

## Topics: C.2-Developments in site investigation and monitoring

### FIELD PORTABLE XRF ANALYSER FOR MINE WASTE AND RED MUD POLLUTED SOIL

Mária Tolner<sup>a</sup>, Mónika Molnár<sup>a</sup>, Emese Vágó<sup>b</sup>, Viktória Feigl<sup>a</sup>, Orsolya Klebercz<sup>a</sup>, Éva Ujaczki<sup>a</sup> and Katalin Gruiz<sup>a</sup>

Budapest University of Technology and Economics,  
Department of Applied Biotechnology and Food Science<sup>a</sup>,  
Department of Chemical and Environmental Process Engineering<sup>b</sup>  
Budapest, HUNGARY;

Phone: +36-14632347 e-mail: [mtolner@mail.bme.hu](mailto:mtolner@mail.bme.hu), [gruiz@mail.bme.hu](mailto:gruiz@mail.bme.hu)

#### Abstract

Preliminary site assessment, characterization and monitoring of soil contamination require fast, cost-efficient and reliable *in situ* and/or *on site metal* analyses methods. The field portable X-ray fluorescence device (FP-XRF) is a viable and effective analytical tool that meets the above demands. The FP-XRF is easy to use and it provides rapid, nondestructive multi-element assessment. For this reason the FP-XRF has become a common analytical technique for *on site* screening.

FP-XRF analysis can be sensitive to physical and chemical matrix effects, spectral interferences, measurement time as well as sample preparation leading to decreased precision and accuracy.

In connection with this topic our research activity aimed at studying the effects of different sample preparation methods and measurement conditions.

We determined the toxic metals concentration of mine waste and mine waste contaminated agricultural soil, of red mud and red mud contaminated soil using the FP-XRF. The effects of the moisture content, particle size distribution and homogeneity of soil samples as well as of the measurement time were investigated. In addition to the FP XRF measurements the As, Ba, Cu, Cr, Ni, Pb and Zn concentration of the samples was determined also by inductively coupled plasma atomic emission spectroscopy (ICP-AES) after Aqua Regia digestion.

One of the most important conclusions of the research is that the soil moisture and the measurement time considerably affect analytical performance. We demonstrated that sample preparation has also slight effects on the mean value of the results. The importance of the independent measurement methods has been emphasized to ensure precise correction of the field values.

#### Keywords

FP-XRF, metal, soil, metal contaminated soil, on site analyses

#### 1. Introduction

The XRF technique is a non-destructive technique which can save costs owing to its rapidity and ability to analyse solid environmental samples *in situ /on site*. Kalnicky and Singhvi (2001) showed that FP-XRF instruments provide an effective analytical approach for many types of environmental samples such as metal contaminated soils and sediments. The information collected *in situ* or *on site* make the decision making process and contaminated land management environmentally and economically more efficient compared to traditional laboratory analyses.

Using the portable device for preliminary assessment, source, hot-spot and transport route identification as well as delineation of metal-contaminated areas the risk manager is able to take *in situ* decisions on the modification of the assessment plan and monitoring concept, to check whether the samples taken for laboratory analyses or microcosm tests represent the hot spots or the average of a certain site, or whether the removal, treatment or other costly manipulations are done at the right place. All these uses significantly decrease the uncertainty of site characterisation, site specific risk

assessment and contaminated site management. Higuera *et al* (2012) showed that FP-XRF instruments can perform well in environmental surveys for heavy metal pollution in large mining districts. They have also rendered new and updated information regarding FP-XRF versatility to operate under both field and laboratory conditions depending on what is required from a time-efficient viewpoint.

The FP-XRF has gained a widespread acceptance nowadays therefore increasing citations are available on application and validation of this field portable device.

