# Field use of X-ray fluorescence spectroscopy for investigation of contaminated soils

Ministry for the Environment
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# Abbreviations

| Abbreviation | Term |
|---|---|
| CLMG 1 | *Contaminated land management guidelines No 1: Reporting on contaminated sites in New Zealand (Revised 2021)* |
| CLMG 5 | *Contaminated land management guidelines No. 5: Site investigation and analysis of soils (Revised 2021)* |
| IANZ | International Accreditation New Zealand |
| keV | kiloelectronvolts |
| mm | millimetre |
| NESCS | Resource Management (National Environmental Standard for Assessing and Managing Contaminants in Soil to Protect Human Health) Regulations 2011 |
| PARCCS | precise, accurate, representative, complete, comparable, and sensitive |
| QA/QC | quality assurance and quality control |
| QMS | quality management system |
| SAP | sampling and analysis plan |
| SCSs | soil contaminant standards |
| SQEP | suitably qualified and experienced practitioner |
| SRM | standard reference material |
| XRF | X-ray fluorescence spectroscopy |

# 1 Introduction

Field portable X-ray fluorescence spectroscopy (XRF) is a non-destructive field analytical technique that can be used to rapidly analyse and quantify the composition of soil samples *in situ*.

## 1.1 Purpose

This guidance covers what constitutes good practice when using field portable XRF instruments to analyse soil samples at known or suspected contaminated sites. It also covers the analysis and interpretation of data collected during such investigations. It is not a training manual or a reference for how XRF works or how to use specific devices.

The use of XRF in contaminated land investigations can meet the requirements for **field screening** techniques in the *Contaminated land management guidelines No. 5: Site investigation and analysis of soils* (CLMG 5) (Ministry for the Environment, 2021b).

Modern portable XRF instruments are literally 'point-and-click', and operators can easily reach incorrect conclusions if they do not understand the limitations of the device. Good XRF practice requires users to implement appropriate quality assurance and quality control (QA/QC) throughout the investigation to ensure data gathered is robust.

Complying with CLMG 5 is a legal requirement for site contamination investigations undertaken under the Resource Management (National Environmental Standard for Assessing and Managing Contaminants in Soil to Protect Human Health) Regulations 2011 (NESCS) and most regional plans.

This guidance sets out situations where field XRF can be used in contaminated land investigations, some situations where it cannot, and a range of controls to help obtain robust results. It covers **qualitative applications**, where the investigator is considering where heavy elements are contaminants of concern, and **semiquantitative applications**, where the investigator wants to supplement laboratory analyses with field XRF data.

This guidance **does not cover quantitative applications** in which field XRF might replace laboratory analyses.

This guidance does not cover field XRF analysis of rock, paint or any material other than soil.

This guidance assumes the use of a modern instrument with an electronic source of X-rays (not a radioactive source) and fundamental parameters calibration.

## 1.2 Use of this guidance

This guidance has been prepared to help contaminated land practitioners to use XRF as a field analytical technique in a way that gives councils assurance it has been applied in an appropriate and scientifically reliable way. Any deviation from this guidance must be explained in the sampling and analysis plan and/or any subsequent reports that rely on data collected using XRF.

This guidance is not a standard and has no regulatory status. Terms such as 'must' are used only to indicate things an investigator needs to do to claim they have followed this guidance.

For NESCS purposes, a suitably qualified and experienced practitioner (SQEP) must supervise investigations and certify reports.

Regulators, land owners, land managers and other stakeholders may find this guidance useful for specifying work to be undertaken or for assessing results. Other soil scientists are welcome to draw on it, although it has been developed for analysis of soil as part of contaminated land investigations, and such users must exercise their own judgement as to whether it meets their needs.

## 1.3 Workplace health and safety

X-rays are dangerous, and X-ray applications such as XRF are regulated accordingly under the:

- Radiation Safety Act 2016
- Radiation Safety Regulations 2016
- Code of practice for irradiating apparatus (ORS C10) (Ministry of Health, 2020).

