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PATTLE DELAMORE PARTNERS LTD

Analysis of Soil Samples Using a Portable X-Ray Fluorescence Spectrometry (XRF)

Marlborough District Council

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Analysis of Soil Samples Using a Portable X-Ray Fluorescence Spectrometry (XRF)

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Limitations:

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Executive Summary

Marlborough District Council (MDC) has requested that Pattle Delamore Partners Limited (PDP) prepare a brief document which outlines the requirements for undertaking an on-site X-ray Fluorescence (XRF) analysis of soils at contaminated sites.

Field portable XRF analysis is an ideal tool to undertake a large number of measurements of elemental concentrations in soil in a very short time. However, the technique is subject to a number of sampling and analytical errors and therefore is regarded as a screening level assessment tool only. The main sources of error affecting accuracy of this technique are sampling error due to heterogeneity in the contaminant distribution in the soil, and moisture content variation in the sample. Therefore, properly preparing the soil sample is vital to assure data quality.

This document outlines the theory of x-ray fluorescence, the interferences and other factors which can influence the reliability of the XRF results, sample analysis procedures (including QA/QC measures), and minimum reporting requirements for undertaking XRF surveys.

In-situ XRF analysis (by placing the XRF directly in contact onto the ground) requires minimal sample preparation but is only a screening level technique. BS/ISO standard 13196 (2013) provides a suitable methodology for undertaking the screening level investigations. Screening level analysis can be used for:

- Identifying potential hotspots on a site,
- Providing an indication of the extent of contamination,
- Preliminary identification of contaminants present,
- Assist with remediation decision making,
- Screening of hazardous waste.

Semi-quantitative XRF analysis can be achieved by implementing more intensive sample preparation, correct QA/QC techniques and correct use of the XRF. Sieving, drying and homogenisation of soil samples removes many of the sampling errors caused by grain size effects, moisture content and other matrix effects, and increases the accuracy and reliability of the results. US EPA Method 6200 provides a methodology for undertaking semi-quantitative investigations.

Semi-quantitative investigations can:

- Assist with determining the appropriate soil sampling density and sampling locations for site investigation works (exploratory level site investigations);
- Provide an indication of degree of heterogeneity of contaminants present on the site;
- Be used to augment data used in assessing potential human health risk of average exposure to the site, provided that data quality objectives (outlined in Section 4.4) are met and suitable verification of results has been undertaken;
- Be used in a Preliminary Site investigation, assisting (with traditional information sources) to determine if it is more likely than not that the site is contaminated.

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1.0   Introduction

Currently in New Zealand there are no guidelines or standards regarding the use of XRF for investigating contaminated sites within New Zealand. Thus, Marlborough District Council (MDC) has requested that Pattle Delamore Partners Limited (PDP) prepare a brief document outlining the use of field portable X-ray Fluorescence Spectrophotometry (XRF) for contaminated site investigations. MDC intends to use the information as a basis for assessing resource applications that include XRF analysis. This document is not intended to be an analytical training manual or to cover laboratory based XRF instruments.

X-ray Fluorescence Spectrometry (XRF) is a quick method for determining of the total elemental composition of soil samples. Unlike many laboratory techniques, XRF does not require any acid digestion techniques before the sample is analysed, therefore it can be a useful screening tool. As this technique is subject to a number of analytical interferences and analytical errors, the results of XRF investigations should only be used to undertake qualitative or semi-quantitative investigations of a contaminated site.

1.1   Scope

The scope of this report includes:

1. Preparing a brief outline on the theory and typical use of a field portable XRF.
2. Outline of the potential physical and analytical interferences associated with XRF analysis.
3. A statement on the health and safety considerations associated with operating XRF.
4. Brief outline on the soil preparation techniques for XRF analysis.
5. Data quality and quality assurance/ quality control measures that should be undertaken for field screening of soil samples with XRF.
6. Minimum reporting requirements associated with undertaking XRF measurements.

1.2   Primary References used to Prepare this Document

The information outlined in this document is based on the following reference documents:

A. Sections 3.9.1 and Section 4 of MfE (2004) to ensure quality assurance procedures outlined in this document are consistent with the QA/QC procedures recommended for other site investigation techniques undertaken in New Zealand.
B. The recommendations outlined in US EPA method 6200 (1998) using a portable or handheld XRF for undertaking semi-quantitative analysis.
C. The recommendations outlined in ISO 13196:2013 Soil Quality – Screening soils for selected elements by energy-dispersive X-ray fluorescence spectrometry using a handheld or portable instrument.
D. BS EN 15309:2007 Characterization of Waste and Soil- Determination of elemental composition by X-ray Fluorescence.

