



Utilization of Portable X-Ray Fluorescence- Spectrometers for the Registration of Contaminated Sites in Vietnam

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1 . Registration of contaminated sites in Vietnam

Contaminated soils are among the main environmental issues in Viet Nam. Persistent organic pollutants (POPs) such as dioxins from the Vietnam war and others; as well as **heavy metals** like lead, cadmium or chromium are among the pollutants mostly found in Vietnamese soils. They derive, among other, from mining, fertilizer use and wastes from industry or so-called craftsmen villages. Many polluted sites lay near to densely populated areas or within sites that are used for agriculture.

The registration of such polluted areas in a **cadastre** would identify and mark these locations and therewith help to prevent their use for activities that pose human health as risk.

The Government of Vietnam responded to these issues with the Law on Environmental Protection (or Environmental Protection Code, 55/2014/QH13 from 1993, revised in 2006 and 2014). It obliges the state to take measures to identify, analyze and classify contaminated sites and, based on this, to develop and implement guidelines for their rehabilitation.

Decree N° 64 (64/2003/QD-TTg) and its prolongation 1788/2013/QD-TTg ordered, among others, the determination and registration of environmentally-relevant companies and sites.

Until recently, there exist only few localities with accurate soil contamination profiles. One of the reasons for this delay is the difficulty that from each potentially polluted site, a higher number of samples have to be collected and transported to professional laboratories for further analysis. This process is not only relatively slow, it is also prone to errors.

Portable X-ray fluorescence (XRF) spectrometers are a tool that allows researchers and responsible agencies to conduct already on the spot a quick and draft analysis of the existing soil conditions. This makes them – if used properly- a suitable option to **diminish errors and inaccuracies**. Portable XRF allows on areas suspected to contamination a quick differentiation of contamination hot spots and non-harmful sections. Therefore, it reduces the number of samples needed for a comprehensive analysis of the area's contamination profile, allows adaptations of the design of a soil analysis already on the spot **and saves so time and money** required for the evaluation of the local heavy metal dissemination.

2 . Purpose of portable XRF-spectrometers for the detection of contaminated sites

Battery-powered portable XRF-spectrometers allow **measurements of contents of heavy metals and arsenic** on collected samples **directly on the site**. This way, a wide range of contaminants can be analyzed quickly, accurately and at low cost. The presence or absence of soil contamination as well as its approximate level can be obtained instantly without having to wait days or weeks for laboratory reports. In this way, the contaminated area can be delimited quickly in order to decide whether:

- directly protective measures (work and environmental protection) are required,
- further investigations must be carried out and
- if there is a need for further hazard prevention.



Figure 1: Deposits of potential environmental hazards in Bien Yen, 2016.
Image: UfU, Kovac.

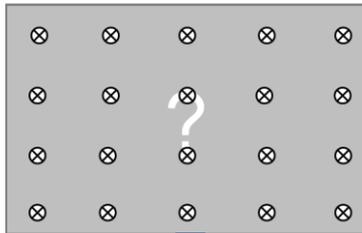
By means of grid or transect sampling (*see excursus*), the extent of contamination can be analyzed in detail and in a short amount of time. Samples for further assessment in the laboratory can be chosen carefully due to previous spatial analysis. Therefore, projects can be processed faster and resampling can be avoided, thus saving time and money. Field data collected with the XRF-analyzer can get immediately transferred to a computer or notebook.

Excursus: Spatial analysis with portable XRF-spectrometers

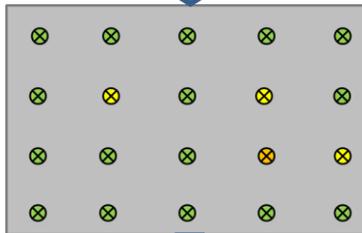
Compared to the standard screening for laboratory investigations, the measurements with portable XRF-analyzers have an advantage due to the directly available results: This allows to adopt the design of the spatial analysis of an area suspected to be contaminated already during the field investigation if this is necessary. It is so possible to gain more detailed information about the scope and dissemination of heavy metals in the soil and to reduce the number of necessary sample evaluations through a laboratory.

Approach 1: Standard grid screening for laboratory investigation with the according results

The area is scaled into measuring points.



Samples from the measurement points are sent to the laboratory for analysis.

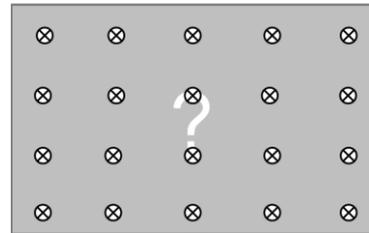


Based on laboratory results, a contamination profile can be developed.