Kilbride *et al* (2006) investigated dual isotope and the X-ray tube FP-XRF instruments and they found that the FP-XRF analyser performance improved with the increase of the analysis time for Cu, Mn and Pb, whilst Fe, Zn, Cd, Ni and As showed no significant improvement. The particle size did not influence FPXRF analyser performance. Parsons *et al* (2012) investigated As polluted soil samples, their study shows that one of the most important sources of error in quantitative FP-XRF analysis of fine soils is the presence of interstitial water which has been underestimated in previous studies. Peinaldo *et al* (2012) found the FP-XRF is a useful tool for the determination of trace element concentrations in the field. They demonstrated that the main mechanism of trace elements dispersion in soils was due to water and wind erosion.

The main objective of our study was to characterise the measurement uncertainties of the portable XRF device. The measurement results of conventional laboratory analyses were compared with those of the portable XRF function of testing time and various environmental conditions, such as, moisture content, particle size distribution and heterogeneity of the tested samples.

The results of XRF measurements were compared to the results of chemical analysis done by ICP-AES on Aqua Regia extracts in case of mine waste contaminated agricultural soil.

## **2. Materials and methods**

### **2.1. FP-XRF theory and instrumentation**

*In situ* FP-XRF analysis can be a cost-effective near-real-time method to increase sampling densities due to the simplicity of the sample preparation. It is easy to operate, light in weight (Sarkadi *et al.*, 2009). The field portable X-ray fluorescence device (FP-XRF) developed for multi-elemental analyses was applied to simultaneously measure metals and semi metals in soils or other solid media without extracting metals from the samples.

The Thermo Scientific Niton XL3t 600S Analyser was used for the measurements. The analyzer is equipped with a 50 kV miniature X-ray tube and multiple primary filters (Thermo Fisher Scientific Inc. 2008). The Thermo Scientific Niton XL3t x-ray fluorescence (XRF) field portable analyzer combines proprietary electronics with an ergonomic design and easy-to-use software, transforming XRF analysis.

The FP-XRF measuring device provides *ex situ*, in the field prepared-sample analysis with an accuracy challenging that of standard laboratory analysis. The FP-XRF analyzers can be used directly on the soil surface, for *in situ* soil analysis this is the ideal way to quickly delineate the boundaries of contamination. Placing samples in plastic bags roughly homogenizes the sample for semi-quantitative results, while drying, grinding and sifting the sample provides a more uniform composition, making quantitative analysis possible. These techniques comply with US EPA Method 6200 for site characterization, on-site clearance screening, soil stabilization and remediation quality control (Thermo Fisher Scientific Inc. 2008).

Limits of detection are dependent on the elements, testing time, soil type, matrix and interelement interferences.

## **2.2. Soil samples**

Four different environmental samples (MS, MW, RMS, RM) were analysed and characterized function of sample preparation method and morphology.

- MS is a metal polluted soil sample from the agricultural area of the Gyöngyösorszi toxic metal polluted site, in the Toka watershed (North-East Hungary) (Tolner et al., 2008). It contains eroded solid material from mining waste and country rock delivered by the Toka creek reaching the hobby gardens along the creek during flooding.(Tolner et al., 2010)
- MW (mine waste material) derives from mine waste heaps left over in the forest at the foot of the Mátra hills in North-East Hungary further to the former mining activity. In addition to the mine waste material, flotation tailings, and precipitates from acid mine drainage treatment were disposed of concentrated or diffusely in the Gyöngyösorszi area. (Gruiz et al., 2007)
- RMS is a red mud polluted soil sample deriving from the red mud flooded area of the Marcal river catchment, in western Hungary The sample was taken following the accidental spill of the bauxite processing residue (red mud) in Ajka.
- RM is a red mud sample taken following the accidental spill of bauxite processing residue (red mud) in Ajka (Hungary). (Klebercz et al., 2012)

## **2.3. Sample preparation**

Results of two sample preparation procedures were compared.

### **2.3.1. Simplified sample preparation procedure**

Soil and waste samples were collected and air dried. Large rock pieces, organic matters such as leaves, twigs, grass or debris were removed. 10 g sample was placed into the X-ray sample cup without grinding and sieving.

