Development and validation of portable X-ray fluorescence spectrometry for elemental routine measurement in geological samples

S Nuchdang¹, B Sukhummek² and D Rattanaphra¹

¹ Research and Development Division, Thailand Institute of Nuclear Technology, Phathumtani, Thailand
² Faculty of Science, Department of Chemistry, King Mongkut's University of Technology Thonburi, Thailand

Abstract. A pressed pellet technique was developed for quantitative analysis of elements in geological samples by portable X-ray fluorescence spectrometry (pXRF). Validation of analytical method was done using eight geological reference materials (BCR-2: basalt, COQ-1: carbonatite, GSP-2: granodiorite, JA-1: andesite, JB-2: basalt, JG-1a: granodiorite, JG-2: granite and JSy-1: Syenite). Minimum concentrations of Al, Ca, Cu, Fe, K, Mn, Pb, Rb, Si, Sr, Ti, Y, Zn and Zr in geological reference materials for pXRF detection were 6.60%, 0.50%, 19 mg/kg, 0.06%, 0.35%, 120 mg/kg, 5.36 mg/kg, 7.37 mg/kg, 1.62%, 17.92 mg/kg, 0.09%, 24.90 mg/kg, 13.60 mg/kg and 51.20 mg/kg, respectively. The accuracy of the developed method was acceptable with the mean error below 18%. The geological samples received from the Department of Mineral Resources (DMR) were also tested using this method. The results showed that the concentration values obtained by the studied method were in good agreement with those obtained by the DMR for K, Mn, Pb, Rb, Si, Sr, Ti, Y and Zn with concentrations ranging of 3.70-4.20%, 90-400 mg/kg, 64-89 mg/kg, 296-404 mg/kg, 24.44-32.17%, 50-180 mg/kg, 0.22-0.28%, 34-47 mg/kg and 30-41 mg/kg, respectively. This method is suitable for elemental routine measurement in geological samples.

1. Introduction

X-ray fluorescence (XRF) spectrometry is a technique for element analysis, widely applied in many fields [1]. One of the applications in the analysis is geological and mineral samples. In this case, the accuracy of the XRF depends on the availability of reliable matrix correction procedures [2]. In addition, high X-ray background scatter could make the XRF difficult to quantify elements at such low concentration [3]. The XRF analysis allows for non-destructive and express quantification of several elements simultaneously. The process of XRF analysis is based on interaction of X-ray radiation with atoms and then ejection of electrons and formation of vacancies occurs as a result of this interaction. These vacancies are filled with electrons from higher orbitals with emission of X-ray radiation with unique energy for a specific element. Generally, X-ray fluorescence derived from transitions of inner electrons is employed. The reason for the high selectivity of this technique is that the number of allowed transitions is limited. The number of spectral lines is rather small, and their overlapping is not common [1]. Two main ways of signal registration in XRF are energy dispersive (EDXRF) and wavelength dispersive (WDXRF).

For EDXRF analysis, it is quite fast and compact. In general, EDXRF is usually applied more often than WDXRF. The spectra are registered by semiconductor detector having rather high energy resolution.
[1]. This technique allows low cost construction and desktop size spectrometers able to reliable and fast determine the element concentrations in different kinds of matrices [4]. Portable XRF (pXRF) equipment is now an EDXRF technique. The pXRF could analyse elements with medium to high atomic mass from K to Pb, Th and U. It has high limitations for light weight elements than laboratory XRF because of instrument constraints and low energy responses [5,6]. However, recent equipment could explore lighter elements including Al, Mg, P and Si by high performance detectors [5]. It allows for direct substrate measurements or loose powder method using special containers for the analyses [6].

In the case of sample preparation technique, in general WDXRF analysis, glass bead method has been widely used for major elements analysis because this method is high reliability in the resulting data and high analysis throughput [4]. The effects of matrix and mineral are eliminated by this method [2]. For trace element determinations, the sample is usually prepared by a pressed pellet method or low dilution glass bead [7] but mineral and matrix effects interference in the measurement [2,4]. According to our previous studies, we found that the grain size, moisture content and film type for loose powder sample preparation affected on element analysis by the pXRF [8,9]. In this study, the pressed pellet method for the pXRF analysis was studied to reduce those effects. The analytical method was validated using geological reference materials. The known concentrations of the geological samples obtained from the Department of Mineral Resources (DMR) were also tested. The developed sample preparation was expected to be the suitable method for routine element measurement by the pXRF.

2. Materials and method

2.1. Geological reference materials
Eight geological reference materials from two locations to get different matrix samples (the components of a sample) including: 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 to validate the method.

2.2. Geological samples
Four known concentrations of geological samples including O-A, A-B, B-C horizon from Thung Kha Wat, Lamae, Chumphon province and D horizon from Pak Chalui, Tha Chang, Surat Thani province, Thailand, respectively (supported by the Department of Mineral Resources, Thailand) were used to test the analytical method.

2.3. Sample preparation
Each sample was dried at 110°C and then homogenized. Eight grams of sample was mixed with 2.00 g of boric acid by an automatic mortar for 5 min. The mixture was pressed under pressure (150 kN) into 40 mm diameter, 7.5 mm thick pellet and held at this pressure for 20-30 s. The mass ratio of sample and boric acid used in this study is the optimum condition obtained from our previous experiment.