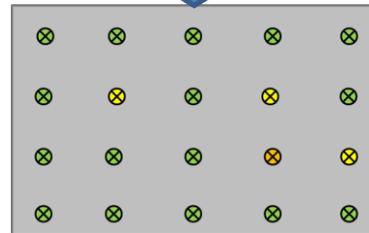


Approach 2: Grid screening with portable XRF analyzers-

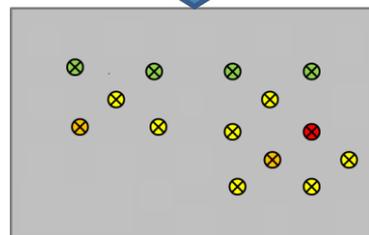
The area is scaled into measuring points.



Samples from measurement points are analyzed with mobile XRF directly on the spot.



Based on results and evaluation of the on-spot-analysis, points for closer analysis in the laboratory are defined.



With the evaluation of all results, a more detailed contamination profile can be developed.



In approach 1, the analysis of 20 soil samples in the laboratory is needed to draw a contamination profile.

In approach 2, only 14 soil samples have to be analyzed in the laboratory and around 25 samples in the field to draw a more detailed contamination profile. In this case, also the sources of the contaminations could be located.

Images: Kerth 2016: Möglichkeiten der Vor-Ort-Analytik bei kontaminierten Flächen. Presentation (with own adjustments).

3 . Design and function of portable XRF-spectrometers

3.1 Technological basis: X-ray fluorescence spectroscopy

In X-ray fluorescence analysis, a soil sample is excited by primary X-ray radiation from the spectrometer to emit fluorescence X-radiation. The spectrum of this emitted radiation gives conclusions on the chemical composition of the sample.

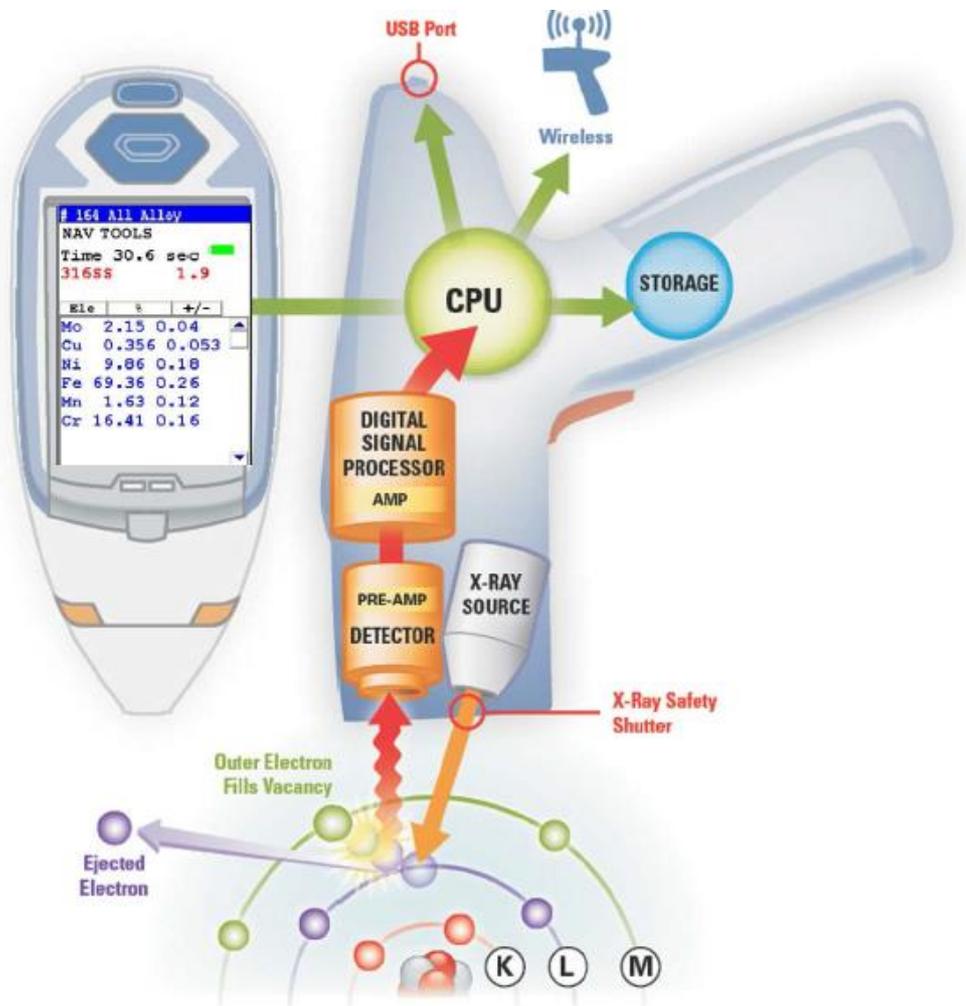


Figure 2: Design of a portable XRF-analyzer and its basic function. Image: Thermo Fisher Scientific / Tewksbury - USA