### **2.3.2. Thorough sample preparation procedure**

Samples were collected and air dried. Large rock pieces, organic matters or debris were removed, the soil samples were ground, and sieved (2-mm sieve) according to Hungarian Standard 21470- 50:2006. 5–10 g homogenous sample was placed into the X-ray sample cup. The cup was kicked lightly against the table top to pack the soil evenly and analyzed with the FP-XRF (Bernick et al., 1995).

## **2.4. Soil sample preparation by adjusting moisture content**

To study the effect of soil moisture on FP-XRF measurements, a series of soils of 6 different moisture contents were analysed. Variation on water content was achieved by drying and grinding the soils and adding variable quantities of water. We added different amount of distilled water to the prepared, homogenised, air dried samples to achieve the 5, 10, 15, 20 and 25 weight percent moisture content.

## **2.5. Measurement time**

To establish the effect of the measurement time on precision and accuracy all samples were measured for 45, 90, 180 and 225 sec, meaning 15, 30, 45, 60, 75 sec/filter. FP-XRF device has 3 filters: low, medium and high. Each filter measures different elements of the sample.

## **2.6. Sample amount**

To determine the effect of sample size (the critical penetration depth in soils) different sample amounts were measured. 5 and 10 g of the prepared sample was placed into an X-ray sample cup and 40 g prepared sample was placed into a 4\*6 cm plastic bag. Bagged and cupped sample measurement results were compared.

### 3. Aqua Regia extractable metal contents

The metal contents of soil samples was measured by MTA TAKI after Aqua Regia digestion (3:1 hydrochloric acid–nitric acid ratio; 1:4 soil extractant ratio; 2 h at 25°C; microwave digestion) (HS 21470-50:2006). The metal content of the extracts was determined with inductively coupled plasma atomic emission spectroscopy (ICP-AES) using an Ultima 2 (HORIBA Jobin Yvon, France) (HS 21470-50:2006).

### 4. Results

The standard deviation of the performed XRF measurements and of the measurement errors was estimated for four various samples (mine waste and mine waste contaminated agricultural soil, red mud and red mud contaminated soil) and in case of the detected metals.

The effect of the moisture content, heterogeneity and grain-size distribution on the resulted standard deviation was examined and compared. The results of measurements performed on samples prepared by the simplified method were compared with the results of the measurements performed on the thoroughly prepared samples (after drying and grinding). The standard deviation of the measurements was determined on the toxic metal containing samples both in case of simplified and thoroughly prepared samples. Variation of the investigated metals (As, Fe, Pb, Zn) in all toxic metal contaminated samples was measured under “on site” conditions at various soil moisture contents. The Scatterplots and Mean Plots were visualised using STATISTICA® 11.0 Software.

#### 4.1. Effect of soil moisture content

Figure 1 shows the Zn concentration and Zn error of the metal polluted agricultural soil (MS) against moisture content.

Our results show that the water content has an important effect on the measured values. The increasing water content resulted in exponential decrease of the measured concentration and of the recorded error for all elements. This is presumably due to the increased density of samples and to the replacement of air by water in the soil pores. This replacement may increase the photoelectric absorption.

Thus where the soil water content varies significantly between the samples we recommend to apply soil moisture effect correction.

