Detecting Heavy Metals in Soil

USING FIELD PORTABLE X-RAY FLUORESCENCE

ENVIRONMENTAL
Analysis

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Figure 1. X-MET3000TXS portable XRF spectrometer

Land contamination has become an increasingly high profile issue on the agenda of environmental and regeneration programmes, especially in Europe and in North America. One significant type of land contamination is pollution by heavy metals. Several incidents have attracted major media attention and as a result many enviromental programs have been initiated to address land contamination problems. Previously, the catastrophic consequences on human health and the environment by land contamination were not considered. Today with greater knowledge, land contamination is not seen as just a few isolated severe incidents, but as a widespread infrastructural problem of varying intensity and significance..

Heavy Elements

Heavy elements are normally considered as those with a density of 4 – 5 g/cm3 and higher. Based on this definition, all elements heavier than titanium (Ti) are heavy elements. However, normally only poisonous heavy elements are considered: arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), vanadinium (V), nickel (Ni), lead (Pb) and zinc (Zn). Some of the metals like Cu and Zn are poisonous only in high concentrations and they exist in normal, non contaminated soil.

Most often, the heavy elements originate from previous use of the land by industry, for instance from waste burning plants, coal power plants, shooting tracks, mining, traffic and fertilizers. Heavy elements can cause harm both to human health and to the environment. Humans can be exposed to heavy elements by food plants, water and air, but animals and vegetation can also be adversely affected.

In different countries there are determined accepted concentration levels (reference value, target value, guideline value, soil quality criteria…) for heavy elements. Levels are determined based on use of the land. A typical classification is for example: 1) play grounds, 2) residential areas, 3) parks, 4) industry areas. Concentration levels may vary significantly from one country to another.

On site heavy element screening

Handheld XRF offers a fast, and inexpensive approach to site characterization for identifying heavy element pollutants in soil. A large number of in situ measurements can be performed quickly, allowing fast pollutant profiling for heavy elements and their levels. XRF is totally non-destructive to the samples, which allows the same sample to be sent to the lab for confirmatory analysis.

Recent advances in electronics and data processing coupled with miniature X-ray tube technology have produced substantial improvements in the precision and speed of analysis of handheld XRF analyzers. Miniature X-ray tubes have only recently become a reality in handheld XRF spectrometers. Higher X-ray flux from miniature X-ray tube provide faster results and better precision than traditionally used radioisotope sources, with all the associated benefits of ease of transportation, storage etc. A modern field portable XRF consists of four main components: X-ray tube, detector, pulse processing electronics, and Personal Data Assistant (PDA) as a user interface.

Oxford Instruments handheld XRF analyzer is a dedicated soil analyzer, designed specifically for measuring heavy metals in soil – offering accurate and reliable identification of pollutant metals and their concentrations. X-MET3000TXS is the perfect tool for the demands of soil screening, were operators perform tests directly on the ground to quickly profile contamination pattern.

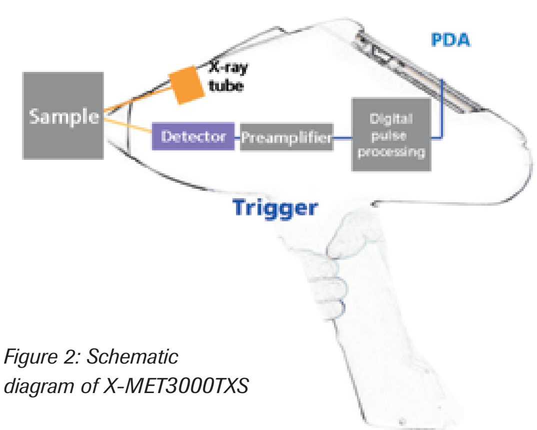
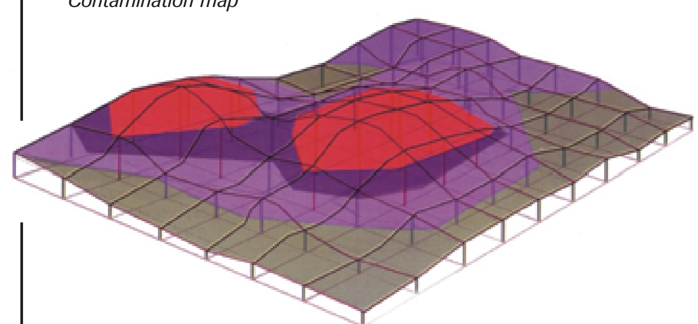