As a general principle, exposure to X-rays should be kept as low as reasonably achievable and, in all cases, within occupational exposure dose limits. Modern XRF instruments use electronic X-ray- sources that only produce X-rays when energised, and therefore are only dangerous if used inappropriately or if shielding is damaged. For these instruments, expected controls include the following.

- Maintain a controlled area around and 'forward' of the instrument during operation in which only the user is permitted. Particular caution is required for older instruments without proximity cutoffs.
- Users must never point the XRF toward any body part, must never hold a sample in the hand for scanning, and must avoid scanning legs and feet through an unshielded work surface.
- People who are (or may be) pregnant should not be using an XRF instrument unless additional precautions can be taken to prevent exposure.

Every location where XRF instruments are held and managed must have a source licence and a radiation safety officer. Every operator must hold a user licence, or work under the direct supervision or written instruction of a user licence holder. All operators must have formal training in radiation safety and instrument use from a training provider recognised by the Office of Radiation Safety.

If in any doubt, consult the instrument manufacturer, a radiation safety specialist and/or the Office of Radiation Safety at the Ministry of Health.

As with all site contamination work, handling soil samples can be dangerous and should be undertaken in compliance with regulatory health and safety requirements.

# 2 X-ray fluorescence spectroscopy

X-rays are a form of electromagnetic radiation with shorter wavelengths and higher energies than ultraviolet light. As X-radiation passes through matter, a proportion is absorbed. Heavy elements absorb much more radiation than light elements. Absorption decreases rapidly as X-ray- energy increases.

When an atom absorbs an X-ray photon, it ejects an inner-shell electron, and an electron from an outer shell ‘falls’ into the place of the ejected electron, releasing more X-ray photons in all directions, which is called ‘fluorescence’.

Fluorescence is always much weaker than the primary beam, and of lower energy, although still in the X-ray range. Although it cannot be seen, fluorescence can be detected by specifically designed instruments.

Each element has a characteristic atomic structure, with electron shells at set energy levels, so its fluorescence also has a characteristic spectrum, with peaks at specific energies corresponding to specific electronic transitions. Heavier elements have more peaks in their X-ray- spectrum, at steadily higher energies. These differences make it possible to distinguish elements within a material, making the technique of XRF possible. In XRF, energies are usually measured in keV (kiloelectronvolts).