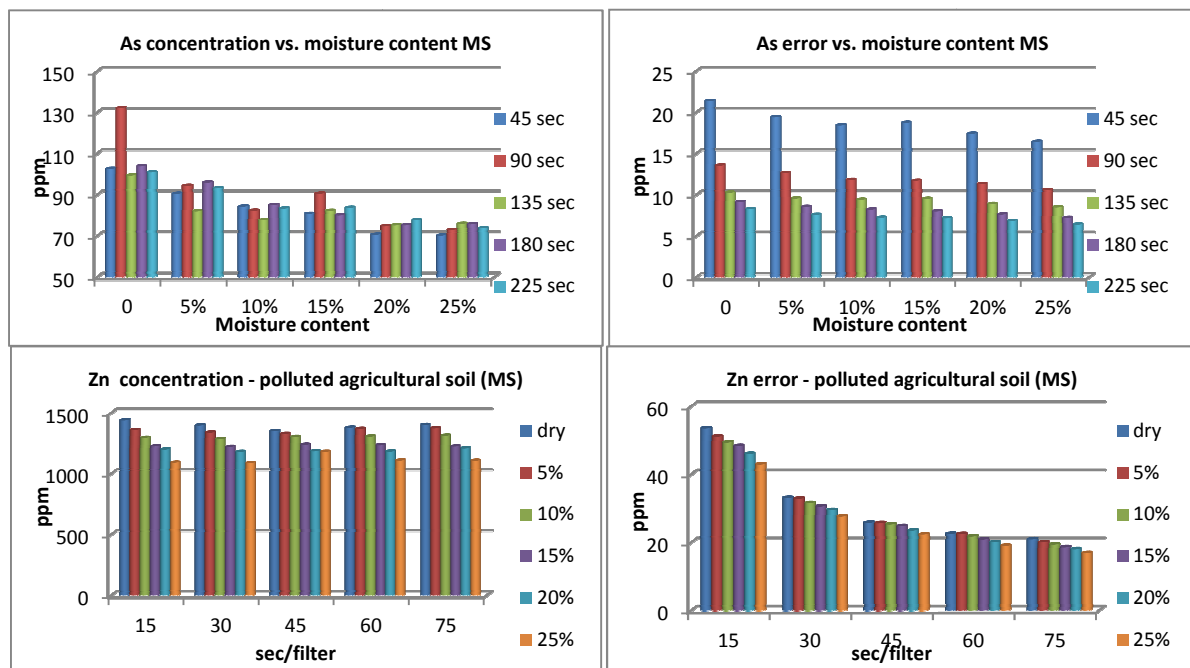
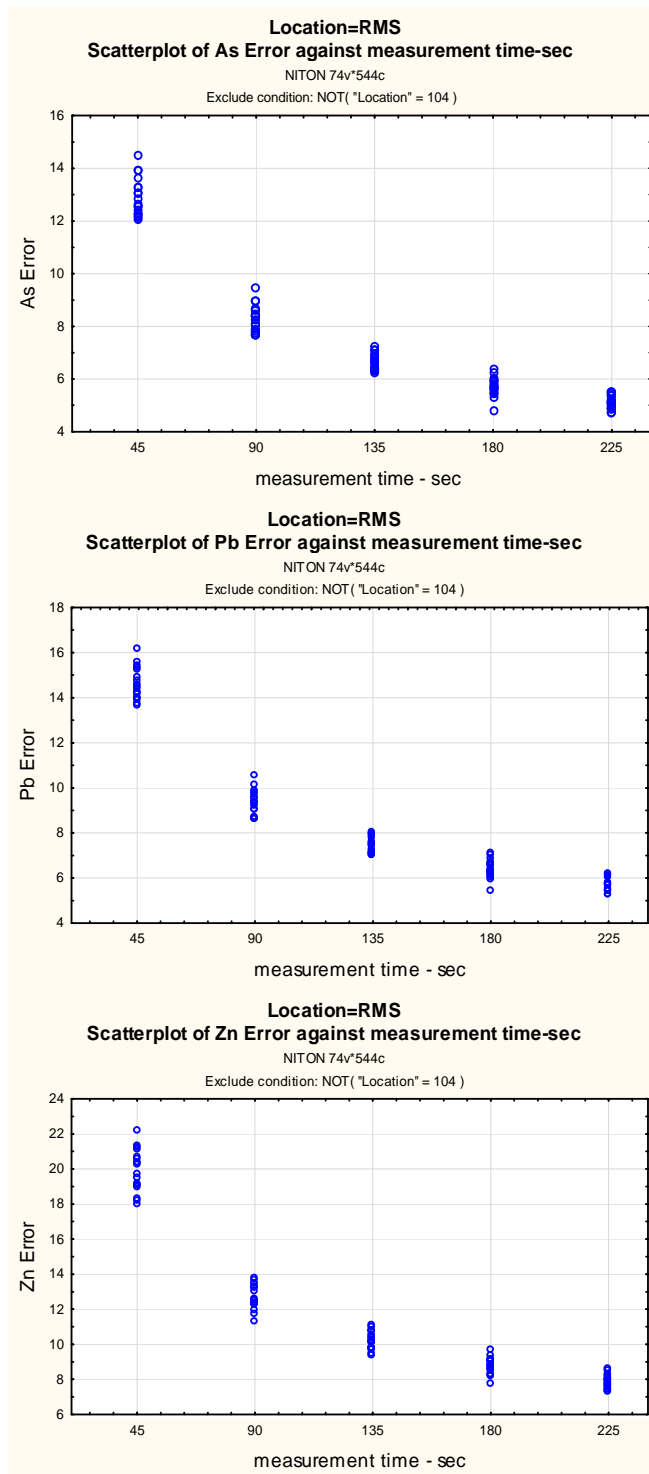


