

## RAPID DETERMINATION OF SOME HEAVY METALS IN SOIL USING AN X-RAY FLUORESCENCE PORTABLE INSTRUMENT

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**Abstract.** Contaminated soils present a major global health problem especially in urban areas with dense population. The common contaminants of soil are heavy metals. Research investigating the risk assessment procedures adopted in different EU member states, suggests that there needs to be greater standardization in the methods of assessing risks from contaminated soils. For risk-assessment studies and follow-up remediation projects is necessary to perform numerous analyses to determine the concentration of metal contaminants. To minimize the need for laboratory analysis of soil samples, the XRF - technology can be used for screening the metal contamination in soil, with significant advantages. This method provided significant accuracy and well documented to support field decision making with reduced overall costs. The new generation of portable XRF instruments is equipped with miniatures X-ray tubes in order to reduce the regulatory demands encountered with radioactive isotopes. The goal of this experiment was to complete the data obtained in the preliminary tests, by observing the correlation between XRF results and laboratory analysis data in heavy metal determination. Soil samples were collected from an old metallurgical industrial area, situated in the vicinity of

Bucharest, Romania. The 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. The collected samples were XRF measured, then dried in air, XRF measured, sieved through the 2 mm sieve to remove non-soil particles and XRF measured again. The samples were homogenized and passed through the 200 microns sieve and XRF measured. After XRF determination, these fine samples were laboratory analyzed (XRF analysis being nondestructive). The XRF results are presented comparatively with laboratory analysis data. From these results is evident that the soil particle size have no important influence upon the XRF data, an important factor appears to be the metal concentration in soil. The results confirm the influence of metal concentration in soil upon the XRF data, smaller is metal concentration in soil sample, higher are the difference between XRF and laboratory analysis results. In all samples laboratory results are many times smaller than XRF data, in chromium and cobalt determination. Best correlation was obtained in lead and manganese determination.

**Key words:** heavy metals, soil, portable X-ray fluorescence instrument

### INTRODUCTION

Soil plays an important role, as a habitat capable of recycling water, carbon and nutrients and a provider of food and raw materials. The same time, soils are vulnerable; the largest disruption and destruction is caused by humans.

Research investigating the risk assessment procedures adopted in different EU member states, suggests that there needs to be greater standardization in the methods of assessing risks from contaminated soils [1].

In 2005, the European Commission Joint Research Centre (JRC) initiated a long - term research network to promote the development of common risk assessment tools for contaminated land in Europe.

In the framework of risk assessment studies and follow - up remediation projects, is necessary to perform numerous laboratory analysis for the determination of metal concentration in soil.

Field methods can offer significant advantages over laboratory methods, provided they are sufficiently accurate and well documented to support field decision - making [2].

The prescribed reference methods for heavy metals determination in soil are: inductively coupled plasma - atomic emission spectrometry (ICP-AES) or atomic absorption spectrometry (AAS), characterized by time - consuming acid digestions, the high analysis costs and they may take a week to complete [3-5].

Field portable X-ray fluorescence (XRF) continues to gain acceptance as a complement to traditional laboratory testing of metal contaminated soil. This analysis is less expensive than laboratory analysis being non time and reagents consumer. It reduces the overall cost of remediation project.

Field portable XRF offer the rapid and efficient screening of heavy metals in soil by *in - situ* measurements, being also versatile to provide *ex-situ*, prepared - sample analysis. Since XRF method is completely non-destructive, the samples collected and measured in the field can be laboratory analyzed.

The principle of X-ray fluorescence 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. After absorption the atoms becomes “excited” and 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-ray 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-ray provides a quantitative indication of the concentration of the metal present in sample.

We have to emphasize that 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 [2].

The new generation of portable XRF instruments is equipped with miniatures 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 determination of metals and metalloids concentration in soil, in laboratory or in field;
- producing a contaminant profile for a site;
- delineating contaminant “hot spot”;
- evaluating the effect of remediation.

The objective of this work was to compare the XRF data with the laboratory analysis results obtained in the determination of some heavy metals concentration in soil.