3.2 Measurement capabilities

With portable XRF-spectrometers, it is possible to measure elements from sulfur (OZ 16) to uranium (OZ 92) with detection limits of less than 100 mg/kg for most heavy metals. For some more common and harmful elements such as lead, cadmium and mercury, mobile XRF-spectrometer can even measure detection limits less than 10 mg/kg. Figure 3 gives an overview over most common soil contaminants in Vietnam for which the utilization of portable XRF spectrometers is useful for an on-site analysis.

| | | | |
|---------------------|----------|---------------------|---------|
| ¹⁶ S | Sulfur | ³⁵ Br | Bromine |
| ¹⁷ Cl | Chlorine | ⁴⁸ Cd | Cadmium |
| ²⁴ Cr | Chromium | ⁸⁰ Hg | Mercury |
| ³³ As | Arsenic | ⁸² Pb | Lead |

Figure 3: Most common contaminants which can be accurately analyzed on-site with portable XRF-analyzers. Figure: UfU.

3.3 Technical features

XRF-spectrometers are able to measure metal contents for different contexts such as soil or metal alloys. These measurement options for sample types are already calibrated in the factory. There is no need to calibrate it manually.

The XRF-analyzers can also only be re-calibrated by the manufacturer. The analyzer must be switched on at least two times a year to prevent deep discharge and therewith damages.

4 . Types of sample analysis

There are different options to measure heavy metals contents of soils with XRF-spectrometers, namely an in-situ measurement or an intrusive measurement at the field, or an intrusive management with prepared samples in the laboratory.

Different measurements options lead to various degrees of preciseness of the analysis. Reason for these differences lays in the function of the XRF- spectroscopy, which only analyses those elements at the surface of the soil (sample).

Thus, mixing the samples to make them as homogeneous as possible has a decisive influence on the accuracy of the results. Consequently, the previous homogenization of samples in the laboratory is the decisive factor that makes them more precise than on-site analysis.

4.1 In-situ measurement

In-situ measurement can take place directly on the soil surface (figure 4a) or on a sample in a plastic bag (figure 4b). Soils are - compared to other measurable surfaces such as metal alloys- usually very inhomogeneous. Measurements directly on the soil are therefore often very imprecise. Direct measurement on the soil can also easily damage or contaminate the detector.

It is strongly recommended to measure on soil samples in plastic bags which have been already thoroughly mixed and pressed for compaction. The even soil is then analyzed by holding the detector for two minutes carefully against the sample.

Results: Both forms of in-situ measurements often result in high inaccuracies. Without test stand, there exists the risk of exposure to x-ray radiation. In-situ measurement should therefore be avoided when a mobile test stand is available.



Figure 4 a (above) and 4 b (below): In-situ measurement at the soil surface (a) and on a sample (b). Image 4a: Thermo-Fisher Scientific / Tewksbury - USA; Image 4b: Bernd Steinweg, UBB Viersen

4.2 Intrusive measurement

In the field:

A sample from an approx. 5 cm x 5 cm area (depth depends on the question) has to be taken, from which plant residues and coarse stones have to be removed. This sample will then be mixed in a separate bucket or in the sample bag and is then filled in the sample container for analysis. If plastic bags are

used, the same batch of plastic bags shall be utilized for the whole measurement campaign.

Results: Samples can still be inhomogeneous and are therefore less precise than in the laboratory. The use of the mobile test stand protects against x-ray-radiation.



Figure 5: Intrusive measurement on-site with a portable XRF-analyzer in a test-stand in Bien Yen, 2016. Image: UfU, Kovac.

In the laboratory:

Before the measurement takes place, samples have to be dried for 72 hours at 40°C. To make the soil samples even more homogeneous, they should be sieved to 2mm and be fine grounded in a mill before they are then analyzed in the test-stand. Due to the intensive preparation of the samples, this type of analysis will have the most precise results.