Figure 1. As and Zn concentrations, As and Zn errors of metal polluted agricultural soil against moisture content.

## 4.2. Effect of measurement time



**Figure 2.** As error, Pb error and Zn error of red mud polluted soil against measurement time

Determination of the optimal measurement time is also important because during field analyses (on site assessment) precision and time are often equally valuable.

“Metal error” %-s was plotted against the measurement time in case of red mud polluted soil sample (RMS) (Figure 2).

Increasing measurement time in most cases led to non-linear decrease in error values. In the case of Ag we didn't find any time-dependency of the measurement. The observed trends were similar for all of the investigated environmental samples. Figure 2 shows the decreasing values of As, Pb and Zn errors measured in the case of the RMS sample.

According to our experimental data the optimal measurement time is usually not dependant on the investigated element and the actual concentration. A suitable compromise between measurement time and precision of metal concentration can be 135 sec (45 sec/filter).

### 4.3. Effect of sample preparation

Results show that the sample-preparation had slight effect on the quality of XRF data. Measured metal concentrations of thoroughly prepared samples are usually lower than of the samples prepared by the simplified preparation method (Figure 3.).

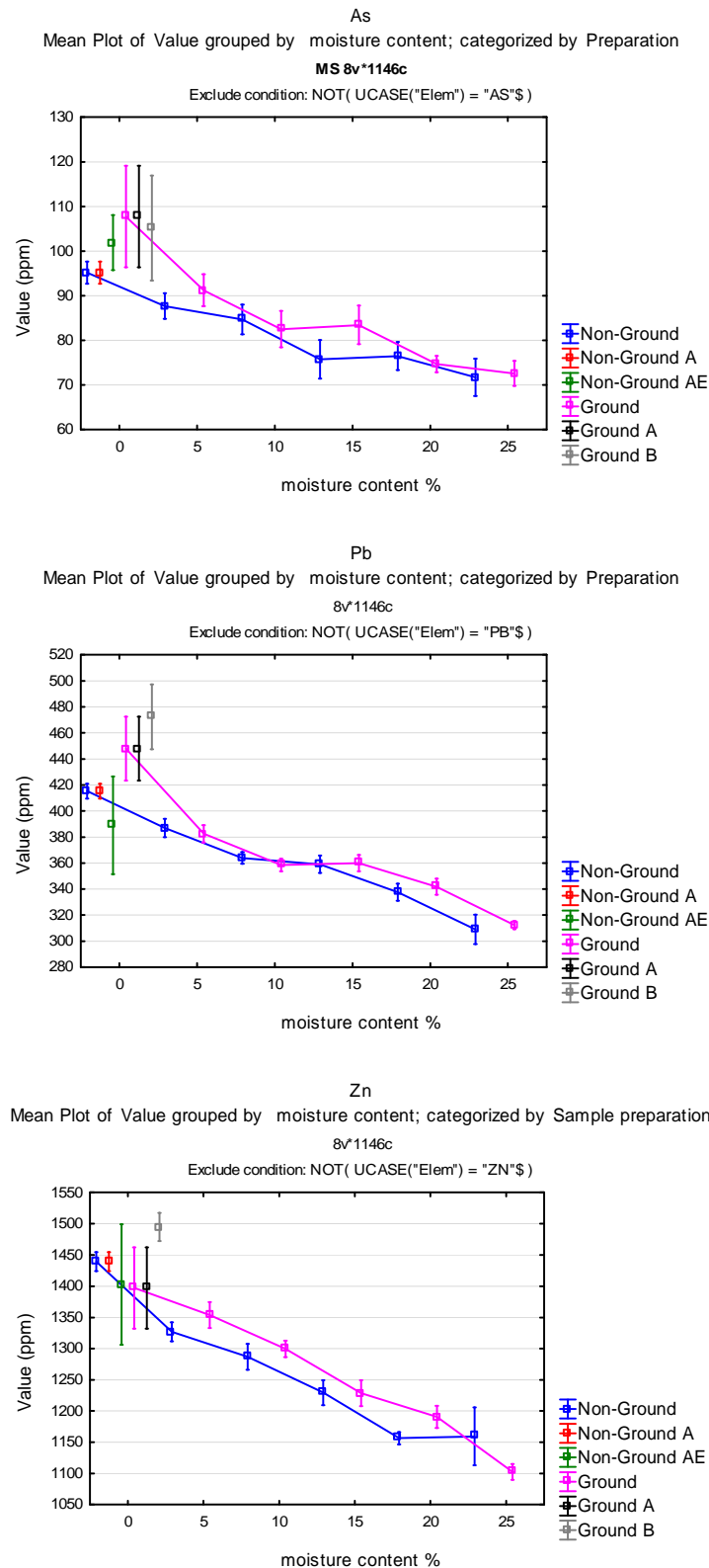
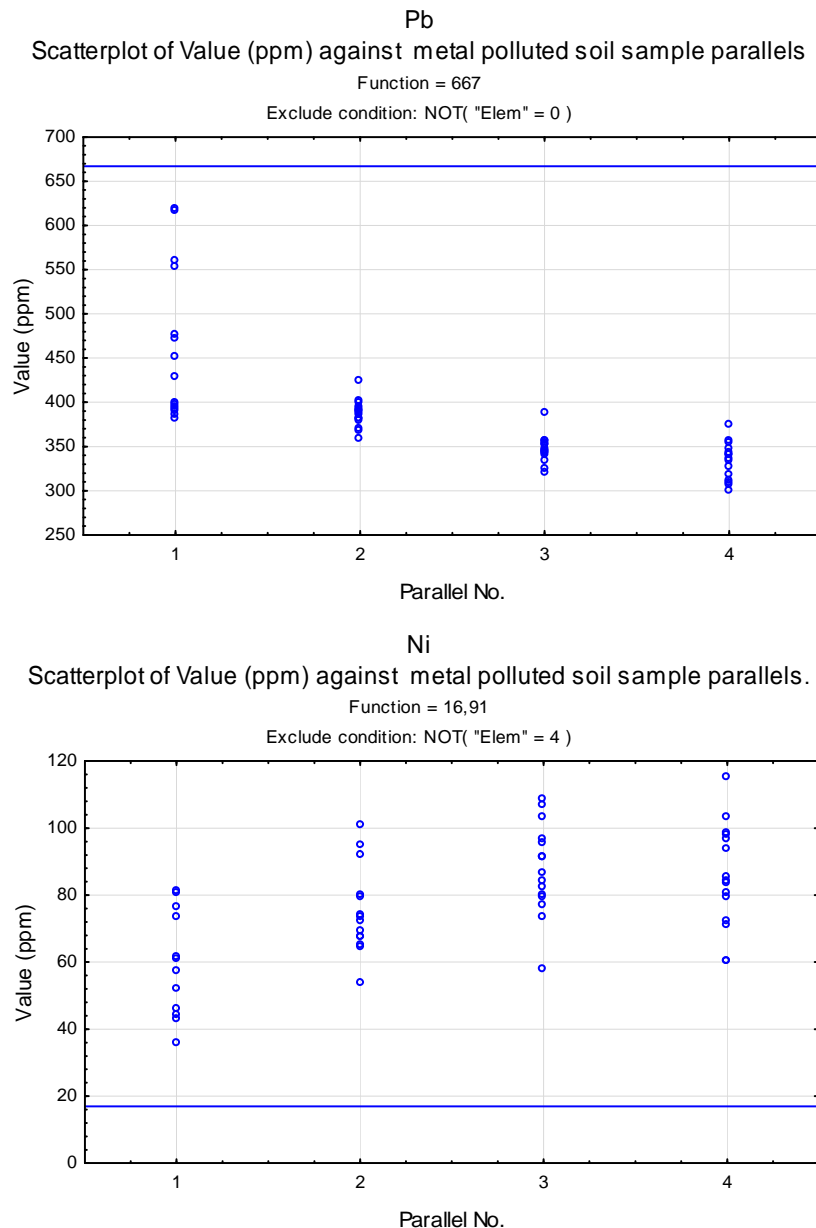


