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# Rapid and Low Cost Determination of Heavy Metals in Soil Using an X-Ray Fluorescence Portable Instrument. I. Preliminary Tests

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## Abstract

*The paper presents the results of preliminary test in lead, copper and zinc determination in contaminated soil samples using an X-ray fluorescence portable instrument. From this preliminary work is evident that portable instrument could be used for the determination of these heavy metals in contaminated soil samples, the correlation factors with laboratory analysis being : 0.82, 1.19 and 1,00, respectively. The analysis time (using XRF instrument) practically do not affect the determination of lead and zinc, but it influence copper determination, especially when small concentration of copper must be determined.*

**Key words:** soil contamination, heavy metals, portable XRF

## Introduction

Soil provides us with food, biomass and raw materials. Unfortunately, soil is subjected to a series of degradation processes or threats. These include erosion, decline in organic matter, local and diffuse contamination, sealing, compaction, and decline in biodiversity, salinisation, floods and landslides. A combination of some of these threats can ultimately lead to desertification under arid or sub – arid climatic conditions [1].

Contaminated soils present a major global health problem especially in urban areas with dense population. Heavy metals are common contaminants and understanding their behavior in soil is central to our ability to predict the extent of their environmental hazard.

In the framework of risk assessment studies and follow – up remediation projects, is necessary to perform numerous analyses for the determination of these metals concentration.

Environmental remediation often includes the removal of metal contamination from surface and removal of metal – contaminated soils, sludge and sediments.

Generally, defining the scope and developing a work plan and methods for decontaminating surfaces or defining the volume of soil and other material to be removed is dependent on the results of laboratory analysis of samples collected in the field. The laboratory analyses have to

be carried out according to the prescribed reference method by inductively coupled plasma – atomic emission spectrometry (ICP – AES) or atomic absorption spectrometry (AAS), proceeded by time – consuming acid digestions which are subject to possible contamination; these analysis can be expensive and may take – up to a week to complete, increasing the time required to complete a remediation project [2-4].

XRF (X-ray fluorescence) technology can be used to screen for metal contamination on surface and in soil, minimizing the need for laboratory analysis of samples. This method can offer significant advantages over laboratory method, provided they are significantly accurate and well – documented to support field decision making. It is frequently less expensive per sample than laboratory analysis because of less need for sample, handling, transportation and chain – for – custody documentation.

In addition, it provide timely support for field decision – making and greatly reduce overall project cost.

Field – portable X-ray fluorescence (XRF) is an exemplary method, offering extremely rapid, cost – effective screening of heavy metals in soil by in – situ (in field) measurements or in ex – situ soil sample. It is also versatile enough to provide ex – situ, prepared – sample analysis in the field with accuracy that can rival that of standard laboratory analysis. Even in the cases where laboratory analysis is required, portable XRF can be used rapidly pre – screened samples (directly through the plastic sample bag) to obtain the optimal utility from the laboratory sampling effort.

Since XRF is completely non destructive, any sample collected and measured in field can be retained for verification by a laboratory [5].

The principle behind this process is simple: when an X – ray emission from a radioactive source strikes a sample, the X – ray can either be absorbed by atoms or scattered through the material. If absorbed the atoms become “excited” and will then give off a characteristic X – ray whose energy level is unique to the element impacted by the incident X – ray. The emission of these characteristic X – rays is called X – ray fluorescence, or XRF. Measurement of the discrete energy of the X – rays emitted is used to identify the metals species present. Measurement of the number of emitted X – rays provides a quantitative indication of the concentration of the metal present.

Each of the atomic elements present in a sample produces a unique set of characteristic X – rays that is a fingerprint for that specific element.

Different metals in soil can be measured quickly and non – destructively using an XRF instrument.

The new generation of field portable XRF instruments is equipped with miniature X – ray tubes in order to reduce the regulatory demands encountered with radioactive isotopes.

Field portable XRF instruments have real potential for [6]:

- quickly and effectively determining soil metal and metalloid concentration on the laboratory or field;
- producing a contaminant profile for a site;
- delineating contaminant “ hot spot”;
- evaluating the effects of remediation.

The goals of this preliminary experiment were:

- to verify the possibility to use the portable X-MET instrument for the determination of some heavy metals in contaminated soil samples;
- to observe the influence of time analysis upon the magnitude of the results;
- to find the correlation factors between the X-MET results and the laboratory analysis results.

## Principles and consideration

### XRF instrumentation

The X – MET 3000 TX XRF analyzer is manufactured by the Portable Division of Oxford Instruments Analytical Lmtd., Finland. The main characteristics of X-MET instrument are presented in table 1.