Figure 2: Schematic diagram of X-MET3000TXS

Advantages of in situ analysis

Use of field portable XRF can offer significant advantages over laboratory methods. Field analysis is significantly less expensive per sample than laboratory analysis because of reduced sample handling, sample transportation to laboratory and documentation. In addition, the almost immediate results provide timely support for field decision-making, and greatly reduce overall project cost. The low cost per sample allows for denser, more complete sampling. Actually in many situations, the field portable XRF provides better overall decision making data than laboratory analysis, because of its ability to overcome spatial variability through increased sampling density.

Figure 3. Contamination map



Handheld XRF can also provide ex-situ, prepared-sample analysis in the field with accuracy that can rival that of standard laboratory analysis. This is achieved by using the analyzer in "benchtop mode" with the sample placed in a plastic bag and placed in the X-MET3000TXS adapter (see Figure 4)

Figure 4. X-MET3000TXS Benchtop system

Even in cases where laboratory analysis is required, handheld XRF can be used to rapidly pre-screen 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 the field can be retained for verification by a laboratory if needed. While handheld XRF cannot generally provide as low detection limits as laboratory methods, it can often provide detection limits well below regulatory levels.

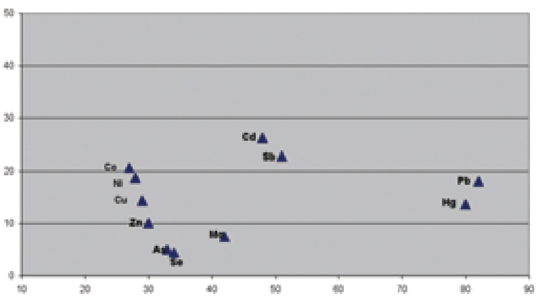


Figure 5. Detection limits

For example, handheld XRF can easily provide detection limits for lead-in-soil of less than 20 ppm, well below typical regulatory levels of 50 to 1000 ppm.

The XRF method is also an efficient tool during the remediation process. Often the remediation process concentrates on removing contaminated soil. Normally, test excavations are made to provide information on the depth of contamination. This will ensure that only contaminated soil is treated or removed, which will reduce the costs of the project. When handheld XRF is used, it allows the operator to stop land removal when results for contamination elements are under the action level. If readings are near or exceed action levels, soil removal or remediation is continued until non-contaminated soil is reached.

Figure 6. Contaminated soil removal

Sample handling and measurement

In the field, direct measurements on the soil without any sample preparation produce the quickest possible screening result. However, minimal sample preparation is often recommended to improve measurement accuracy. The field operator should first remove any debris, such as leaves, grass and stones from the measurement surface. If there is lot of debris in the soil, the operator can sieve the loose soil using a 2 mm mesh which will remove the larger objects. In addition, the operator should loosen the soil to a depth of a few centimeters and stir the loosened soil to obtain a representative homogenous sample. To reduce the effect of soil moisture, the loosened soil may be allowed to dry for a few hours or dried with absorbent paper before the measurement. Just before the measurement, the operator can mix the loose soil and pack it down gently in a plastic bag for analysis. This procedure will give the highest level of accuracy on a representative sample.