Figure 3. Effects of sample preparation in case of metal polluted agricultural soil

#### 4.4. Validation measurements

We compared by statistical analyses the results of FP-XRF measurements with the results of chemical analysis done by ICP-AES on Aqua Regia extracts. The scatterplots present the result in case of dried and sieved metal polluted agricultural soil (MS). Four parallel soil samples were taken and measured 3 times in parallel at different measurement times. We found that the FP-XRF underestimated the Pb, Cu and Zn concentrations, while in the case of Ni higher values were measured by FP-XRF than by ICP-AES on Aqua Regia extracts.

The measured As and Cd contents (not shown here) were similar with both measuring methods (Fig. 4). This confirms the need for cross-validation with an alternative technique such as ICP-AES.



**Figure 4.** As and Pb concentrations changes in parallel metal polluted soil samples compared with results done by ICP-AES on Aqua Regia extracts

## 5. Conclusion

FP-XRF can be a rapid and appropriate analytical support to analyze environmental samples in a timely fashion. The simultaneous analysis of multiple elements saves time and money over traditional, laboratory techniques.

However this study demonstrated that the effects of different sample preparation methods and measurement conditions should be investigated and corrected, because soil moisture and measurement time have a significant impact on the accuracy of FP-XRF analysis.

This study shows that one of the most important sources of error in quantitative FP-XRF analysis of environmental samples is the variable soil moisture content. Drying of all soils may be an acceptable alternative to eliminate the errors connected with different soil water contents.

Our experimental results proved the importance of cross-validation with an alternative technique such as ICP-AES.

## References

Bernick, M. B., Getty D, Prince G. and Sprenger, M.: Statistical evaluation of field-portable X-ray fluorescence soil preparation methods In: *Journal of Hazardous Materials* 43. pp. 111-116, Published by Elsevier Science B.V. 1995

Bernick M.B., Kalnicky D.J., Prince G. and Singhvi R.: Results of field-portable X-ray fluorescence analysis of metal contaminants in soil and sediment In: *Journal of Hazardous Materials* 43. pp. 101-110, Published by Elsevier Science B.V. 1995