E. Innov-X system (2003). Metals in Soil Analysis Using Field Portable X-ray Fluorescence. A guideline to using portable XRF according to EPA method 6200, basic overview of the technique of x-ray fluorescence (XRF), appropriate data quality assurance protocols and sample preparation steps for operators analysing prepared soil samples.
F. Effective XRF Field Screening of Lead in Soil (Johnson, et al, 1995).
G. Advanced Design Application & Data Analysis for Field-Portable XRF (US EPA, 2005).

In some cases the recommendations in this document are not identical to those made in the above reference documents. These changes have been made based on the review of a number of published scientific journals articles on the performance of XRF and changes have been made to make the methodology consistent for use in a NZ regulatory environment (in particular the recommendations in MfE (2004).

2.0 Theory of X-Ray Spectrophotometry

2.1 Typical Use of Field Portable X-ray fluorescence in Contaminated Site Investigations

XRF instruments can be used for in-situ soil measurements of inorganic elements only, for qualitative or screening level assessments only (ISO 13196:2013; Innov-X, 2003). With limited sample pre-treatment (sieving and homogenising of the soil sample), XRF can provide semi-quantitative results.

If quantitative results are needed, sample pre-treatment with drying, sieving, homogenization and particle size reduction is necessary (See EN 15309) and analysis should be undertaken with laboratory equipment by an IANZ accredited laboratory. (The methodology for doing this is beyond the scope of this document.)

As neither XRF screening level nor semi-quantitative assessments meet the requirements of MfE (2004), XRF should not be relied upon as the sole source of information for undertaking human health risk assessments or site validation.

2.1.1 Screening Level Assessments

Screening level assessments are a rapid, non-rigorous site investigation method, which does not offer a definitive quantification of the concentration of the elements present. Therefore the results of these types of investigations by themselves **cannot be used to verify compliance with threshold limits or site remediation goals**.

Typically, screening level assessments are used to:

⸫ Identify potential hotspots on a site,
⸫ Provide an indication of the extent of contamination,
⸫ Provide preliminary identification of contaminants present,
⸫ Assist with remediation decision making,
⸫ Assist with screening of hazardous waste.

Screening level assessment should be undertaken in accordance with the requirements of ISO-13196 as a minimum.

2.1.2 Semi-Quantitative Level Assessments

Semi-quantitative level assessments provide an indication of the concentration of contaminants of concern.

Typically, semi-quantitative investigations can be used to:

- Assist with determining the appropriate soil sampling density and sampling locations for site investigation works (exploratory site investigations);
- Provide an indication of degree of heterogeneity of contaminants present on the site;
- Augment data used in assessing potential human health risk of average exposure to the site, provided that data quality objectives (outlined in Section 4.2) are met and a suitable verification of results has been undertaken;
- Undertake a Preliminary Site investigation assisting (with traditional information sources) to determine if it is more likely than not that the site is contaminated[1].

Semi-quantitative assessments should be undertaken to the necessary standard to meet the data quality objectives outlined in US EPA method 6200 (US EPA, 1998) and QA2 data quality objectives outlined in OSWER Directive 9360.4-01 (US EPA, 1990).

Semi-quantitative XRF investigations, which have acceptable QA/QC results can also be used to determine if a site is highly unlikely that there will be a risk to human health if the activity is done to the piece of land. However, this requires that:

- The investigation will need to be undertaken by a suitably qualified person with experience in undertaking contaminated site investigations and use of XRF.
- An intensive sampling approach has been undertaken on the site and no hotspots have been detected. The size of the grid will vary according to the size of the site, the sensitivity of the land use and the heterogeneity of the contamination present. For residential land use, grid sizes of between 10 and 30 m are typically used for XRF investigation, but in highly heterogeneous sites, grid sizes of less than 10 m are sometimes used.
- The guideline value or soil contaminants standard (SCS) is higher than the limit of quantification (3 to 5 times the instrument detection limit) of the XRF.
- At least three confirmatory laboratory samples[2] (usually the highest value) are analysed at an IANZ accredited laboratory.
- All the results of the XRF survey should be lower than the NES SCS (using the method outlined in Appendix J of CLMG#5).
- None of the laboratory results shall exceed the NES SCS.