Figure 6: Preparation of homogeneous samples for intrusive measurement with mobile XRF in the laboratory. Hanoi, 2017. Image: UfU, Nguyen

Results: Strictly spoken, the measurement in the laboratory does not present an on-site analysis any more. For the preparation of samples in the laboratory, laboratory equipment such as mortars, bowls and an oven are needed.

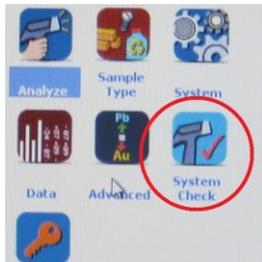
Excursus: Intrusive on-site measurement explained Step – by - Step

After the prepared sample is inserted into the mobile test-stand, the measurement process can be initiated:



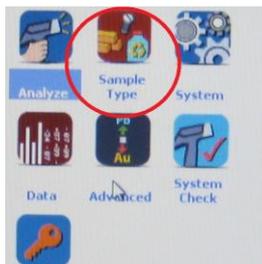
Step 1:

Start the spectrometer by pushing the "Start"-Button for some seconds. Then answer the questions related to security and enter the password. Wait some seconds while the spectrometer starts the initialization.



Step 2:

Carry out a **System Check** by pushing the button at the Menu and confirming your entry. The System Check takes 2 minutes. When the software shows "OK", return to the Menu by pushing the "Return" button at the left.



Step 3:

Select under the Menu button "Sample Type" the option "Soil" and confirm your choice by pushing the "Return" button. Note: The different options here already include all necessary calibrations – there is no need to calibrate yourself.



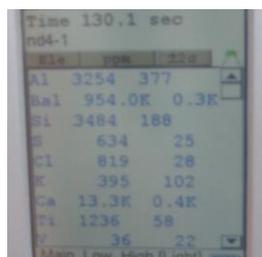
Step 4:

Select the option "Analyze" in the Menu. Now you can name the sample and include further information such as GPS data and the name of the researcher.



Step 5:

Press the orange button on the analyzer and **keep holding it for at least 120 seconds!** During this time, the sample is measured and first results for each metal are shown at the monitor. After release of the orange button, the analysis ends and results are saved automatically.



Step 6:

Repeat step 4 and 5 with all samples. You can transfer the results to your PC by connecting the mobile XRF analyzer with it and using the **Software NDT**. With this program, you can also transfer the results into an Excel table.

Images: UfU, Kovac

4.3 Safety precautions during operation

X-ray radiation is emitted from the device only when the user starts a measurement. The primary beam shows a high radiation dose. The secondary (scattered) beam shows a relatively low dose compared to the primary beam (Fig.5).

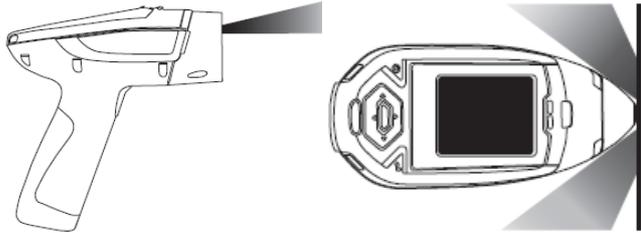


Figure 7: Primary beam (left) and secondary beam (right) Images: Manual Niton XL3t XRF-analyzer, ThermoFisher Scientific / Tewksbury - USA

The dose of the secondary beam is higher for samples with a low density (plastics, wood, soil samples) and samples that do not completely cover the measure window. For such samples, a test stand (fig. 5) and/or backscatter shield is appropriate. For measurements of metals and metallurgies, the backscattered radiation is of negligible dose.

The measurable dose during a measurement is small around the plastic housing as well as the handle. The dose per year does not exceed the limit values for persons who are not exposed to radiation due to their occupation, even if the spectrometer is operated by a user about 2000 hours per year and the X-ray tube is in operation during this time. Despite these low doses, XRF-spectrometer shall not be used during pregnancy.

Also never operate the device with a part of your body in the primary beam or the primary beam directed at anyone else.



In some countries, persons who work with equipments operating with x-ray technology require a special approval from state authorities.

Please check the legal instructions in your country before using an XRF-spectrometer.

4.4 Conditions for on-site analysis

In contrast to laboratory samples, the measurements on the spot are carried out on non-dried and non-ground samples. Due to these altered boundary conditions, the measurement can be disturbed by influences of the soil matrix, soil moisture, temperature, humidity and other contaminants such as oil-containing substances on the surface, which makes them less precise than laboratory measurements.