Feigl, V.; Atkári, Á., Anton, A. and Gruiz, K.: Chemical stabilisation combined with phytostabilisation applied to mine waste contaminated soil in Hungary. – In: *Advanced Materials Research Vols. 20–21*, pp. 315–318, Trans Tech Publications, Switzerland 2007

Gruiz, K.; Vaszita, E. and Siki, Z.: Tiered risk assessment of point and diffuse pollution source of mining origin, – In: *Summaries of Interventions of the Difpolmine Conference, 12–14 December, 2006*, Montpellier, France, 2006

Gruiz, K., Vaszita, E., Siki, Z. and Feigl, V.: Environmental risk management of an abandoned mining site in Hungary – In: *Advanced Materials Research Vols. 20–21*, Trans Tech Publications, Switzerland, pp. 221–225, 2007

Higuera, P., Oyarzun, R., Iraizoz, J.M., Lorenzo, S., Esbrí, J.M., Martínez-Coronado, A.: Low-cost geochemical surveys for environmental studies in developing countries: Testing a field portable XRF instrument under quasi-realistic conditions In: *Journal of Geochemical Exploration* 113 3–12, Elsevier B.V. 2012

Kalniczy, D. J. and Singhvi, R.: Field portable XRF analysis of environmental samples. In: *Journal of Hazardous Materials* 83 pp. 93-122, Published by Elsevier Science B. V. 2001

Kilbride, C., Poole, J., and Hutchings, T.R.: A comparison of Cu, Pb, As, Cd, Zn, Fe, Ni and Mn determined by acid extraction/ICP–OES and ex situ field portable X-ray fluorescence analyses In: *Environmental Pollution Volume 143*, Issue 1, pp 16–23, 2006

Klebercz, O., Mayes, W. M., Anton, Á., D., Feigl, V., Jarvis, A. P., Gruiz, K.: Ecotoxicity of fluvial sediments downstream of the Ajka red mud spill, Hungary In: *Journal of Environmental Monitoring*, 14 (8), 2063-71, 2012

United States Environmental Protection Agency: Field Portable X-RAY Fluorescence Spectrometry for the determination of elemental concentrations in soil and sediment Method 6200 2007

Parsons, C., Margui Grabulosa, E., Pili, E., Floor, G. H., Roman-Ross, G., Charlet L.: Quantification of trace arsenic in soils by field-portable X-ray fluorescence spectrometry: Considerations for sample preparation and measurement conditions In: *Journal of Hazardous Materials*, Published by Elsevier Science B. V. 2012 In Press

Peinado, F.M., Morales Ruano, S., Bagur González M.G., Estepa Molina C.: A rapid field procedure for screening trace elements in polluted soil using portable X-ray fluorescence (PXRF) In: *Geoderma* 159 pp.76–82 Published by Elsevier Science B. V. 2010



Sarkadi, A; Vaszita E.; Tolner M. and Gruiz K.: In situ site assessment: a short overview and description of the field-portable XRF and its application. In: Land Contamination & Reclamation, 17 (3-4) pp 431-442, EPP Publications Ltd. 2009

Thermo Fisher Scientific Inc.: On-site Screening of Environmental Contaminants N3 6-301 05/2008

Tolner, M., Nagy, G., Vaszita, E., and Gruiz, K.: In situ delineation of point sources and high resolution mapping of polluted sites by X-ray fluorescence field –portable handheld device. In: R. Sarsby (ed.), *Paper Abstracts, Green5 Conference 'Construction for a sustainable Environment'* 1-4 July 2008, Vilnius, Lithuania, p.35

Tolner, M.;Vaszita, E., Gruiz, K.: On-site screening and monitoring of pollution by a field-portable X-ray fluorescence measuring device ConSoil 2010 Conference, Salzburg, Austria 22-24 September 2010

#### **ACKNOWLEDGEMENT**

*The financial support of Hungarian Research & Development Program (TECH\_09-A4-2009-0129, SOILUTIL project and NKFP-3/020/2005 MOKKA project) is greatly acknowledged.*