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

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Introduction

Fast, efficient and reliable *in situ* and/or on site metal analyses methods are required for preliminary site assessment, for characterization and monitoring of soil contamination. This study provides a comparative statistical evaluation of the As, Ba, Cu, Cr, Ni, Pb and Zn concentrations of a series of samples measured both by a Thermo Scientific Niton XL3t 600S field portable X-ray fluorescence Analyser (FP-XRF) and by traditional analytical methods after Aqua Regia digestion, using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

We determined the toxic metal concentration of mine waste and mine waste contaminated agricultural soil, red mud and red mud contaminated soil. The effect of moisture content, particle size distribution and homogeneity of soil samples as well as the measuring time were evaluated.

Analysed samples

Four different samples were analysed and compared versus the measuring time and moisture content.

- **MS** is a metal polluted soil sample from the toxic metal polluted area of Gyöngyösoroszi, Toka watershed (North-East Hungary). The eroded solid material from mine waste and country rock was delivered downstream by the Toka creek reaching an agricultural area.
- **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.
- **RMS** is a red mud polluted soil sample from the Marcal river catchment, red mud flooded area in western Hungary the. The sample was taken following the accidental spill of 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).

Sample preparation

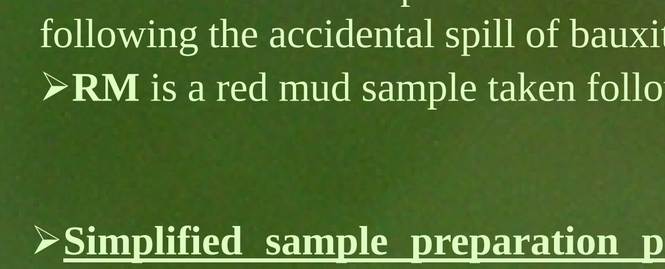
- **Simplified sample preparation procedure** Soil and waste samples were collected and air dried. Large rocks, organic matters such as leaves, twigs, grass or debris were removed. 10 g sample was placed into the X-ray sample cup without grinding and sieving.
- **Thorough sample preparation procedure** Samples were collected and air dried. Large rocks, organic matters or debris were removed, ground, and sieved (2-mm sieve) (Hungarian Standard 21470 50:2006).
- Each sample was analysed after wetting the soil at 6 different moisture contents (air dried and 5-25 w%).
- To establish the effect of measurement time on precision and accuracy all samples were measured for 45, 90, 180 and 225 secs (15, 30, 45, 60, 75 sec/filter).

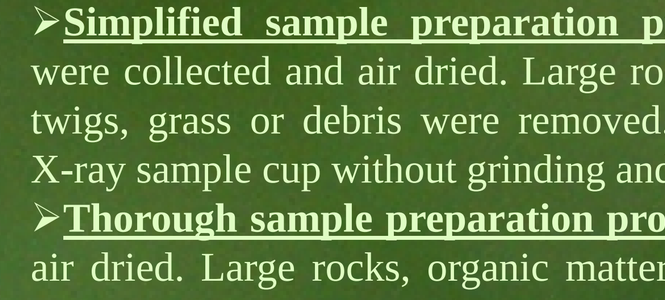
Results

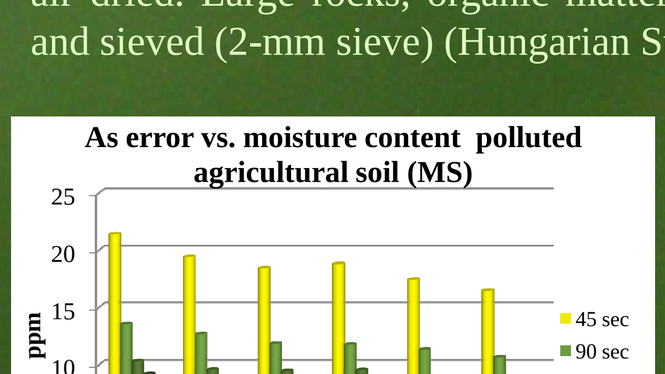
Effect of soil moisture content The increasing water content resulted in exponential decrease in measured concentration and recorded error for all elements. It is due to presumably the increased density of samples and the replacement of air with water in soil pores. This replacement may increase the photoelectric absorption.