In general, wet soils cannot be analyzed with XRF-analyzers. After heavy rains, measurements can start on the third rain-free day. Furthermore, the **infrastructure** regarding the power supply and the weather protection for the portable XRF-spectrometer should be considered. To ensure a qualified assessment of the results and the according decision making on-site, it is important that users have the necessary educational background to interpret the results from the XRF-spectrometer.

On-site measurements show a reduced accuracy in comparison with laboratory results due to **simplified or no sample preparation** as well as **deviation from laboratory standards and directives**. Main reason for the reduced precision is the inhomogeneity of unprepared samples from the field.

However, there are international standards for the screening of selected elements in soils with handheld or portable XRF-spectrometers (ISO 13196:2013). They can be applied on-site to obtain qualitative or semi-quantitative data that assists decisions on a further sampling strategy for soil quality assessments, as well as to ensure a basic comparability of the measurement campaigns.



Figure 8: On-site analysis in Da Hoi village near Hanoi. Image: UfU, Kovac.

5 . Software and data transfer to the PC

Measurements can take place only with the portable XRF-spectrometer itself, or via notebook directly connected to the XRF-analyzer (see Figure 8).



Figure 9: Measurement directly with the XRF-spectrometer (left) or via a connected notebook (right). Images: Ufu, Kovac.

There are two software programs supporting the data analysis with the XRF-spectrometer alone and/or with your PC.

Analysis Software NDT runs the soil analysis of the spectrometer. It can be ordered with settings for the analysis of different sample types, e.g. of soils or of metal alloys. NDT allows also the naming of samples on-site and has a long-term memory for analytical data.

Data Transfer Software NDT supports the transfer of analytical data from the XRF-spectrometer to programs of your PC such as Excel. The software also allows that analytical data and recorded GPS data from site investigations can be transmitted wireless via Bluetooth to a PC or printer.

| Index | Reading No | Time | Type | Duration | Units | Sign | Sequence | Flags | SAMPLE | LOCATION | INSPECTOR | CCCC | MI | NC | Mo | Mo Error | Zr | Zr Error | Sr | Sr Error | U | U Error | Rb | Rb Error |
|-------|------------|------------------|------|----------|-------|------|----------|-------|--------|----------|-----------|------|----|----|------|----------|--------|----------|-------|----------|------|---------|--------|----------|
| 1 | 129 | 10.11.2017 09:58 | Soil | 120,69 | ppm | 2 | Final | a1 | da hoi | | | | | | 4,79 | 1,58 | 241,46 | 3,55 | 45,79 | 1,75 | <LOD | 4,4 | 63,16 | |
| 2 | 130 | 10.11.2017 10:02 | Soil | 120,77 | ppm | 2 | Final | a2 | da hoi | | | | | | 6,37 | 1,6 | 252,54 | 3,6 | 41,64 | 1,68 | <LOD | 4,43 | 62,76 | |
| 3 | 131 | 10.11.2017 10:06 | Soil | 120,85 | ppm | 2 | Final | a3 | da hoi | | | | | | 6,48 | 1,56 | 300,11 | 3,71 | 43,89 | 1,64 | <LOD | 4,39 | 73,2 | |
| 4 | 132 | 10.11.2017 10:09 | Soil | 120,5 | ppm | 2 | Final | a4 | da hoi | | | | | | 2,29 | 1,49 | 381,9 | 3,92 | 43,43 | 1,55 | 4,22 | 2,72 | 68,11 | |
| 5 | 133 | 10.11.2017 10:12 | Soil | 120,8 | ppm | 2 | Final | a5 | da hoi | | | | | | <LOD | 2,15 | 358,96 | 3,72 | 40,65 | 1,47 | 4,15 | 2,58 | 61,25 | |
| 6 | 134 | 10.11.2017 10:16 | Soil | 120,85 | ppm | 2 | Final | a6 | da hoi | | | | | | <LOD | 2,21 | 377,92 | 3,9 | 40,59 | 1,51 | 7,33 | 2,72 | 61,99 | |
| 7 | 135 | 10.11.2017 10:19 | Soil | 120,54 | ppm | 2 | Final | a7 | da hoi | | | | | | <LOD | 2,07 | 207,44 | 3,04 | 60,9 | 1,79 | 9,43 | 3,05 | 86,92 | |
| 8 | 136 | 10.11.2017 10:22 | Soil | 120,5 | ppm | 2 | Final | a8 | da hoi | | | | | | 5,13 | 1,49 | 273,07 | 3,48 | 61,7 | 1,82 | 8,38 | 3,21 | 100,37 | |

Figure 10: Example for a measurement output on MS Excel. Image: Ufu, Kovac.

6 . Sources and figures

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