## **MATERIAL AND METHODS**

### *Soil Samples*

Soil samples were collected from an old metallurgical industrial area, situated in the vicinity of Bucharest, Romania.

### *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 the table 1.

The 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*

For laboratory analysis was used as method: Atomic Absorption Spectrometry, using an instrument ANALYTIC JENA AG-AAS-ZEEnit 700 in the determination of cobalt, cadmium and lead concentrations and by induced coupled plasma, using an instrument ICP - OES Spectro Flame P for copper, chromium, iron, manganese and zinc determination, in agreement with national standards prescriptions.

For samples disintegration, was used an acid mixture: HNO<sub>3</sub> - HClO<sub>4</sub> - H<sub>2</sub>SO<sub>4</sub>, in the ratio: 2:1:0.2. The resulting data were considered to be the total forms content of heavy metals.

Table 1

Some 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 (64 MB memory)
Sample chamber	1 sample
X - ray source	Mini X-ray tube: 40 kV, 40 microA
Detector	Diode Si -PiN, 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
Elements domain	From titan to uranium
Memory	64 MB
Operation media	Temperature range: -10 to +50 <sup>0</sup> C
Security element	IR sensor
Used software	Windows CE
Transfer data	USB or Bluetooth without fill

*Soil sample collection and preparation*

10 soil samples were collected from an old metallurgical industrial area in Romania, using a GPS instrument to establish the exact coordination points. The soil samples were collected and prepared in agreement with actual Romanian standards.

The collected samples were XRF measured, then dried in air, XRF measured, sieved through the 2 mm sieve to remove non-soil particles and XRF measured again. The samples were homogenized and passed through the 200 microns sieve and XRF measured. After XRF determination, these fine samples were laboratory analyzed (XRF analysis being nondestructive).

The samples humidity ranged between 4.3 and 9.2%.

**RESULTS AND DISCUSSIONS**

*Laboratory analysis*

Table 2 presents the metal concentrations in ten soil samples, minim and maxim

values, determined by atomic absorption spectroscopy, and induces coupled plasma, in comparison with the limit values predicted by Romanian Environment Protection Law.

From table 2 is evident that the concentration of cadmium, copper and lead in contaminated soil samples is higher than the limit predicted in Romanian legislation, even for less sensible areas (meaning non agricultural areas); the concentration of chromium and cobalt is higher than the limit for normal level; zinc concentration is higher than the limit for sensible areas (meaning agricultural areas) and manganese is in the limit for normal areas.

*XRF results*

To find the influence of soil particle size, the soil samples have been XRF measured as follows: the initial collected (humid) soil samples, the dried soil samples, the soil samples after passing through 2mm sieve and samples having the particle size less than 200 microns. The analysis time was constant and equal to 120 seconds. The data presented in this paper represents the mean of five measurements with XRF instrument.

Table 2

Concentration range for heavy metals in contaminated soil samples determined by AAS and ICP methods and the limit values predicted by Romanian Environment Protection Law, Order nr. 756/03.11.1997, (mg metal/kg soil)

Element	Metal concentration (AAS or ICP analyses), mg/kg soil		Limit of alert (Romanian legislation), mg/kg soil		
	Min.	Max	Normal	Sensible areas	Less sensible areas
Cadmium	29	44	1	3	5
Chromium	55	60	30	100	300
Cobalt	17	23	15	30	100
Copper	62	259	20	100	250
Lead	216	895	20	50	250
Manganese	716	916	900	1500	2000
Zinc	189	599	100	300	700

The results are presented in figures 1-7, comparatively with the laboratory analysis data.

In figures 1-7: *Humid* refers to the soil samples fresh collected; *Dry* refers to the soil samples dried at room temperature; less than 2 mm and less to 0.2 mm are the sieved dried soil samples and *Lab.* are the results of laboratory analysis.

