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DEVELOPMENT OF HANDHELD X-RAY FLUORESCENCE (hXRF) SPECTROMETRY FOR MAJOR AND MINOR ELEMENTS ANALYSIS IN GEOLOGICAL SAMPLES FROM PHUKET PROVINCE, THAILAND

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INTRODUCTION

Soils and rocks have a complex matrix composition and their contained-element chemical analysis is interested in geochemical and environmental studies. A well-established and commonly technique to obtain chemical composition in geological sample is X-ray fluorescence (XRF) spectroscopy [1]. The XRF technique has been used to eliminate matrix effects and sample heterogeneity but analytical precision and the ultimate accuracy of the results depend on several factors. These factors includes 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 [2]. For providing the higher quality data possible, the measurements can be costly, require intensive sample preparation and analysis time [1].

Field handheld instruments can be a new application for in and out of standard laboratory setting [1]. The hXRF has precisions comparable to benchtop models. Moreover, it allows for direct substrate measurements without the need to collect samples or the use of special containers for the analyses. The hXRF is less expensive than benchtop model [3,4]. In recent years, the hXRF has been used to analyze major and minor elements in different materials (rocks, soil, sediment, wood and archeological [5].

However, the hXRF analysis has some limitations in the efficient application which constrain its reliable uses for optimal element analysis of different types of materials. The hXRF limitations are: (1) calibration of a small number of element analyses; (2) measurement based on the instrument's internal calibration; (3) a priori measuring-time determination based on the relative deviation as a determinant factor and (4) absence of criteria to establish the minimum amount of sample that can be measured and its container material [3].

In this study, handheld XRF (hXRF) was developed to determine major and minor elements in soil and rock samples at the different horizontal soil profiles. Effect of film type on chemical compositions of samples was investigated. The accuracy of the methods was done by using geological reference materials.

MATERIALS AND METHODS

Sample preparation

Ten samples were taken per horizon which varied in thickness 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 (2.0-3.0), C2A (3.0-5.0), C2B (5.0-8.0), C3 (8.0-12.0), D (12.0-20.0) and RK (> 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 manually homogenized and passed through a 250 µm sieve. The sample was dried to constant weight at 110°C before the element analyses.

Wavelength dispersive X-ray fluorescence spectrometry (WD-XRF) analysis

The sample was prepared by 2 methods following;

Fused bead method: The dried sample and flux were weighed in an exact ratio into the platinum crucible (0.62 g of sample, 1.24 g of lithium metaborate, 4.96 g of lithium tetraborate and 0.08 g of ammonium iodide). The fusion was performed at 1000°C for 2.30 min in a furnace.

Loose powder method: Two types of film were used in this study including (1) 4 µm Prolene® thin film and (2) 6 µm Mylar® polyester film. Each cup was covered with thin film. The fine powder sample was then filled into the cup.

Handheld X-ray fluorescence spectrometry (hXRF) analysis

The sample was prepared by the loose powder method with two film types. A Delta Professional hXRF 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 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 (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 K-α count on a 316-stainless steel coin every day of use. Each sample was analyzed three times.

The hXRF was calibrated after measuring intensities in the following seven geological reference materials: JA-1, JG-1a, JG-2, JSy-1 (andesite, granodiorite, granite, syenite, GSJ, Japan); BCR-2, COQ-1, GSP-2 (basalt, carbonatite, granodiorite, USGS, rseton). Each reference material was analysed ten times.

RESULTS AND DISCUSSION

Calibration curves

The collected data of the reference materials were constructed linear calibration curve for each element. It was found that the calibration curves of Ag, As, Cd, Cr, Hg, Mg, Mo, Ni, S, Sb, Se, Sn, U, V and W measured using hXRF were poor because of their restricted rang in the standard materials for both film types. Whereas those of Al, Ca, Fe, K, Si, Ti, Mn, Nb, Pb, Sr, Th and Zn were acceptable with $R^2 \geq 0.95$ except for Cu, P and Y. The calibration curves of Nb and Rb analyzed using 4 µm Prolene® thin film ($R^2 \geq 0.95$). The slopes of the regression line for each element was inputted into the hXRF analyser software for automatic correction of sample data, if the difference between the hXRF analysed value and the CRM recommend value was more than 10%. When 4 µm Prolene® thin film was used for the analysis, 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. In the case of 6 µm Mylar® polyester film, these elements including Al, Fe, K, Si, Ti and Th were recalibrated with 1.8805, 0.8969, 1.0251, 1.4803, 1.1013 and 0.8689, respectively.

P and Na could not be detected by hXRF spectrometer. For P, it is due to its concentration found in the geological reference materials were very low. In case of Na, it was too light to be detected by the hXRF model [1]. Hunt and Speakman [6] suggested that Na-X rays were extremely low energy, Kα 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 hXRF analysis and the results at low concentration [7].

Measurement of major and minor elements in soil and rock samples by hXRF and WD-XRF techniques

The major elements including Si (20-27 wt%), Al (13-17 wt%), Fe (1-4 wt%) and K (1-3 wt%) could be detected. The minor elements were composed of Mn (135-793 g/kg), Th (128-188 g/kg), Zr (65-89 g/kg) and Sr (25-63 g/kg). It can be also noted that the concentrations of Th found in the studied samples were very high and over the calibrated range (> 105 ppm). There was variation of each element in difference soil and rock horizon.

For the hXRF analysis using the 6 µm Mylar® polyester film without recalibration, Al and Si concentrations were lowest values but these values could be improved by the recalibration method. However, the recalibration was not required for the hXRF analysis using the 4 µm Prolene® thin film. Therefore, efficiency of element analysis by the hXRF depended on film type and film thickness. Some elements i.e. Al, Fe, Ti, Pb, Sr, Th and Zr were reliable when compared to WD-XRF results (fused bead and loose powder techniques) but other elements (such as K, Si and Mn) differed from the laboratory values (> 20%). The concentrations of K, Si and Mn obtained using the hXRF tend to be significantly underestimated. The variance in Pb, Sr, Th and Zr related directly to small concentrations contained in these samples. Though the hXRF was able to dependable measure some geologically important elements (such as Al, Fe, Ti, Pb, Sr, Th and Zr) but the instrument was unable to detect other important elements reliably (i.e. Ca and Mg). This was due to the particle size, mineralogical, the coexisting component effects (matrix effect) when hXRF 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 [8].

CONCLUSION

The results demonstrated that the hXRF could provide data consistent with laboratory reported values. The hXRF measurement of geological reference material by both film types were in satisfactory agreement with certified values for all elements except for Cu, Nb, Ni, P, U, V, W, Y, Zn. The recalibration was required for 6 µm Mylar film analysis. The accuracy and precision of the elements in geological reference materials by hXRF after recalibration were acceptable. The elements such as Al, Ca, Fe, K, Mn, Si, Sr, Th, Zn in geological samples were detected by pXRF technique. Good agreement between the result values obtained by pXRF and by WD-XRF was found for some elements including Al, Fe, Ti, Pb, Sr Th and Zn. The study showed that the hXRF had significant potential as a geochemical tool. For the future work, the effect of particle size, sample preparation and moisture content will be investigated for reliable quantitative analysis.

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