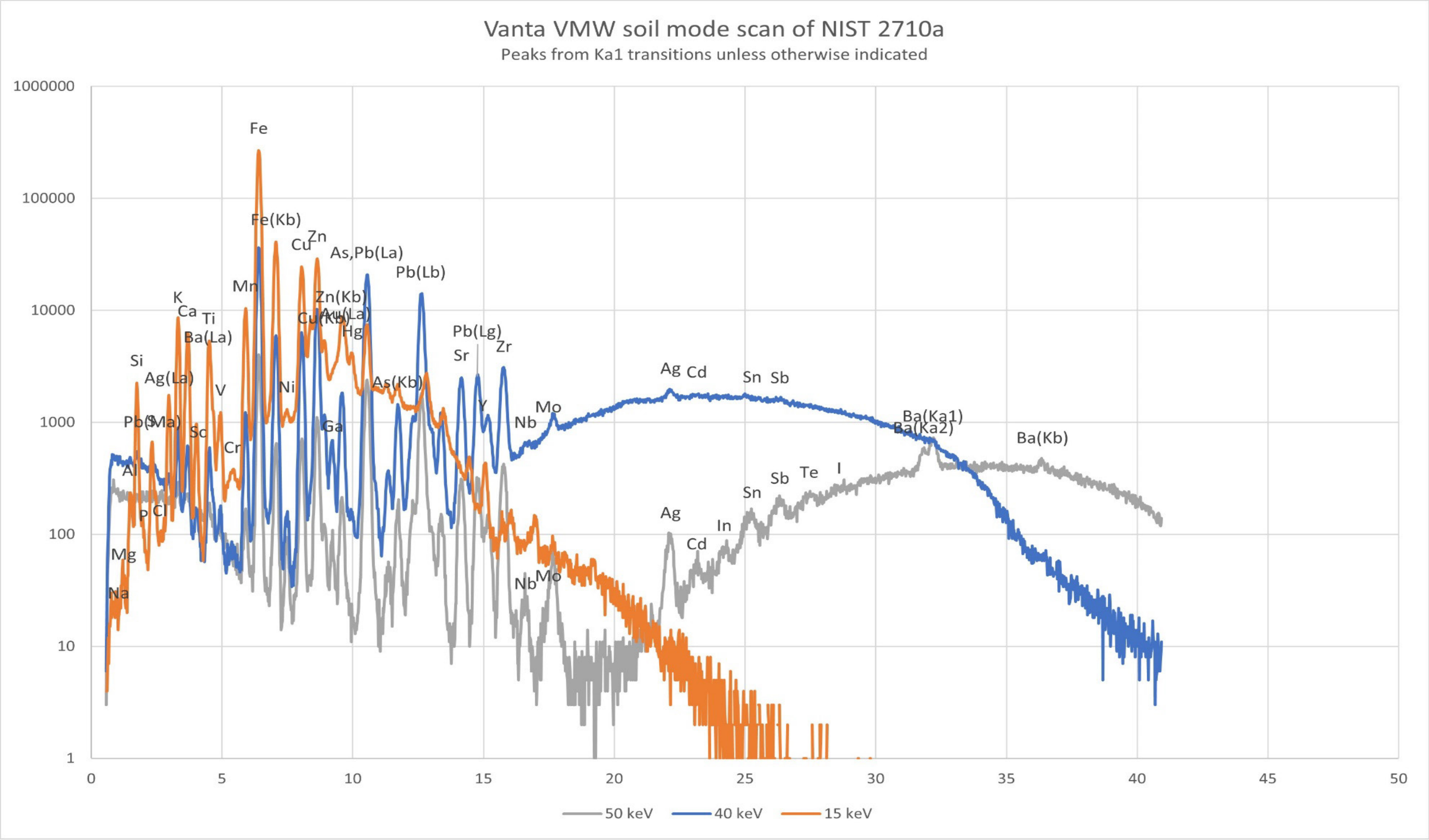
However, some elements can be difficult to distinguish because the peaks on their X-ray spectra partly overlap. This is referred to as ‘interference’, which is almost always the case for adjacent elements on the periodic table, which necessarily have very similar spectra with a lot of overlap (the ‘$Z$+1 problem’). Additionally, heavy elements with multiple peaks in their spectra are more likely to overlap with other elements, purely by chance. For example, lead (a very heavy element, with atomic number $Z = 82$) has at least four peaks in the field XRF energy range; one of these (the ‘Lα’ peak) happens to overlap with the primary peak (‘Kα’) of arsenic ($Z = 33$).

The more of an element contained in a material, the more it will fluoresce when exposed to X-rays. Therefore, interference permitting, XRF can be used to determine concentration as well as composition. At high concentrations, processes such as shielding and multiple absorption become perceptible (as does detector overload), so the relationship between fluorescence and concentration is sublinear over orders of magnitude: XRF tends to under-report high concentrations.

Complicating matters further, XRF fluorescence depends on the primary beam energy as well as the composition of the material being irradiated. The best response is obtained for peaks about half the energy of the primary beam. Therefore, some XRF instruments make multiple scans using different primary beam energies. For particularly heavy elements, the highest energy peaks (Kα and Kβ) are more than 30 keV and cannot be efficiently generated or detected in field instruments at all. These elements are identified and quantified from lower-energy L peaks that are in the working range.

Figure 1 presents field XRF scans of a standard reference soil at three different primary beam energies.

**Figure 1:** **Field X-ray spectra of a standard reference material at different primary beam energies**



# 3 Applying XRF to contaminated soils

Modern field portable XRF instruments are designed to be simple to use. The operator should, however, be fully aware of the potential issues that can arise from improper use of the instrument, or errors that can occur when the circumstances surrounding its use are not fully understood and accounted for.