**Table 1.** Main characteristics of portable X-MET instrument

Characteristic	
Power supply	Two lithium ion – batteries of 220 AC power
Weight	1.8 kg
Data storage capacity	Up to 10 000 tests (64MB memory)
Sample chamber	1 sample
X – ray source	Mini X-ray tube
Detector	To convert X-ray emitted from the sample into measurable electronic signals
Data processing unit	Records the emission (fluorescence energy signals) and calculate the elemental concentrations in the sample
Measurement time	15...360 seconds

X – ray tube based sources offer a faster analytical time because the X – ray flux can be higher than most isotope based sources. They can also be used over a wider range of excitation energies, eliminating the need for multiple isotope sources to produce X – ray over the entire excitation spectrum [7].

### Laboratory analysis

Heavy metals contents of soil samples were determined in hydrochloric acid solution (0.5N) using an open-tube digestion method with acid mixture  $\text{HNO}_3\text{-HClO}_4\text{-H}_2\text{SO}_4$ .

For quality control three replicates of quality control material (LGCQC 3004) were included in batch of samples analyzed.

The F-AAS measurements (GBC Scientific Equipment Pty Ltd, Australia) were performed with an AVANTA 932 AA system.

As calibration standards, were used 5 multi-element solutions in hydrochloric acid solution (0.5N) containing lead, copper and zinc, using CertiPUR salts delivered by Merck.

## Results and discussion

### Sample collection and preparation

Soil samples were collected from an old metallurgical industrial area in Romania. The soil samples were air dried, at ambient temperature.

The samples were XRF measured to observe the effect of analyses time, than the samples were homogenized. The homogenized dried samples were ground with a mortar and pestle and passed through a 60 mesh sieve to achieve a uniform particle size.

The influence of time upon the magnitude of the results was determined directly on the dried samples, by measuring the heavy metal concentration with XRF instrument.

For the determination of correlation factors between laboratory analysis and XRF data, the homogenized and sieved samples were used. So, the samples were XRF measured and analyzed by AAS method. A broad concentration range exists for contaminants lead, copper and zinc; these data together with the Soil Guideline Value, in agreement with Romanian Legislation, are presented in table 2

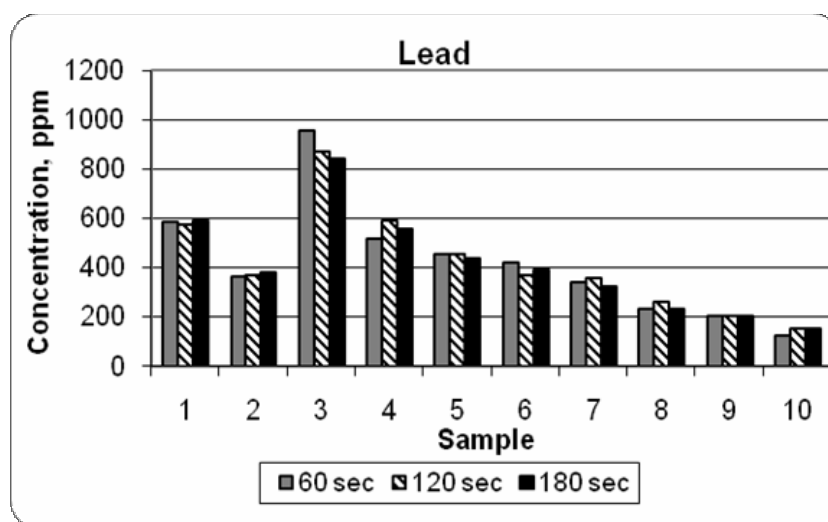
**Table 2.** Concentration range for lead, copper and zinc in contaminated soil samples determined by AAS method and the limit values predicted by Romanian Environment Protection Law (mg metal/kg soil).

Element	Metal concentration (AAS analyses), mg/kg soil		Limit of alert (Romanian legislation), mg/kg soil		
	Min.	Max	Normal	Sensible areas	Less sensible areas
Copper	55	283	20	100	250
Lead	115	786	20	50	250
Zinc	157	577	100	300	700