Effect of measurement time Increasing measurement time in most cases led to non-linear decrease in error values. In the case of Ag we didn't found any measurement time-dependency. The observed trends were similar for all of investigated environmental samples.

Effect of sample preparation Results show that the sample-preparation had slight effect on the quality of XRF data. Measured metal concentrations in thoroughly prepared samples are usually lower than following simplified preparation .







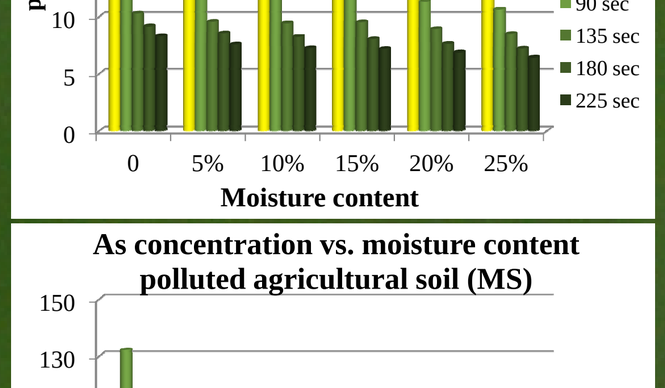
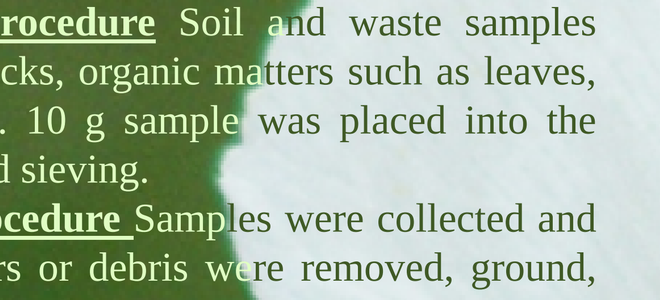
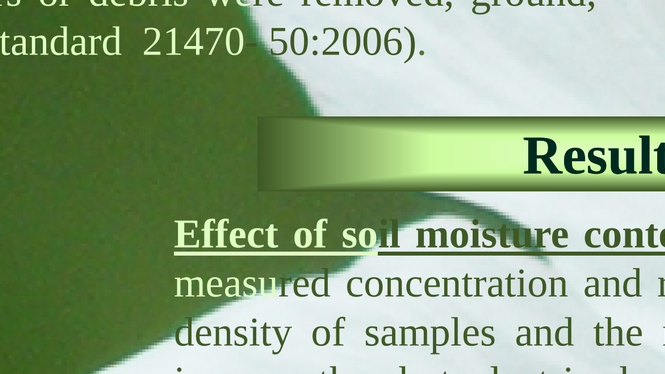


Fig. 1. As and Zn concentrations, As and Zn errors of metal polluted agricultural soil against moisture content.





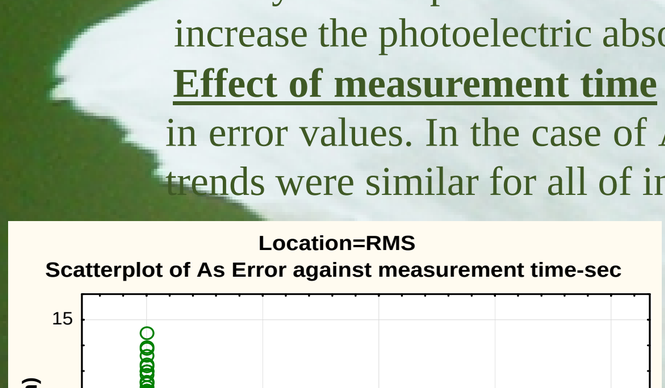


Fig. 2. As error, Pb error and Zn error of red mud polluted soil against measurement time