When using XRF instruments, characteristics and variables that affect the results must be taken into consideration when determining the suitability of XRF as an analytical technique.

## 3.1 Concentrations are totals

Because XRF involves only non-bonding electrons, it does not provide any information about chemical bonding and chemical form. For example, XRF cannot distinguish between metallic chromium $Cr^0$, trivalent chromic ion $Cr^{3+}$ or hexavalent chromate $CrO_4^{2-}$.

In soils, some elements may be present in forms that cannot be extracted by a ‘total recoverable’ chemical analysis, such as chromium or uranium as impurities within a silicate matrix. These forms can still be detected by XRF. As a result, concentrations determined by XRF can be significantly higher than concentrations determined by a laboratory.

## 3.2 Detection limits vary for each element

The characteristic fluorescence energies of lighter elements are so low that, in solids such as soils, the emitted X-rays are absorbed almost immediately by the surrounding material. Because so much of the fluorescence is absorbed, the lightest elements (up to at least neon, atomic number $Z = 10$) cannot be detected at all; detection limits are relatively poor up to at least calcium ($Z = 20$) and, for some instruments, to manganese ($Z = 25$).

In practice, a second group of elements are also detected using low-energy fluorescence and therefore also have poor detection limits. Depending on the instrument’s source and detector technology, this group may begin as soon as rhodium ($Z = 45$) and continue into the lanthanides ($Z = 57–71$).

Some elements are more toxic than others and therefore of greater interest in a contaminated-site investigation. Poor detection limits may be a problem, depending on whether the element in question is of interest to the investigator.

As a general rule, **XRF is only an appropriate analytical technique if the soil guideline value of an element of interest is at least three times the instrument’s detection limit**.

Any investigation report that relies on XRF should state the detection limit for all elements of interest and should clearly state all results that are less than three times the detection limit of the XRF device used.

## 3.3 X-ray penetration depth affects results

The XRF detector can only analyse material a short distance into the sample because the soil matrix strongly absorbs low-energy X-rays. Although penetration depths depend on many factors, **for elements with low-energy fluorescence, that depth is a small fraction of a millimetre**. This can make field XRF quite unreliable unless the element is evenly distributed within the soil, because only the surface of the soil particles is scanned. Where the composition of a soil particle differs at the surface and in the centre, the XRF result may not represent the bulk of the sample.

## 3.4 Soil matrix affects X-ray absorption

Different soils absorb X-rays differently. An organic soil comprised principally of light elements will absorb less than a mineralised soil with high levels of heavier elements such as iron. Modern approaches to XRF calibration via 'fundamental parameter analysis' can alleviate this problem but not eliminate it.

In practice, **moisture content** can be a major source of matrix effects. Soil absorbs more X-rays when wet, because water is an additional absorber. Consequently, a wet sample will appear to contain less contaminant. This is particularly important when different samples from the same site have different moisture contents.

## 3.5 Soil heterogeneity

Soils are complex materials. Soil properties, including contaminant concentrations, may vary on many scales. The main advantage of field XRF is that many more measurements can be taken in a given time than with traditional soil sampling and laboratory analysis. Thus, XRF can help measure and understand soil variation on the 10-metre, metre and 10-centimetre scales. However, with a field of vision several millimetres wide and some millimetres deep at best, XRF is highly vulnerable to matrix variation on the centimetre scale. If penetration depth is short, then even submillimetre variation will cause problems.

## 3.6 Interference

Because of the '*Z*+1 problem' (see section 2), it is difficult to quantify an element when its neighbour on the periodic table is present at a significantly greater concentration, say 10 times or more.

High concentrations of heavy elements may also cause interference problems; for example, arsenic can be difficult to quantify in the presence of lead.

The XRF provides a list of characteristic X-ray fluorescence energies that can be used to check for possible interferents.

Interference problems are reduced in modern XRF instruments, which have better detectors and signal processing and may determine concentration based on multiple peaks.

## 3.7 Instrument effects

Detectors can become overloaded at high count rates, leading to XRF instruments under-reporting high concentrations. This is a different mechanism from the other causes of sub-linearity mentioned in section 2.