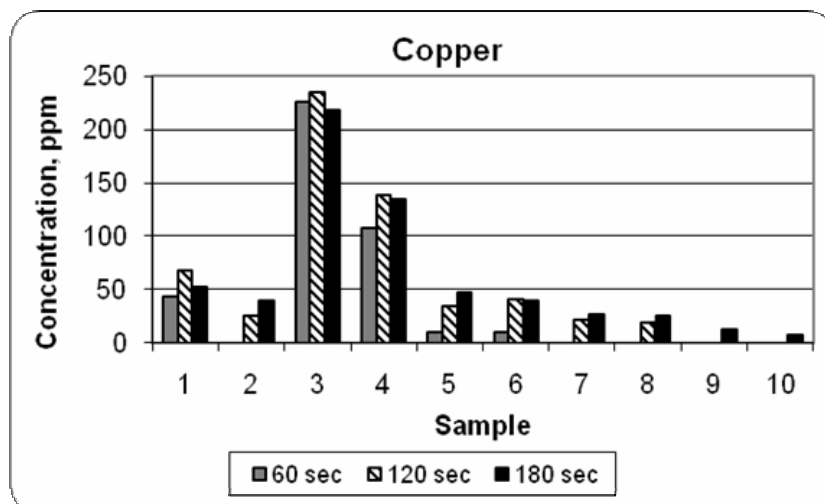
From table 2 is evident that the concentration of heavy metals in contaminated soil samples is higher than the prediction of Romanian legislation, even for less sensible areas (meaning non agricultural areas).

### Effect of Analysis Time

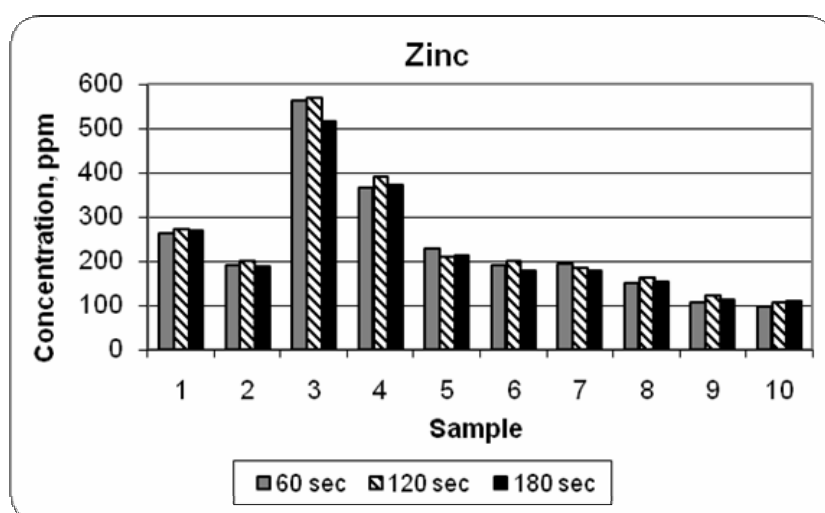
To observe the effect of analysis time upon the magnitude of the results, a set of 10 samples were analyzed for 60, 120 and 180 seconds, using X-MET instrument. The samples were only air dried. The results are presented in figures 1-3.



**Fig. 1.** Influence of analysis time upon the magnitude of the results in lead determination



**Fig. 2.** Influence of analysis time upon the magnitude of the results in copper determination



**Fig. 3.** Influence of analysis time upon the magnitude of the results in zinc determination

The following conclusions are evident from these graphs:

- the influence of analysis time do not affect practically the determination of lead and zinc;
- in copper determination, the time analysis of 60 seconds is not enough for copper determination, for concentration less than 50 ppm, 180 seconds for analysis time being necessary.

### The correlation factors determination

Linear regression analyses on the XRF data determined at 120 seconds analysis time compared with the results from aqua regia extraction analysis was used to evaluate the effect of count time. From linear regression analysis results the correlation factors between XRF data and laboratory analysis data. Figures 4, 5 and 6 present these data for lead, copper and zinc, respectively.