Figure 7. Soil samples in plastic bags

Measurement itself is easy - just point the instrument at the sample (field measurement) or place the sample bag in the holder (field lab measurements), pull the trigger and read the result. Measurement time is 15 – 300 seconds depending on required level of accuracy. Normally three different measurements from different portions of the sample is made when working in the field. Error due to counting statistics can be seen in the analyser display, and represents the main source of instrumental error in analyses.

Calibration principle

X-MET3000TXS is calibrated by a fundamental parameters (FP) method. FP is a universal calculation method which takes into account the X-ray interactions in the sample, for example primary and secondary fluorescenses, spectral overlap, background in the detector etc.. It is a versatile calibration, which can be used for all different soil types, without the need for site specific calibration adjustments. By using FP calibration, all heavy elements can be measured covering a wide concentration range. Excellent correlation (shown in Figure 8) can be achieved between results of field portable XRF and the common laboratory analysis method of Inductively Coupled Plasma Spectroscopy (ICP). If required, empirical calibration can be also done by a factory calibration sample set or by customers' own sample set.

Soil remediation projects

In Finland problems related to contaminated soils have been studied systematically for the last decade. Some 20,000 sites, where contamination is a possibility, have been measured and their environmental and health impacts estimated. Attention has focused on contamination problems created by sawmills, impregnation plants and oil-polluted sites. Nearly 1,000 urgent sites have so far been cleaned up. Use of field portable XRF for contamination

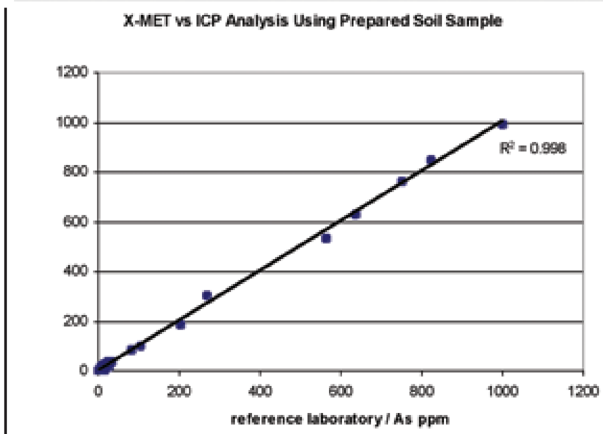


Figure 8. Comparison of Oxford Instruments' X-MET results to laboratory results for Arsenic in soil.

screening and controlling remediation procedures is standard practice in Finland. One of these cleaned up sites is located in the eastern part of the Helsinki. Heavy element contamination was one of the problems in this residental area, which was built on the old dump area.

In this land remediation project, Oxford Instruments' X-MET3000TXS was used for quick mapping the heavy metal level in the area before remediation work was started. From one test excavation, about 2 kg of collection samples were taken from the excavator bucket. Besides removing stones, roots, broken glass, metal fragments etc., no special sample preparation was made before measuring the sample. Three measurements were made from different points on the sample. The following table shows an example of typical X-MET3000TXS results with a comparison to ICP laboratory analysis.. (see table one)

In these samples, Cu and Pb results were above the reference value but below the action limit value. Zn result was above the action limit value, which meant that this case test area was remediated. Results show excellent agreement with the laboratory method, even when the in-situ analysis was carried out without any significant sample preparation.

Summary

New generation field portable XRF analyzer is a fast, inexpensive site characterization tool for identifying heavy element pollutants in soil. A large number of in-situ tests can be performed quickly, allowing thorough pollutant profiling for heavy elements and their levels. Contamination hot spots can be quickly mapped, which allows the remediation process to begin immediately. In many situations, the field portable XRF provides better overall decision making data than laboratory analysis, because of its ability to overcome spatial variability through increased sampling density.

Soil sample X-MET3000TXS results	Cu / ppm	Zn / ppm	Pb / ppm
	167	751	187
	118	768	195
	146	743	191
Average value	143	754	191
Laboratory ICP analysis	120	800	230
Reference value	100	150	60
Action Limit value	400	700	300

Table One