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[1] For certain elements (i.e. As, Cd, etc.) some XRF may not be sensitive enough to undertake semi-quantitative assessments of residential sites.
[2] Note: For some sites this may mean that more samples need to be analysed for the site than recommended in Section 6.2.3.

2.2   Theory of X-ray fluorescence

X-ray fluorescence spectroscopy uses high energy photons (x-rays) to bombard an atom
and excite electrons orbiting the atom. Some of these photons have sufficient energy to
eject an electron which is bound to the nucleus of the atom. When an inner orbital
electron is ejected from an atom, an electron from a higher energy orbital will be
transferred to the lower energy orbital. During this transition, photons (x-rays) may be
emitted from the atom. This process is known as fluorescence, and the x-rays emitted
from the atom will be characteristic of that particular element. The energy (and therefore
wavelength) of the photon will be the difference between the two orbitals of the electron
making the transition. Because the energy difference between two specific orbitals, in a
given element, is always the same then the photon (x-ray) emitted from a particular
element will always have the same energy. Thus by measuring the energy of the photons
emitted, the XRF can determine the element that is emitting the photons, and the
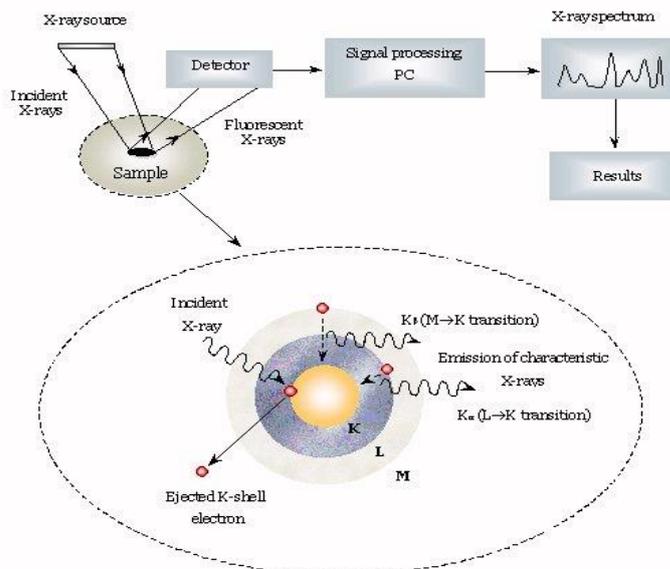concentration of element in the soil.

Figure 1: *The principle of XRF and the typical XRF detection arrangement*

3.0   Elements suitable for XRF analysis

Theoretically, an XRF is capable of analysing a variety of different elements, usually
between magnesium (Mg) and uranium (U) the periodic table. However the elements that
a particular type of XRF instrument can measure (and is calibrated for) can vary between
manufacturers. Many instruments are only calibrated for analysis between 20 to 25
elements and some instruments are not designed to detect light elements (magnesium to
sulphur) or bromine.

Typically the detection limit for XRF varies between 5 to 100 ppm. However, the
detection limit for an element is dependent on the element being analysed, x-ray source
and detector used by the instrument.

For antimony (Sb), cadmium (Cd), cobalt (Co), molybdenum (Mo) and vanadium (V) the XRF may not be sensitive enough (i.e. the lower limits of qualification of the instrument for those elements are too high) when compared to environmental or human health guideline limits or thresholds. Ideally, the instrument limit of detection (LOD) should be between 3 to 5 times less than the guideline value that are being used to assess the site[3].

4.0   Factors Affecting XRF Analysis

4.1   Interferences and Sources of Error

Inferences in X-ray fluorescence are due to spectral line overlaps, matrix effects, spectral artefacts, soil moisture and particle size or mineralogical effects.

4.1.1   Spectral Inferences and Spectral Artefacts

Spectral inferences occur when an elemental spectral line for one element overlaps with another element's line. Examples of spectra inferences include overlaps of spectra lines for sulphur and molybdenum, chloride and rhodium and arsenic and lead.

Another common spectra interference is adjacent element overlap (Z-1 and Z+1, where Z is the atomic number of the element of interest). This is called a Kα/Kß inference.