XRF instruments generally report concentrations only when the signal is at least three times the estimated measurement error (σ). When this is not achieved, the instrument reports a ‘less than’ concentration of 3σ. Note that this is not the same as a practical detection limit and, moreover, can vary from sample to sample.

XRF instruments generally allow users to control the duration of the scan. The longer the scan, the more data collected, and the more precise the measurement. In theory, doubling the scan time should reduce measurement error by about 30 per cent.

Instrument performance can vary. Gradual and even sudden drifts have been reported, especially in older instruments with poor temperature control.

## 3.8 Handling effects

XRF requires samples to be located at a standardised small distance from the tube window and at a known angle of incidence (ideally perpendicular). The tolerances for instrument placement and for the flatness of the surface must be very tight to maintain a repeatable X-ray flux.

# 4 XRF as a field investigation technique

## 4.1 Applications for XRF in field investigations

Field XRF can measure some common contaminant elements in soil and sediment in real time, with great ease and at low operating cost, making it a powerful tool for investigating site contamination. Used appropriately, field XRF gives investigators the ability to collect much more data for a given budget and to make sampling decisions in the field. Accordingly, it is well suited to **qualitative objectives**, such as:

- helping the investigator choose **where to collect soil samples** and **what to analyse for**
- providing one line of **evidence that a hazardous activity or industry is likely to have occurred** at a site
- checking for **'hotspots'** and small areas or volumes of significantly more contaminated soil.

Field XRF can also be extremely useful for **semiquantitative objectives**, such as:

- **delineating a contaminated area, depth or volume** of soil
- estimating **supporting chemical parameters**, such as iron concentrations, that may be a geochemical parameter that is part of a conceptual site model but not a contaminant of concern.

Nonetheless, field XRF has several important limitations, including the following.

- Concentrations are totals, giving no information about chemical speciation or leachability.
- Detection limits vary according to the element and, for many elements, are poor; the penetration depth of the X-ray beam into the sample may be only a fraction of a millimetre.
- Effective sample volume is very small, on the order of a cubic centimetre at best.
- Results can be compromised by various factors, including interfering elements, soil conditions and poor instrument handling.
- Many contaminants exist that are not measurable with XRF, including some NESCS priority contaminants.
- The investigator must do their own QA/QC, rather than delegating it to a laboratory as with conventional chemical analysis.
- Field XRF instruments are expensive.

Consequently, even in ideal conditions, considerable care is needed to get precise, accurate, representative, complete, comparable, and sensitive (PARCCS) data.

**Field XRF is a field screening technique** as defined in CLMG 5 (Ministry for the Environment, 2021b).

Field XRF generates **quick data at the expense of quality data**.

For the avoidance of doubt, field XRF is **not a quantitative technique** and **should not be considered to be equivalent to a laboratory analysis** for the purposes of the NESCS, **unless** investigators are:

- International Accreditation New Zealand (IANZ) accredited under ISO 9001:2015 *Quality management systems*, and
- IANZ accredited under ISO 17025:2017 *General requirements for testing and calibration laboratories* to analyse soils by field XRF, and
- working strictly in accordance with the above accreditations.

## 4.2 Contaminants

Field XRF can generally be applied to the following contaminants of concern:

- **copper** and **zinc**, potentially subject to mutual interference
- **arsenic**, potentially subject to interference from high lead
- **mercury**
- **lead**.

This short list captures contaminants of concern for around half the categories on the *Hazardous Activities and Industries List (HAIL)* (Ministry for the Environment, 2011).

Field XRF is often useful for contaminated sites such as timber treatment sites that used chromated copper arsenate, sheep dips that used arsenic, pipfruit orchards that used lead arsenate, and epithermal gold or silver mines. It can also be used on soils with naturally elevated arsenic.