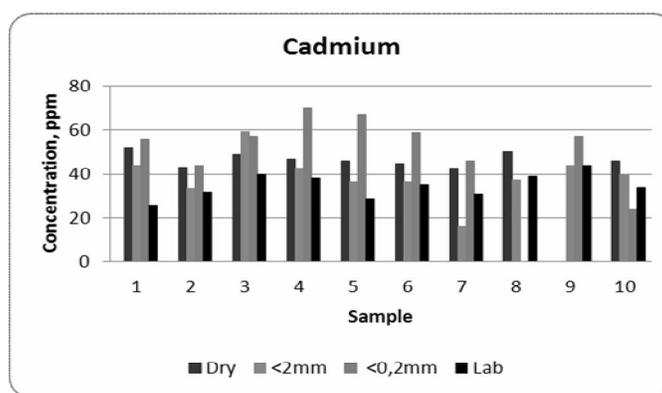


Figure 1: Cadmium concentration in soil samples, XRF data versus laboratory analysis data

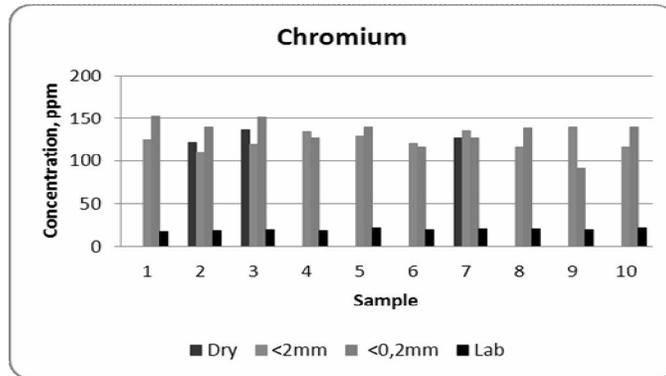


Figure 2: Chromium concentration in soil samples, XRF data versus laboratory analysis data

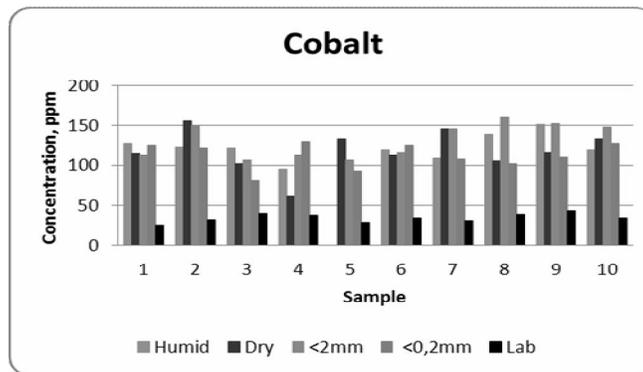


Figure 3: Cobalt concentration in soil samples, XRF data versus laboratory analysis data

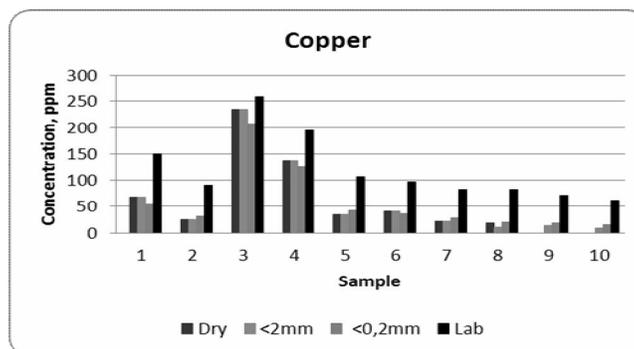


Figure 4: Copper concentration in soil samples, XRF data versus laboratory analysis data

From the figures 1, 2 and 4 result that in humid samples there are no XRF indication about the cadmium, chromium and copper content.

In all 10 samples laboratory results are many times smaller than XRF data, in chromium and cobalt determination. The XRF results for lead and manganese are closed to

laboratory data. In copper and zinc determination, the metal concentration is an influencing factor; smaller is metal concentration in soil sample, higher is the difference between XRF and laboratory analysis results. Generally, any correlation results between sample particle size and the XRF data.