If the resolution of the detection is not sufficient to resolve the difference between the two element peaks then the instrument will potentially over-report the concentration of the element of interest. Two examples of this involves the presence of large concentrations of vanadium (V) when attempting to measure chromium (Cr) or the presence of large concentrations of iron (Fe) when measuring cobalt (Co). The peaks of vanadium and iron overlap with the peaks for chromium and cobalt respectively and therefore high concentrations of vanadium and iron will interfere with the quantification of these elements.

Because each element emits a variety of x-rays with different energies, another type of inference that can arise when some of these secondary peaks is overlap with various peaks of a different element (these types of interferences are called K/L, K/M and L/M peak overlaps depending on which energy levels within the atom a causing these peak overlaps). The most common example of this type of interference involves the overlap of the arsenic (As) Kα peak with the lead (Pb) Lα peak. The inference between arsenic and lead can be corrected by software using a mathematical correction factor over a certain range of lead concentrations. However, due to limitations of this mathematical technique, arsenic concentrations can not be effectively calculated for samples with a Pb/As ratio of greater than 10:1 (US EPA, 1998).

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[3] The detection limit for arsenic varies between 5 to 15 ppm for most instruments; however it is also influenced by the presence of soil moisture and the presence of lead. In samples with lead concentrations greater than 200 ppm the detection limit for arsenic could exceed 20 ppm and for samples with lead concentrations of greater than 1000 ppm the detection limit for arsenic may be greater than 45 ppm. Therefore, care is needed to determine if an XRF is used for investigating residential sites for arsenic contamination in the soil.

4.1.2   Matrix Effects

There are two main types of matrix effects, adsorption and enhancement effects.
Absorption effects occur when another element absorbs or scatters the fluorescence of
the element of interest. This results in the XRF detecting a lower concentration of the
element of interest.

Enhancement effects occur when the x-ray emitted from one element excites another
element, causing it to fluoresce. This results in the XRF reading a higher concentration of
the second element.

At very high concentrations of an element, one atom of the element can shield another
atom of that element from the x-ray emitted from the XRF. This results in the XRF under-
reading the true concentration of the element in the soil. This effect occurs only at a very
high concentration of a particular element and therefore may not be important for
screening level purposes; however it can be important when undertaking human health
risk assessments (because it results in the risk assessor underestimating the risk from
that element).

4.1.3   Soil Moisture

Soil moisture content of the sample can affect the accuracy of the analysis of a sample.
Generally the concentration of an analyte will appear to decrease as the moisture content
of the soil sample increases because the water in the sample absorbs x-rays (Kalnicky et
al, 2001). The overall error associated with soil moisture may be minor if the soil
moisture content is small (5 to 20%) but it becomes significant when the soil is saturated
with water (Kalnicky et al, 2001).

4.1.4   Particle size and Mineralogical Effects

Soil heterogeneity has the largest influence on the accuracy of XRF results (Argyranki *et
al*, 1997; VanCott *et al*, 1999, Johnson *et al*, 1995; US EPA, 1998). Physical matrix
effects such as changes in particle size, sample uniformity, heterogeneity and presence of
particles of high concentration of metals (i.e. lead shot, mineralised particles or lead
paint chips) can have a significant influence in the variability of sample results. This is
partly because the amount of sample analysed by a typical XRF is very small (typical size
of an XRF analyser window is less than 1 cm^2 and the depth of analysis is less than 2
mm). The inference effects of grain size, moisture, etc can be reduced by proper sample
preparation.

Sieving and homogenising of the samples are the two most common techniques employed
to minimise these effects.

4.1.5   Depth of X-ray penetration

X-ray fluorescence is a surface analysis technique, with the X-rays only penetrating
between 2 and 5 mm into the sample (Kalnicky et al, 2001). Therefore, if the soil being
analysed is covered by a thin layer of clean soil or organic matter (i.e. grass or organic

detritus) then the measurement of the sample may not be representative of the bulk of the underlying soil.

4.1.6   Interferences due to analysing a soil sample though a ziplock plastic bags

For most elements the use of thin ziplock bags does not have a significantly effect on the measurements undertaken using XRF. However, for barium (Ba), chromium (Cr) and vanadium (V), the use of a plastic bag can lower the results obtained by XRF by an additional 20-30%. This effect is due to the plastic adsorbing some of the x-rays emitted by the XRF at specific energy levels which would excite these atoms. Therefore, use of plastic bag for determining the concentration of these elements is generally not recommended.