**Field XRF must not be used for chromium or any other contaminant element with low characteristic peak energies** (less than around 7 keV). This proscription includes silver, cadmium and antimony, unless the instrument scans up to 45 keV. It also includes barium, unless the instrument scans up to 50 keV. At these low peak energies, penetration depths in most soils are minimal (mean free path likely less than 0.1 mm); results are sensitive to water content; and major elements, such as iron, titanium and calcium, may cause significant interference.

Moreover, for most such elements, detection limits are poor, relative to natural background concentrations and relative to soil contaminant standards for sensitive land uses. For chromium specifically, XRF cannot distinguish between the more toxic chromium (VI) form and less toxic chromium (III) and metallic forms; or between 'total recoverable' chromium and the matrix chromium in soils derived from ultramafic rock.

Although, in principle, some instruments can be used for cadmium, detection limits may still be inadequate for sensitive land uses, such as typical rural–residential or residential scenarios. Some instruments may also have inadequate detection limits for arsenic in these scenarios, especially if scan times are short.

Even for applicable elements, field XRF **should not be used for contaminants in particulate form**, such as shotgun pellets, paint chips and metal droplets (such as welding spatter). In these circumstances, results will be entirely dependent on whether there are any contaminant particles in the soil volume being scanned. If an elevated concentration is detected by XRF, and closer inspection reveals this is due to a highly enriched particle, that could be a useful finding and could add significant information to the conceptual site model.

Light elements, asbestos, and organic compounds, such as petroleum hydrocarbons or organochlorine pesticides, cannot be analysed by XRF. **An investigator must not assume a site is not contaminated on the sole basis that XRF measurements have not detected any contaminants at levels that exceed the relevant guideline value or soil contaminant standard.**

## 4.3 Soils

Field XRF is best suited for use on visually homogeneous soils with a low moisture content.

**Field XRF cannot be applied to coarse sands and gravels or to fills containing waste materials**. Heterogeneity, matrix effects and handling effects have a greater impact on results in these soils. Clean gravel, shell, roots and other inert material must be avoided or removed by sieving or hand picking. Any actions taken – such as picking, sieving or sorting – must be recorded in the investigation report in sufficient detail for a reader to be able to replicate the process.

Similarly, **mottled or finely banded soils should not be scanned *in situ***, though *ex situ* analysis should still be valid.

**Field XRF should not be applied to sediments and wet soils *in situ***; *ex situ* analysis with drying should still be valid.

# 5 Sampling and analysis plan

XRF can readily complement desk-based research and conventional sampling via a well-designed sampling and analysis plan (SAP).

Field XRF can be part of any sampling strategy: judgemental, grid, transect or patterned. 'Ranked set' sampling (USEPA, 2002) was devised to take advantage of the real-time information provided by rapid-measurement techniques such as XRF. Special considerations to take into account when using field XRF include the following.

- Plan to take **enough laboratory samples to characterise the site**. If the investigation needs to determine whether a site meets acceptance criteria, that decision must be based on appropriate laboratory analyses, unless field screening clearly shows that contaminant concentrations are well above or below criteria. See section 6.6.
- Planning for this eventuality can save time and expense by ensuring sample containers, labels and equipment are available to the investigator, rather than undertaking a second field visit to gather laboratory samples.
- **Make use of adaptive sampling**. Revise the conceptual site model as data is collected; add extra sampling locations and even contaminants of interest accordingly. Do not assume that a lone elevated result indicates a large area or volume of contamination. Make multiple measurements in the vicinity, and at greater depth, to confirm the result and inform any subsequent assessment or action. This is where field screening comes into its own. Refer to Ministry for the Environment (2021b) and Barnes (2009).
- **Never composite samples for XRF analysis**. Taking individual measurements is likely to be quicker and simpler than preparing and analysing a sufficiently homogeneous composite.
- **Only use field XRF as appropriate**. Deploy other field screening methods, or sampling and laboratory analysis, as needed to assess contaminants in particulate form, contaminants that cannot be detected by field XRF, and soils or substrates for which XRF is not appropriate.