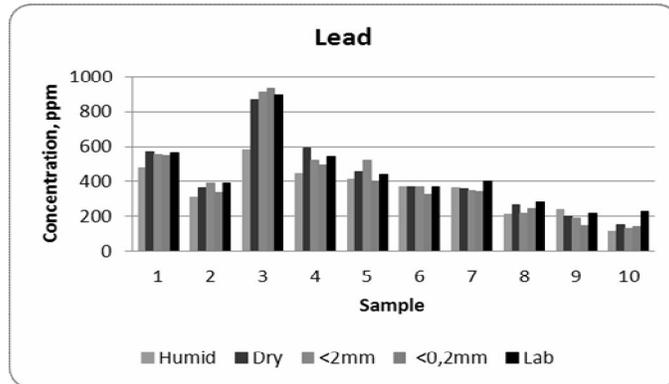


Figure 5: Lead concentration in soil samples, XRF data versus laboratory analysis data

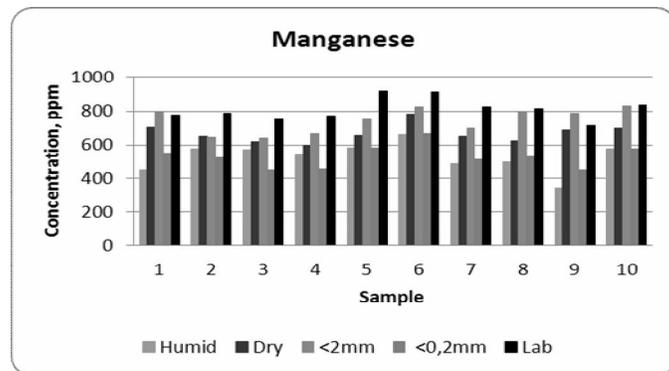


Figure 6: Manganese concentration in soil samples, XRF data versus laboratory analysis data

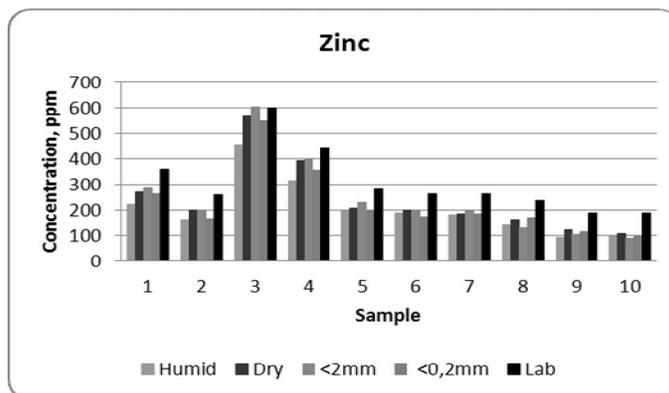


Figure 7: Zinc concentration in soil samples, XRF data versus laboratory analysis data

### CONCLUSIONS

The goal of this experiment was to complete the data obtained in the preliminary tests, by comparing the XRF and laboratory analysis results in some heavy metal concentration determination.

Ten soil samples were collected from an old metallurgical industrial area, situated in south east of Bucharest, using a GPS instrument to have the exact coordination points and were prepared in agreement with actual Romanian standards.

Were XRF measured the collected samples (humid), the dried samples, the samples sieved, with the particle dimension less than 2 mm and finally the fine samples with de particle dimension less than 0.2mm. These finest samples were analyzed in laboratory, by Atomic Absorption Spectroscopy, and by Induced Coupled Plasma in agreement with Romanian Standards.

The results XRF are presented comparatively with laboratory analysis data.

From these results is evident that the soil particle size have no important influence upon the XRF data, an important factor appears to be the metal concentration in soil.

The results confirm the influence of metal concentration in soil upon the XRF data, smaller is metal concentration in soil sample, higher are the difference between XRF and laboratory analysis results.

In all samples laboratory results are many times smaller than XRF data, in chromium and cobalt determination.

The XRF results for lead and manganese are closed to laboratory data.

In copper and zinc determination, the metal concentration is an influencing factor; smaller is metal concentration in soil sample, higher is the difference between XRF and laboratory analysis results.

Generally, any correlation results between sample particle size and the XRF data.

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