4.1.7   Influence of Contact Angle on XRF results

The contact angle of the XRF with the soil influences the degree of accuracy of the sample results. When performing on-site measurements, the XRF analyser window should be placed parallel with the sample surface, which must be flat to achieve maximum contact between the XRF and the sample. Failure to achieve a suitable contact with the soil can result in attenuation of the x-rays and therefore lower the accuracy of the results.

5.0   Safety Considerations

Soil samples may contain toxic concentrations of various contaminants; therefore site personnel should avoid direct contact with soil samples with exposed skin. It may be necessary to take appropriate measures to avoid ingestion and inhalation of soil contaminants.

Exposure to x-rays may give rise to dermal and haematological diseases, therefore X-ray instruments shall comply with the National Radiation Protection Act (1965) and the National Radiation Protection Regulations (1982) and must be operated within the appropriate codes of safe practice. Users of the XRF must either hold a licence under the Radiation Protection Act, or act under the supervision or instructions of a licence-holder.

6.0   Sample Analysis Procedures

6.1   On-site Analysis

While XRF can measure undisturbed soil directly, it is recommended that a minimal soil preparation protocol is followed. On-site XRF measurements should be used for qualitative or semi-quantitative purposes only.

Operation of the XRF instruments will vary depending on the instrument type. Many instruments need a warm up period of 15 to 30 minutes before analysing the sample to help prevent drift or energy calibration problems later during analysis. Therefore it is important to follow the instrument manufacturer's protocols in operating the equipment when using XRF.

There are two ways to measure elements concentrations in soil using a XRF, these are in-situ and grab sampling. In-situ sampling is where the XRF is used to measure the soil in place. A grab sample is where a sample removed from the ground and undergoes some preparation before analysis. In-situ analysis is only a screening level methodology, whereas grab sampling can be either a screening level investigation or a semi-quantitative investigation depending on the level of homogenisation that a sample has been subjected to before analysis.

6.1.1   Sampling Protocol for In-situ analysis (Screening analysis only)

1. At the beginning of the day the field operator should check the functionality of the instrument and determined the accuracy of the instruments as outlined in section 6.2.2.

2. The field operator should undertake necessary instrument checks and check the integrity of the XRF window of the instrument. The visual check of the XRF window should confirm that the window is not torn and there is no residual soil present on the sampling window.

3. Analysis times of between 30 and 60 seconds are usually sufficient for screening level analysis.

4. The field operator should select a suitable sampling location for undertaking XRF measurements. The size of the area where XRF measurements are going to be undertaken should cover an area of approximately 10cm in diameter. XRF should not be undertaken on soils with free water present on the surface as this could result a non – representative measurement being obtained (see Section 4.1.3).

5. The field operator should identify the sample with a unique identifier and record the location where the sample was located (in accordance with section 3.7 of MfE (2004)).

6. The field operator should then remove any debris, such as leaves, stones, twigs and soils from the measurement area. In grassed areas, the top layer of soil should be removed so that the both the grass and the root zone of the grass is removed. Typically this would involve removing the upper 2 to 5 cm of soil.

7. The field operator should then loosen the soil to a depth of 15 to 25 mm over the measurement area.

8. For damp or very moist soils it may be advisable to allow the soil to dry for a few hours before measurement to improve accuracy.

9. Just before measurement, the operator should level the measurement area and gently pack down the soil.

10. At the end of the day the field operator should check the functionality of the instrument and determined the accuracy of the instruments as outlined in section 6.2.2.

6.1.2   Grab sample analysis

Grab sample analysis involves a sample being removed from the soil and analysed in an XRF cup or a ziplock plastic bag. Grab sampling method offers several advantages over in-situ measurements as they allow:

a) The same sample to be sent the laboratory for independent sample concentration verification,

b) May be easier to dry sample to below 20-30% moisture content,

c) Retains sample for repeated measurements to determine sample homogeneity.

6.1.2.1   Soil Preparation Protocol for Grab analysis (screening methodology)

1. At the beginning of the day the field operator should check the functionality of the instrument and determined the accuracy of the instruments as outlined in section 6.2.2.

2. The field operator should undertake necessary instrument check and check the integrity of the XRF window of the instrument. The visual check of the XRF window should confirm that the window is not torn and there is no residual soil present on the sampling window.