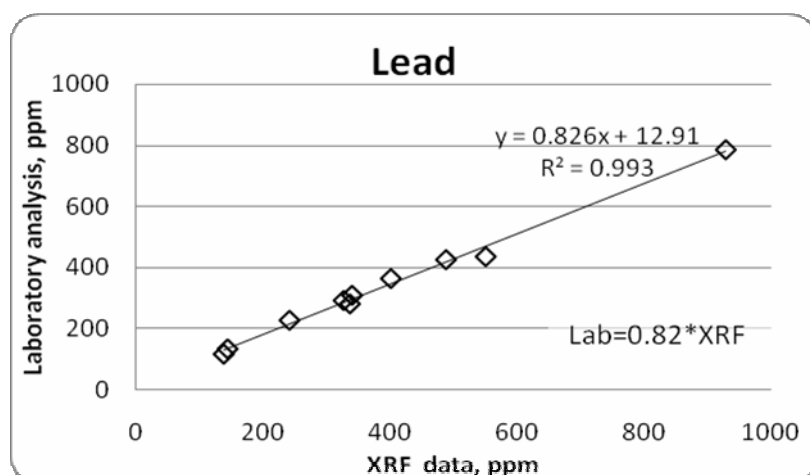


Fig. 4. Linear regression data for lead

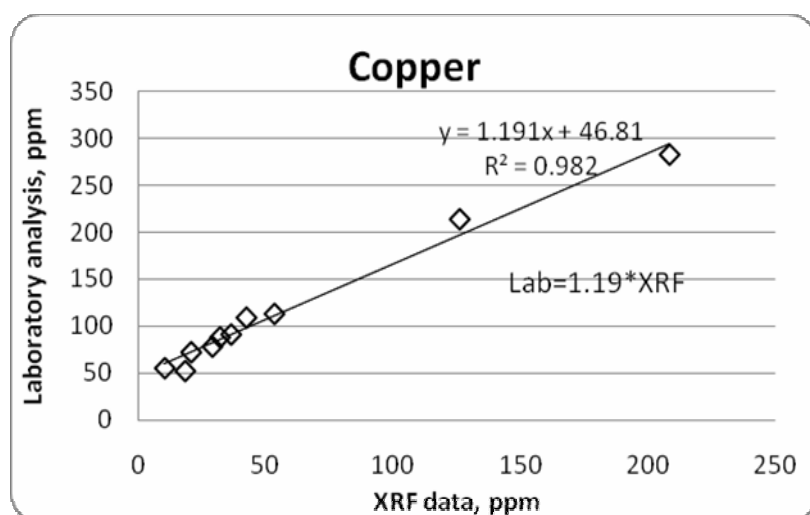


Fig. 5. Linear regression data for copper

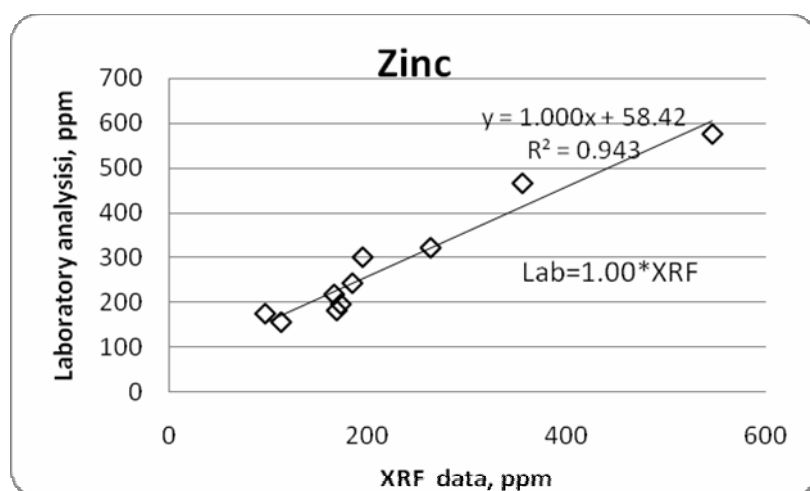


Fig. 6. Linear regression data for zinc

From these data, the correlation factor between laboratory analyses and XRF data for lead, copper and zinc were calculated and they are: 0.82, 1.19 and 1.00, respectively.

The correlation curves are used “to correct” future testing results from the site in question [8]. A comparison of the XRF results and laboratory results reveals a bias in the XRF data, in the case of lead and copper determination. The correlation factors determined showed that laboratory results are lower in the case of lead with 18%, higher in the case of copper with 19% and for zinc the results are similar.

## **Conclusions**

From this preliminary work is evident that portable instrument X-MET based on XRF techniques (a non destructive method) could be used for the determination of lead, copper and zinc from contaminated soil, the correlation factors with laboratory analyses being : 0.82, 1.19 and 1,00, respectively.

The analysis time practically do not affect the determination of lead and zinc, but it influence copper determination, especially when small concentration of copper must be determined.

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## Determinarea rapidă și ieftină a conținutului de metale grele din sol utilizând un instrument portabil de fluorescență de raze X. I. Teste preliminare

### Rezumat

*Lucrarea prezintă rezultatele preliminare obținute în măsurarea concentrației plumbului, cuprului și zincului din probe de sol poluat, folosind un instrument portabil bazat pe fluorescența de raze X.*

*Lucrările efectuate au evidențiat influența timpului de măsurare asupra mărimii rezultatelor în cazul determinării celor trei metale.*

*Au fost determinați factorii de corelare dintre rezultatele analizei de laborator și rezultatele XRF pentru plumb, cupru și zinc, valorile obținute fiind de 0.82, 1.19 și 1.00, respectiv.*