2.4. Portable X-ray fluorescence spectrometry (pXRF) analysis
Elements in the sample were analysed by a Delta Professional pXRF Analyzer, DPO 2000 (Olympus Scientific Solutions Americas, Inc.) using Geochem mode with 40 and 10 kV. The measured time was 120 s. 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, Mn, Mg, Al, Si, P, S, Cl, K, Ca, Ti and Mn were analyzed. Each sample was analysed three times.

2.5. Calculation
Percentage error of measurements were calculated according to equation (1). This study accepted the percentage error at less than 30%.
\[
\text{Error} \; (\%) = \frac{|C_{\text{pXRF}} - C_{\text{rec}}|}{C_{\text{rec}}} \times 100
\]  
(1)

where \(C_{\text{pXRF}}\) and \(C_{\text{rec}}\) are the mean concentrations of measured results for pXRF and recommended values, respectively.

3. Results and discussion

The pressed pellet method was developed for the elemental analysis in geological samples by pXRF. This method is expected to minimize the particle size and mineral effects. The geological reference materials were used to verified the analytical method. Correlation equation was observed by linear calibration curves between the recommended (x) and measured (y) values. The results showed that the elements; Al, Ca, Cu, Fe, K, Mn, Pb, Rb, Si, Sr, Ti, Y, Zn, and Zr could be quantified by the pXRF. The correlation between the recommended and measured values for the analysed geological reference materials are illustrated in table 1. As can be seen in table 1, a good correlation between the measured and recommended results with \(R^2 > 0.95\) (The measured values from pXRF analysis were fitted with regression line curve) was observed for all elements except for Al and Zn. Mean percentage error could be calculated by the average of percentage errors. The accuracy of method for Mn, Rb, Sr, Y and Zr were better than 10% of mean percentage error. In case of Al, Ca, Cu Fe, K Pb, Si and Zn measurements, a poor accuracy with the mean percentage error greater than 10% was noted.

Table 1. Correlation equation between the recommended (x) and measured (y) values, the concentration ranges and the mean average error for the pXRF measurements.

| Element | Unit | Concentration range of reference materials | Minimum concentration detection | Correlation equation | \(R^2\) | Mean percentage error (%) |
|---------|------|------------------------------------------|---------------------------------|----------------------|--------|--------------------------|
| Al      | %    | 0.20 – 12.26                            | 6.60                            | \(y = 1.1159x - 1.4842\) | 0.86   | 11                       |
| Ca      | %    | 0.50 – 34.52                            | 0.50                            | \(y = 1.1023x - 0.3916\) | 0.99   | 12                       |
| Cu      | mg/kg| 19 – 225                                | 19                              | \(y = 1.2601x - 1.1317\) | 0.99   | 13                       |
| Fe      | %    | 0.06 – 9.97                             | 0.06                            | \(y = 1.0964x + 0.1392\) | 0.99   | 18                       |
| K       | %    | 0.13 – 4.48                             | 0.35                            | \(y = 1.0690x - 0.2590\) | 0.99   | 17                       |
| Mn      | mg/kg| 18.6 – 3330                             | 120                             | \(y = 0.9648x - 7.6585\) | 0.99   | 5                        |
| Pb      | mg/kg| 5.36 – 42                               | 5.36                            | \(y = 1.0260x + 1.5477\) | 0.99   | 15                       |
| Rb      | mg/kg| 7.37 – 301                              | 7.37                            | \(y = 0.9908x - 1.1265\) | 0.99   | 6                        |
| Si      | %    | 1.62 – 35.91                            | 1.62                            | \(y = 0.9192x - 0.2750\) | 0.80   | 11                       |
| Sr      | mg/kg| 17.9 – 12000                            | 17.9                            | \(y = 0.8486x + 23.555\) | 1.00   | 4                        |
| Ti      | %    | 0.03 – 1.35                             | 0.09                            | \(y = 0.9053x + 0.0336\) | 0.96   | 8                        |
| Y       | mg/kg| 24.9 – 86.50                            | 24.9                            | \(y = 1.0641x - 0.8003\) | 0.99   | 7                        |
| Zn      | mg/kg| 13.6 – 127                              | 13.6                            | \(y = 1.3921x - 19.509\) | 0.75   | 16                       |
| Zr      | mg/kg| 51.2 – 550                              | 51.2                            | \(y = 0.9495x - 1.9438\) | 0.99   | 7                        |