3. Increase instrument analysis times of 200 to 300 seconds to improve accuracy and precision of the instrument.

4. Label the bag with a unique sample identification number and fill out the necessary sample documentation (in accordance with MfE (2004).

5. The field operator should then remove any debris, such as leaves, stones, twigs and soils from the sample before placing the sample within the plastic bag.

6. If samples are moist, allow the samples to air dry for several hours.

7. The field operator should mix the bag by kneading the sample (for clay soils) and/or turn the bag end-over-end. Visually inspect the soil sample in the bag to judge uniformity of the particle size. Do not shake the bag as this can cause particle segregation and increase the data variability.

8. Create a smooth flat surface for analysis (if the sample contains a significant amount of clay then the sample may need to be moulded flat). Ensure there are no airspaces in the sample and fold bag over tightly to enclose the sample. The thickness of the soil sample should be no less than 5 mm and ideally more than 10 mm.

9. Do not through creases or crinkles in the plastic bag as this can increase the data variability.

10. The field operator should undertake necessary instrument check and check the integrity of the XRF window of the instrument. The visual check of the XRF window should confirm that the window is not torn and there is no residual soil present on the sampling window.

6.1.2.2   Soil Preparation Protocol for intrusive sample analysis (semi-quantitative methodology)

1. The field operator should undertake necessary instrument check and check the integrity of the XRF window of the instrument. The visual check of the XRF window should confirm that the window is not torn and there is no residual soil present on the sampling window.

2. Label the bag with a unique sample identification number and fill out the necessary sample documentation (in accordance with MfE (2004).

3. The field operator should then pass the sample though a 2 mm sieve to remove any debris, such as leaves, stones, twigs and soils from the sample before placing the sample within the plastic bag.

4. Sample should be homogenised in accordance with the methodology outlined below[4]:

   ∴ For samples which are already relatively well homogenised, the samples can be fully homogenised by mixing the sample for 3 to 5 minutes or by using a coning & quartering process.

   ∴ For moist samples with high clay content kneading of the sample in a plastic bag for 3 to 5 minutes per sample may be sufficient.

   ∴ For highly heterogeneous samples, sample drying, grinding with a mortar and pestle (until the sample pass through 60-mesh sample) and sieving may be required.

   ∴ Visually inspect the soil sample in the bag to judge uniformity of the particle size. Do not shake the bag as this can cause particle segregation and increase the data variability.

5. A 10 to 20 g portion of the sample could be air dried under ambient temperature if the sample is dry or slightly moist. Alternatively, if the sample is wet or taken from saturated soils, the sample could be dried for 2 to 4 hours either using a convection or toaster oven or a suitable infra-red heat lamp at a temperature of no greater than 150 ° C.

6. Create a smooth flat surface for analysis. Ensure there are no airspaces in the sample and fold bag over tightly to enclose the sample. The thickness of the soil sample should be no less than 5 mm and ideally more than 10 mm.

7. Do not through creases or crinkles in the plastic bag as this can increase the data variability.

6.2   Quality Assurance/ Quality Control

The aim of any quality assurance/quality control programme is to determine if the precision and accuracy of the data obtained from the instrument is adequate to meet the project's data quality objectives.

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[4] The level of effort required for homogenization required will be dependent on the project data quality objectives and the intrinsic heterogeneity of the sample.

6.2.1 Determining Precision

Precision is determined by repeated measurement (replicate analysis) of a sample which is at or near the action level or level of concern.

Screening Level Assessment (US EPA QA1 Data Quality Objective)

ISO - 13196 and US EPA (1999) do not require precision samples[5] to be analysed for screening level assessments.

However, if the operator wishes to understand the potential variability in the data to assist with decision making, the recommended approach to determine the precision of in-situ analysis is to take triplicate adjacent analysis from the sampling area at a frequency of 1:10 samples (for a small sampling project) or 1:20 samples (for a larger project i.e. >100 sampling locations). Undertaking a precision check can be useful for determining when the results of the screening assessment are above or below a critical trigger value. This can allow the operator to make better decisions when remediating a site or which areas of a site may require additional measurements.

Semi-Quantitative (US EPA QA2 Data Quality Objective)

At least eight non-consecutive analyse of the precision sample should be undertaken each day of the project. For larger jobs (more than 80 samples) it would be typical to analyse this sample after every 10 samples or sampling locations.

