

## **RAPID AND LOW-COST DETERMINATION OF HEAVY METALS IN SOIL USING AN X-RAY PORTABLE INSTRUMENT**

**MIHAELA ULMANU\*, ILDIKO ANGER\*, EUGENIA GAMENT\*\*, M. MIHALACHE\*\*\*, ELEONORA NEAGU\*, L. ILIE\*\*\***

\*National Research and Development Institute for Nonferrous and Rare Metals of Pantelimon

\*\*National Research and Development Institute for Soil Science, Agrochemistry and Environment Protection of Bucharest

\*\*\*University of Agronomic Sciences and Veterinary Medicine of Bucharest

**Keywords:** *heavy metals, polluted soil, portable X-ray fluorescence instrument*

### **Abstract**

*Contaminated soils present a major global health problem especially in urban areas with dense population. The common contaminants of soil are heavy metals. 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 influence of soil particle size and the metal concentration in soil upon the XRF results.*

*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.*

### **INTRODUCTION**

The soil forms the outer skin of the land masses of Planet Earth; it is our life - support system. Soil is a vulnerable resource, the largest disruption and destruction being caused by humans.

Contaminated soils present a major global health problem especially in urban areas with dense population. The common contaminants of soil are heavy metals. For risk - assessment studies and follow-up remediation projects is necessary to perform numerous analyses to determine the concentration of metal contaminants. The remediation projects could include the removal of metal contaminants from

soil or the removal of surface - contaminated soils. The way selected for environmental remediation is dependent on the results of laboratory analysis of samples collected from the contaminated field. 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 [1-3].

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 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. Different metals in soil can be measured quickly and non - destructively using an XRF instrument. Since XRF is completely non destructive, any sample collected and measured in field can be retained for verification by a laboratory [4].

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 [5]:

- 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 goal of this experiment was to complete the data obtained in the preliminary tests [6], by observing the influence of soil particle size upon the XRF results.

## MATERIAL AND METHODS

### *Soil Samples*

Soil samples were collected from an old metallurgical industrial area, situated in South East 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 table 1.

**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: 40kV, 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°C
Security element	IR sensor
Used software	Windows CE
Transfer data	USB or Bluetooth without fill

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].

The main variables affecting the precision and accuracy of XRF analysis are [8]:

- physical properties of soil matrix, more exactly the variation of sample physical properties;
- chemical properties of the soil matrix - the absorption and spectral interferences;
- soil humidity higher than 10% influence the X rays transmission.

### *Laboratory analysis*

For laboratory analysis was used as method Atomic Absorption Spectrometry, using an instrument ANALYTIC JENA AG - AAS - ZEE nit 700 in the determination of lead, copper and zinc concentrations, 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.

## **RESULTS AND DISCUSSION**

### *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%.

### *Laboratory analysis*

Table 2 presents the metal concentrations in soil samples (10), minim and maxim values, determined by atomic absorption spectroscopy, in comparison with the limit values predicted by Romanian Environment Protection Law.

**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, Order nr.756/ 03.11.1997 (mg metal/kg soil)**

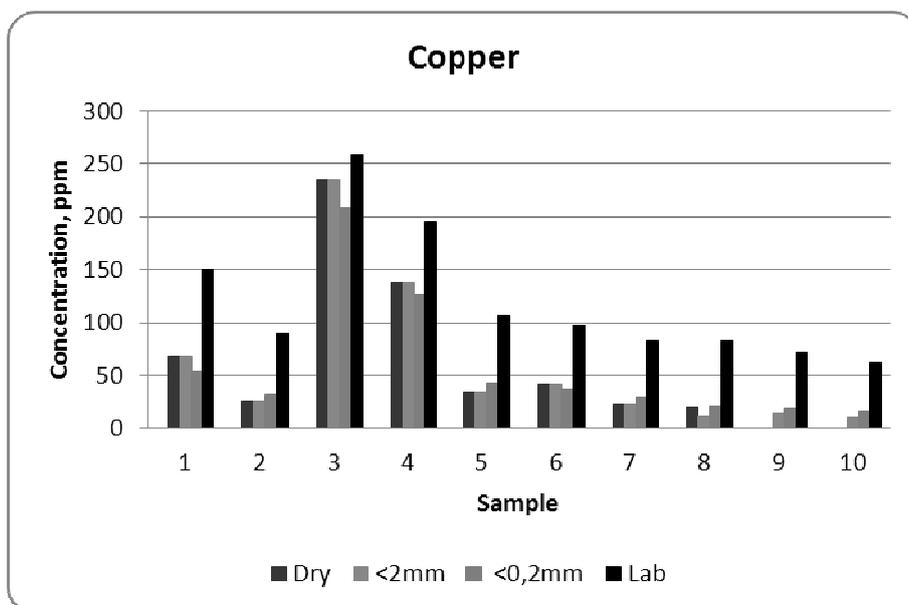
Element	Metal concentration (AAS analyses), mg/kg soil		Limit of alert (Romanian legislation), mg/kg soil		
	Min.	Max	Normal	Sensible areas	Less sensible areas
Copper	62	259	20	100	250
Lead	216	895	20	50	250
Zinc	189	599	100	300	700