\(R^2\)-Coefficient of determination, nd. – not detected

Four known concentrations of geological samples were tested using the pXRF measurement by pressed pellet method and the results are shown in table 2. It can be seen that the concentration ranges of Al, Ca, Cu, Fe, K, Mn, Pb, Rb, Si, Sr, Ti, Y, Zn and Zr in the geological samples were 7.25 -9.93%, 0.10 -1.70%, 10 mg/kg, 1.89 -2.77%, 3.70 -4.20%, 90 -400 mg/kg, 64 -89 mg/kg, 296 -404 mg/kg, 24.44 -32.17%, 50 -180 mg/kg, 0.22 -0.28%, 34 -47 mg/kg, 30 -41 mg/kg and 526 -1020 mg/kg, respectively. The precision for all measurements can be considered good (better than 5% RSD) except for Zn and Y. The concentrations of K, Mn, Pb, Rb and Si for all samples measured by the studied method were in good agreement with those measured by the DMR Laboratory (error better than 10%), except for Mn, Pb and Ti (in D-horizon) as well as Si (in A-B horizon). An acceptable difference in concentration values between the studied method and those by DMR (error < 20%) was observed for Y, Sr and Zn. For Al, Fe and Zr, the error values were greater than 30% for all samples. The most concentrations of Ca and
Cu in the samples were lower than the detection limit in pXRF analysis (0.50% Ca and 19 mg/kg Cu). In the case of Al and Fe, Lemiere [10] reported that pXRF analysis had limitations for light atomic mass.

### Table 2. Results obtained from the known concentration geological samples by pXRF measurement with pressed pellet method.

| Horizon | Element | Al | Ca | Cu | Fe | K | Mn | Pb | Rb | Si | Sr | Ti | Y | Zn | Zr |
|---------|---------|----|----|----|----|---|----|----|----|----|----|----|---|----|----|
|         | Unit    | %  | %  | mg/kg | %  | %  | mg/kg | %  | mg/kg | %  | mg/kg | %  | mg/kg | %  | mg/kg |
| O-A     | Conc.   | 9.28 | 0.10 | 10 | 2.13 | 4.00 | 90 | 68 | 402 | 29.22 | 50 | 0.28 | 34 | 30 | 610 |
|         | (DMR)   |    |     | 8.28 | nd. | nd. | 3.19 | 3.71 | 98 | 67 | 393 | 29.74 | 44 | 0.29 | 39 | 35 | 278 |
|         | (this study) | Error (%) | 41 | 50 | 7 | 9 | 0.1 | 2 | 2 | 8 | 2 | 13 | 17 | 54 |
|         | RSD (%) | 1 | 1 | 0.1 | 11 | 1 | 0.8 | 1 | 2 | 5 | 5 | 18 | 3 | 1 |
| A-B     | Conc.   | 9.38 | 0.10 | 10 | 2.39 | 3.70 | 90 | 69 | 404 | 24.44 | 50 | 0.26 | 44 | 32 | 526 |
|         | (DMR)   |    |     | 13.3 | nd. | nd. | 3.72 | 3.56 | 96 | 69 | 403 | 30.32 | 45 | 0.29 | 47 | 40 | 255 |
|         | (this study) | Error (%) | 42 | 56 | 4 | 7 | 0.3 | 0.04 | 24 | 11 | 6 | 25 | 52 |
|         | RSD (%) | 1 | nd. | 0.5 | 0.4 | 9 | 1 | 0.8 | 0.6 | 2 | 7 | 4 | 5 | 1 |
| B-C     | Conc.   | 9.93 | 0.10 | 10 | 2.77 | 4.20 | 90 | 64 | 394 | 28.89 | 50 | 0.27 | 47 | 41 | 546 |
|         | (DMR)   |    |     | 12.8 | nd. | nd. | 3.82 | 3.76 | 90 | 69 | 397 | 29.14 | 50 | 0.27 | 54 | 39 | 243 |
|         | (this study) | Error (%) | 30 | 38 | 10 | 0.01 | 7 | 0.8 | 0.9 | 0.8 | 0.3 | 15 | 5 | 55 |
|         | RSD (%) | 0.6 | nd. | 0.4 | 0.4 | 29 | 3 | 0.5 | 1 | 1 | 2 | 5 | 6 | 1 |
| D       | Conc.   | 7.25 | 1.70 | 10 | 1.89 | 3.70 | 400 | 89 | 296 | 32.17 | 180 | 0.22 | 34 | 40 | 1020 |
|         | (DMR)   |    |     | 7.62 | 1.51 | nd. | 2.75 | 4.08 | 492 | 195 | 303 | 33.15 | 185 | 0.26 | 39 | 48 | 191 |
|         | (this study) | Error (%) | 5 | 46 | 10 | 23 | 119 | 2 | 3 | 3 | 19 | 16 | 20 | 81 |
|         | RSD (%) | 1 | 1 | nd. | 0.5 | 0.6 | 0.8 | 1 | 0.9 | 1 | 1 | 4 | 12 | 3 | 2 |

nd. – not detected, RSD - relative standard deviation

4. Conclusion

The geological samples were prepared with pressed pellet method to solve matrix problem in the samples for pXRF analysis. This strategy successfully applied for element analysis in various horizon of soil profile samples. The method could be applied to routine element measurement by pXRF without requirement of recalibration for K, Mn, Pb, Rb, Si, Sr, Ti, Y and Zn except for Al, Ca, Fe and Zr measurements. The pXRF showed a tendency for better results in trace elements analysis. In future work, a matrix match calibration will be studied to improve reliable quantitative analysis by pXRF analysis with the pressed pellet method and more samples will be required for the test.

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