The precision of the methodology is assessed by calculating the relative standard deviation (RSD) of the replicate measurements for the analyte. The RSD values should be less than 20 percent for most analytes, except chromium, for which the value should be less than 30 percent.

The data from the precision sample analysis can be used to calculate the uncertainty of analysis using the methodology outlined in Appendix J of MfE (2004). This will allow investigators to determine areas of the site which are likely to be lower than guidelines (or background concentrations) values and areas of the site which are likely to higher than guideline (background concentration) values.

6.2.2 Determining Accuracy

There are 3 basic checks that should be performed (and documented) every time a XRF is used. These are undertaking a blank sample analysis using a silicon dioxide (SiO_2) blank, energy calibration check and analysis of reference material.

Analysis of Blank Sample - This is used periodically to check that there is no contamination on the XRF window. It is recommended that this check is undertaken for

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[5] A precision sample is a sample which undergoes multiple analysis to determine the precision of the xrf measurements.

at least 1 sample in every batch of 20 samples for any in-situ measurements of samples[6] or at least twice per day for analysis of bagged samples.

Energy Calibration Check – An energy calibration check should be undertaken every time the instrument is turned on and at least once per day. Many analysers perform this check automatically.

Analysis of a Standard Reference Material – Analysis of a standard reference material beginning of the day and end of each day. On larger jobs it may be more appropriate and cost effective to prepare reference material from the site. Reference material should be selected containing the elements of interest and covering the concentration range of interest. Additionally, where available, reference materials with a similar composition of the samples under investigation should be selected.

For XRF to be considered accurate, the measured value should be within 20 % of the certified value for the reference material (for chromium and nickel $\pm$ 30% is acceptable). The percentage difference between the certified and measured value of the reference material can be calculated using the following formula:

$$\%D = \left(\frac{C_s - C_k}{C_k}\right) x\ 100$$

%D = Percent difference

C_k = Certified concentration of standard sample

C_s = Measured concentration of standard sample

6.2.3 Determining Data Comparability

Determining data comparability can be undertaken by using two different techniques. The first method is designed to determine when the data generated from the XRF will exceed or be below a certain guideline or trigger value. The methodology for determining this is outlined in Appendix J of MfE (2004).

The second method for determining data comparability is sending samples to an off-site laboratory for formal analysis (this is called a confirmatory sample). One confirmatory sample should be collected for every 20 samples analysed by XRF. For semi-quantitative assessments a regression analysis should be undertaken. The calculated regression co-efficient (r^2) should be between 0.7-1.0 (Q2 criteria US EPA, 1990).

The first method is suitable for field screening techniques and when using a XRF to make real time decision on soil remediation. This technique should be used to asses at what concentration ranges you can be certain to be above or below guideline levels or trigger values.

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[6] A minimum of at least two blank samples should be analysed for any in-situ investigation regardless of the number of samples being undertaken. One of the blank analyses should be undertaken at the start of day to verify that the instrument is working correctly.

Both the first and second method should be undertaken to determine data comparability when XRF is being used to undertake a semi-quantitative assessment of the site.

7.0   Data Analysis and Reporting of Results

Reporting of the result from an XRF investigation would need to comply with the reporting requirements of MfE (2003). In addition to these requirements the following information would also need to be provided:

- Rationale for the sampling location or sampling density used in the investigation;
- The type of instrument used in the survey;
- The type of calibration method used to calibrate the instrument and provide a calibration certificate for the instrument;
- The analysis time for each test;
- Note any special features of the type of instrument for dealing with interferences (i.e. Compton normalisation to correct for soil moisture effects, As/Pb mathematical corrections, etc.) would may affected the results;
- Type of investigation method employed (i.e. screening or semi-quantitative);
- Provide a brief outline of methodology used to prepare soil sample and undertake analysis, including:
    - Standard methodology used (i.e. ISO 13196:2013, BS EN 16424, US EPA Method 6200, BS EN 15309 or other),
    - State any variations from the method and how they may potentially affected the analysis results,
    - Quality assurance/quality control testing undertaken.
- Results of quality assurance/quality control testing;
- Sample location plan;
- Complete identification of samples;
- The results of Investigation;
- Statement of the fitness of purpose of the results with respect to accuracy and precision of analysis (for semi-quantitative investigations).

8.0   References

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