# 6 Quality assurance and quality control

## 6.1 General principles

Quality assurance and quality control are essential elements of the systematic planning process for site investigation (Ministry for the Environment, 2012b). This is particularly true for field XRF where considerable care is needed to get PARCCS data. Nonetheless, the QA/QC should be proportionate to the needs of the investigation.

The focus of an investigation using field XRF should be on collecting data that are fit for purpose and support defensible decisions, rather than on achieving analytical precision at any cost. A large set of lower-quality data points may have a higher information value than a small set of high-quality data points, if the less-precise dataset is collected using good technique and appropriately recorded, analysed, and the findings documented.

**Always report all QA/QC controls and measurements.** Reviewers should reject all field XRF data that are not accompanied by QA/QC information.

## 6.2 User factors

All users must be trained and licensed to operate the XRF. Inexperienced users should be supervised by an experienced operator until they are competent. Instrument manufacturers and professional bodies may be able to help source appropriate training. Evidence of training and certification should be provided as part of reporting.

Training records, including details of courses, examinations and certifications or licences held by each operator must be kept by the operator and/or their employer.

Written operating procedures for field use of XRF should be created and made available for all XRF operators.

## 6.3 Instrument factors

Keep the XRF instrument clean, maintained and independently calibrated according to the manufacturer's instructions. Recalibration by the service agent is typically recommended every two-to-three years.

Records of performance of the XRF must be kept and made available for applicable contaminants against standard reference materials (SRMs) and blanks (see section 7.4). Check the instrument for physical causes (for example, a dirty window) and recalibrate promptly if significant instrument drift is observed.

Instrument drift refers to the instrument reading a different value for an SRM over time. Significant instrument drift would be where a result from an SRM differs by more than 30 per cent from previous analyses of the same SRM.

## 6.4 Systems and processes

Good quality results are usually supported by a quality management system (QMS) that:

- focuses on meeting the requirements of good science, contaminated site regulations and guidance, and this guidance
- provides for an XRF practice leader
- supports and engages field staff in following operating procedures
- manages XRF use as a process
- seeks continuous improvement
- requires evidence-based decision-making
- maintains good relationships with instrument manufacturers and regulators.

Consider adopting a laboratory QMS compatible with ISO 9001:2015 and ISO 17025:2017.

An efficient workflow process should be documented and followed.

## 6.5 Precision

Precision refers to the closeness of agreement between test results obtained under stipulated conditions (ISO 5725-1:2023), or agreement between repeated measurements of the same measurand. When poorly handled and/or used in unsuitable situations, field XRF can generate very imprecise results. Therefore, it is important to understand the precision of all field XRF measurements. Precision can be critical when delineating contamination.

Precision is assessed simply by making many replicate measurements and observing how well they agree.

**The minimum requirement for all field XRF is one replicate measurement per ten sampling points, or six replicate measurements per soil type, whichever is the larger.**

How this is achieved is up to the investigator; six duplicate measurements of separate sampling points, or six replicate measurements of a single sampling point, are usually equally valid.

A variation of more than 50 per cent within any set of replicate measurements should always give the user immediate cause for significant concern. This most likely indicates that the soil is excessively heterogeneous and could also indicate that instrument handling is poor.

If variation is high, the following steps should be taken.

- Inspect the soil carefully to see if any reason is visible for the high variation, such as particles of contaminated material. If so, field XRF is not an appropriate field method for this soil.
- Make replicate measurements of a standard reference material to determine whether the variation is due to instrument or handling effects.
- If the variation is the result of operator error, retrain the user and treat all their results with great caution. If the instrument is faulty, ensure it is serviced or replaced.
- Collect more data: make more replicate measurements at the same sampling point(s) to determine whether the mean variation is excessive.

If variation is still high, implement some or all of the following controls (refer to section 7 as necessary).

- Use a soil foot or instrument stand to reduce handling effects.
- Increase scan duration.
- Make measurements *ex situ*.
- Increase soil-mixing time.
- Air-dry samples.
- Collect larger samples.

These measures should reduce variation, compared to *in situ* measurement (compare with USEPA, 2007). If these measures do not reduce variation, field XRF is not a suitable field method for that soil.