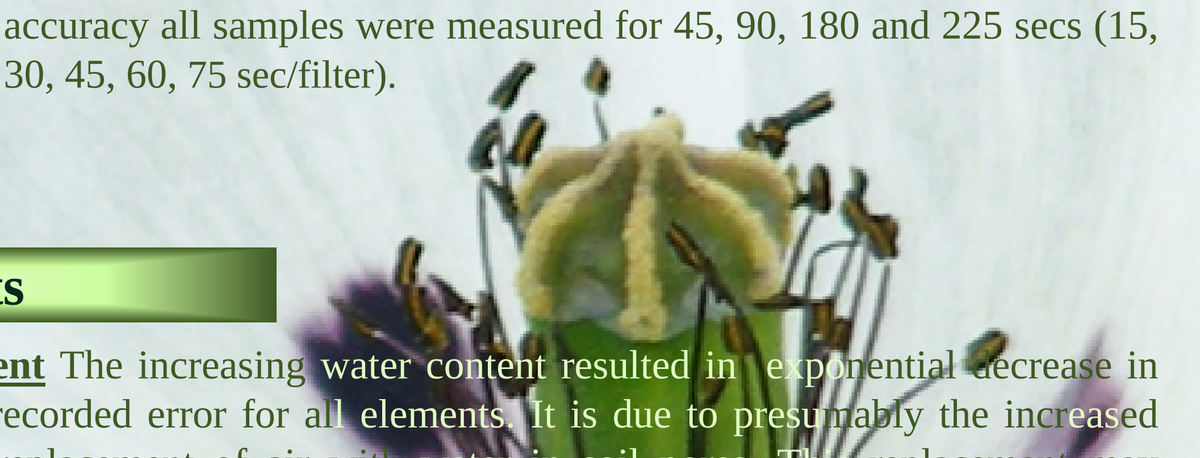


Fig.3. Effects of sample preparation in case of metal polluted agricultural soil

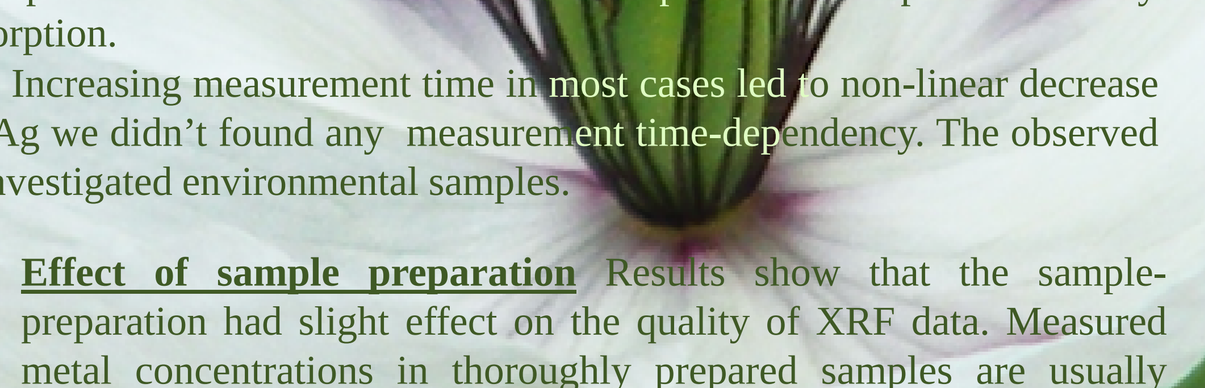


Fig. 4. As and Pb concentration changes in parallel metal polluted soil samples compared with results done by ICP-AES on Aqua Regia extracts

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 our preliminary 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 confirmed the importance of cross-validating the results with an alternative technique such as ICP-AES.

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