 |               |

(3.6 µm Mylar® polyester film)

| Element | Concentration (ppm) | Slope | Intercept | R² | DL_met | Recalibration |
|---------|---------------------|-------|-----------|----|--------|---------------|
| Cu      | 0 - 225             | 0.8463| -0.0003   | 0.9957 | 7.5297 | ✓             |
| Mn      | 18.59 - 3330        | 1.1048| -0.0071   | 0.9971 | 45.0214|               |
| Pb      | 0 - 42              | 0.9453|           | 0.9699 | 6.1022 |               |
| Rb      | 0 - 301             | 0.9938|           | 0.996 | 1.4870 |               |
| Sr      | 17.9 - 12,000       | 1.2568| -0.0047   | 0.9997 | 2.3228 |               |
| Th      | 0.23 - 105          | 0.906 | -0.0004   | 0.9920 | 6.1600 | ✓             |
| Y       | 2.6 – 86.5          | 1.1129| -0.0001   | 0.9029 | 1.6016 |               |
| Zn      | 3.2 - 127           | 0.8820| 0.0009    | 0.9312 | 6.8854 |               |
| Zr      | 51.2 - 550          | 1.0492| -0.0008   | 0.9786 | 4.1637 |               |
Table 4. Concentration interval (wt% or mg.kg⁻¹), detection limit, slope, intercept and correlation coefficients for the analysed geological reference materials using 6.0 µm Mylar® polyester film.

| Element | Concentration (%) | 6.0 µm Mylar® polyester film | Recalibration |
|---------|-------------------|-------------------------------|---------------|
|        |                   | Slope | Intercept | R² | DLmet |                  |
| Al     | 0.20 - 12.26      | 1.8919 | 0.1401 | 0.9472 | 0.1914 | ✓                  |
| Ca     | 0.18 – 34.52      | 1.0384 | 0.0024 | 0.9990 | 0.0202 |                  |
| Fe     | 0.06 - 9.97       | 0.8831 | 0.0577 | 0.9974 | 0.1943 | ✓                  |
| K      | 0.13 - 4.48       | 0.9166 | 0.4828 | 0.9663 | 0.0081 | ✓                  |
| Si     | 1.62 - 35.91      | 1.5118 | 0.2880 | 0.9721 | 0.0655 | ✓                  |
| Ti     | 0.001 - 1.35      | 1.2831 | -0.0670 | 0.9555 | 0.0128 |                  |

3.2. Effect of plastic film type on the chemical analysis

It was found from Figure 1 that both plastic film types (Prolene® thin film and Mylar® polyester film) could be used for scientifically element determinations in the geological samples with different value ≤ 30%. The calculated detection limits (DLmet) results demonstrated that the most detection limits provided by the Prolene® thin film were higher than those obtained by the Mylar® polyester for Ca, Fe, K, Si, Cu, Sr, Th, Y and Zr. According to label on the film boxes, the 4 µm Prolene® thin film contains more impurities than the Mylar plastic film. The Prolene® thin film contains with the amounts of Ca, P, Fe, Cu, Zr, Ti, Al while the Mylar film composes of Ca, P, Sb, Fe, Zn impurities. In this study, some elements were required for recalibration method with different film types. The measurements of Fe, Cu and Th concentration were required for recalibration for 4 µm Prolene® thin film (table 2). For the Mylar® polyester film (table 3 and 4), the recalibration method was applied for the measurements of Al, Fe, K, Si, Cu and Th. These results showed that the pXRF analysis using Prolene® thin film and Mylar® polyester film with recalibration method were not significantly difference. To minimize the measurement errors, each plastic film type was recommended to calibrate. If plastic films are used to collect and measure rock samples, the XRF analyzer must have been calibrated using the same plastic to minimize these effects.

3.3. Effect of plastic film thickness on the chemical analysis

Two different thickness films (3.6 µm and 6.0 µm Mylar film) were used to study the effect of plastic film thickness on the chemical analysis. For the pXRF analysis using both different thickness films without recalibration, Al and Si concentrations were low values but these results could be improved by the recalibration method (Figure 1). The results using plastic films of different thickness in empty containers indicated that the thickness of film effected on the element analysis. In the case of Ca measurement, the detection limits provided by the 6.0 µm thickness film was lower than that obtained by the 3.6 µm thickness film. Thus, the small amount of Ca (0.20 g/kg in SR08rk sample) could be detected by only 6.0 µm thickness film. The pXRF analysis using the different thickness of plastic films with recalibration method were not significantly different.
4. Conclusion
The results established that the pXRF could be used for providing the data consistent with the reported values. The pXRF measurement of geological reference material using different film types and thickness were in satisfactory agreement with the certified values for all elements except for Mg, Ag, As, Cd, Cr, Hg, Mo, Nb, Ni, P, Sb, Se, Sn, U, V, and W. The accuracy and precision of the elements in geological reference materials by pXRF after recalibration were acceptable. The elements including Al, Ca, Fe, K, Si, Ti, Cu, Mn, Pb, Rb, Sr, Th, Y, Zn and Zr in rock samples could be detected by the pXRF technique. Good agreement between the measured results and the recommended values were found for some elements including Al, K, Si, Rb, Sr, Th and Y. The study showed that the pXRF had the potential to estimate the rock composition. However, the calibration method was required for the pXRF measurement. Therefore, if each plastic films are used to analyze the samples, the XRF analyzer should be calibrated using the same plastic to minimize these effects.

5. References
Acknowledgments
Authors would like to acknowledge the Department of Mineral Resources, Thailand for supporting the rock samples.