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

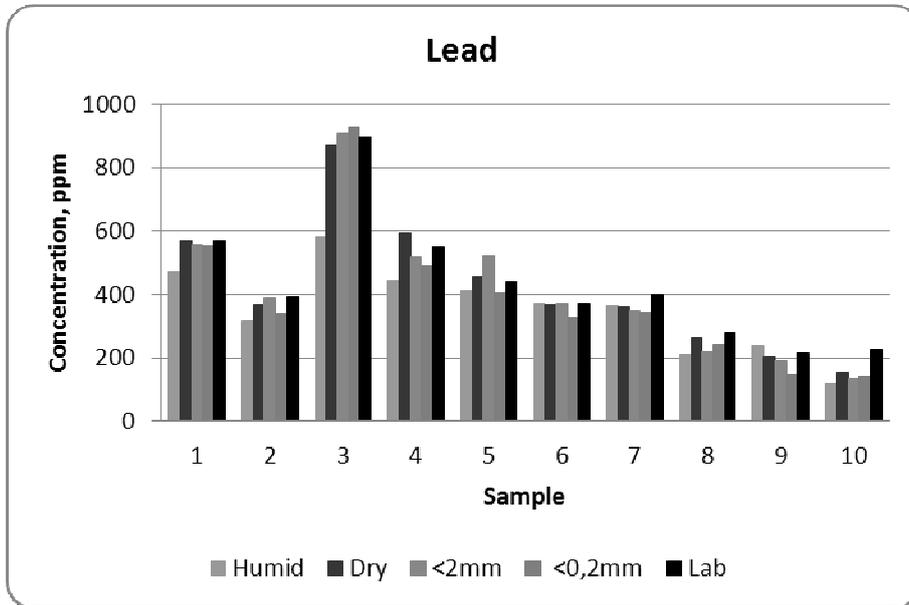
*XRF results*

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 2 mm 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.

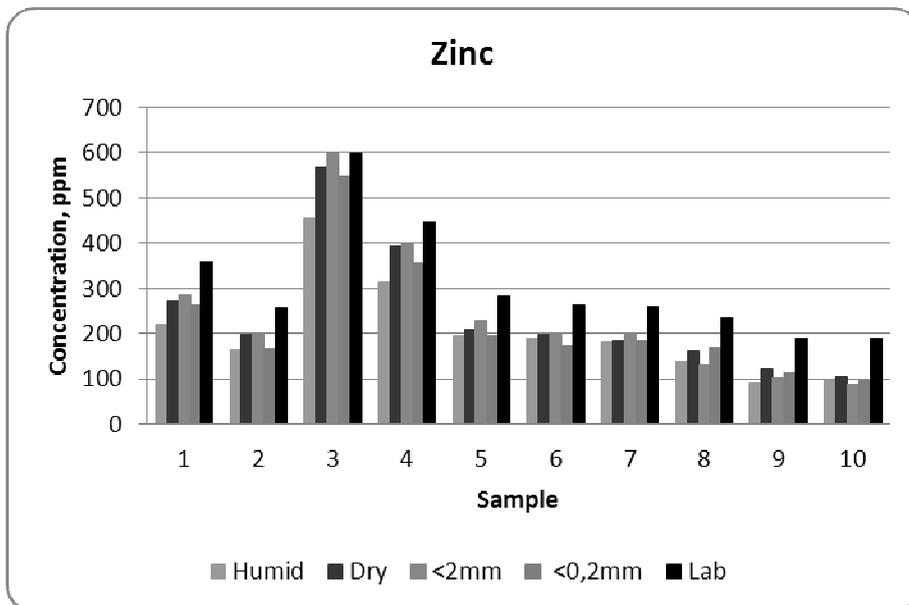
The results are presented in figures 1, 2 and 3, comparatively with the laboratory analysis data.



**Fig. 1. Copper concentration in soil samples, XRF data versus laboratory analysis data**



**Fig. 2. Lead concentration in soil samples, XRF data versus laboratory analysis data**



**Fig. 3. Zinc concentration in soil samples, XRF data versus laboratory analysis data**

In figures 1, 2 and 3: *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.

From the figure 1 results that in humid samples there are no XRF indication about the copper content, even in sample 3 in which the laboratory analysis give the highest concentration (about 250 ppm).

In the samples 9 and 10, in which the copper concentration determined in laboratory is less than 80 ppm, we have no XRF data in dry samples.

In all 10 samples laboratory results are higher than XRF data. Smaller is copper concentration in soil sample, higher are the difference between XRF and laboratory analysis results.

Referring to the influence of soil dimension particle upon the XRF data in copper concentration determination is evident that this characteristic have no an important influence, the copper concentration in soil sample being the determinant factor.

In figure 2 is illustrated the data for lead concentration determinate using XRF instrument comparatively with the laboratory data. The lead concentration in all soil samples is higher than copper concentration and the presence of lead is detected in all humid samples. The XRF data are very closed to laboratory analysis, with one exception, the sample 10 in which the lead concentration is only about 200 ppm, the maximum concentration of lead being higher than 800 ppm (sample 3).

The soil particle size did not affect the XRF measurements in the case of lead concentration determination.

In the case of zinc determination, figure 3, the same observation is valid. The soil dimension particle size is not an important influence factor in XRF results, the decisive factor being the metal concentration in soil. Good agreement exists in the case of sample 3, in which zinc concentration is the highest (600 ppm).

## CONCLUSION

1. The goal of this experiment was to complete the data obtained in the preliminary tests, by observing the influence of soil particle size upon the XRF results in copper, lead and zinc concentration determination.
2. Ten soil samples were collected from an old metallurgical industrial area, situated in southeastern Bucharest, using a GPS instrument to have the exact coordination points, and were prepared in agreement with the actual Romanian standards.
3. To verify the influence of particle size of soil upon the XRF data were 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 0.2 mm. These finest samples

were analyzed in laboratory, by Atomic Absorption Spectroscopy, in agreement with Romanian Standards.

4. The results XRF are presented comparatively with laboratory analysis data.
5. 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.
6. 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.

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