**For semiquantitative applications, when comparing field XRF measurements to assessment criteria, the coefficient of variation must be less than 30 per cent in the vicinity of the corresponding criterion.** (When soil concentrations are significantly higher or lower than assessment criteria, precision is relatively unimportant.) If this cannot be achieved, field XRF is not applicable. Therefore, in this kind of investigation, the user must be prepared to:

- implement some or all of the QA/QC controls above from the outset
- reject the field XRF dataset and begin the investigation again, using a different approach.

## 6.6 Accuracy

Accuracy refers to how close mean measurements are to true values, and is a combination of trueness and precision. Field XRF results rarely exhibit high accuracy, because of matrix effects that vary from soil to soil. However, it is also rare that field XRF measurements diverge far from laboratory results. Accordingly, **it is only necessary to assess accuracy when using field XRF semiquantitatively**, that is, when comparing measurements to criteria. There is no need to assess accuracy when using field XRF qualitatively, including situations when measured concentrations are well above or below criteria (indicatively less than half or more than double).

When qualitatively characterising a site using XRF:

- if the XRF results are less than half the relevant soil contaminant standard, the soil is very unlikely to exceed the relevant soil contaminant standard (SCS)
- if the XRF result is more than twice the SCS, the soil very likely exceeds the relevant SCS
- for cases where the results are not clearly above or below SCSs, appropriate laboratory analyses would be necessary to confirm the field results.

Accuracy is estimated by comparing field XRF measurements to laboratory analyses for the same samples. Although laboratory analyses also have limited precision and accuracy, typically they are superior to field XRF, because they are much more tightly controlled, and samples are prepared for laboratory analysis in accordance with strict protocols. **For semiquantitative applications, the minimum requirement is one matched laboratory analysis per ten XRF sampling points, or six matched laboratory analyses for each soil type, whichever is the larger. These samples must be selected from the lower, middle and upper range of concentrations encountered at the site and must bracket assessment criteria.**

Unbalanced datasets (where most of the points are clustered together, with only one or two distinct values) will yield unstable and likely misleading regressions. As a rough test, if removing any one data point would give a significantly different arithmetic mean or correlation coefficient, the dataset is unbalanced.

Evaluate the matched results for each soil type separately using linear least squares regression analysis. Field XRF measurements should be the independent variable ($x$) and laboratory analyses should be the dependent variable ($y$). The best-fit regression line must have a Pearson correlation coefficient ($r$ statistic) of 0.9 or greater,[*] a slope between 0.5 and 1.5, and an intercept of no more than ± 20 per cent of the assessment criterion (if any).

Because XRF response is sublinear at high concentrations, the relationship between field XRF measurements and laboratory analyses may not fall on a line. In such cases, the matched data may be 'trimmed' by discarding values more than 10 times greater than the assessment criterion, provided the minimum requirement above is still met.

The investigator may use more sophisticated statistics, such as nonlinear regression and/or different measures of correlation, if they have sufficient data (substantially more than the minimum) and provide justification.

**Always check for interferents.** High concentrations of copper relative to zinc (and vice versa) and high concentrations of lead relative to arsenic (and potentially vice versa) would be expected to result in some degree of interference.

A table of characteristic peak energies is provided in the *X-ray data booklet* (Lawrence Berkeley National Laboratory, 2009, table 1-2).

If interference is affecting the whole dataset, it will be evident through the accuracy evaluation described above. However, if only a small proportion of samples contain interferents at high concentration relative to the contaminant element (say, 10 times greater or more), most likely only those results are affected. **Check laboratory analyses of representative samples analysis for the contaminant and potential interferent.**

**If the XRF is significantly over- or under-reporting contaminant concentration in those samples, all such samples must be analysed by chemical means.**

## 6.7 Representativeness

As with almost any investigation methodology, field XRF measurements sample a negligible proportion of site soils. Ensure that sample locations are representative of site soils generally; if field XRF is not applicable to some soils or fills, use conventional sampling and analysis to assess those materials.

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[*] Some investigators may prefer to calculate $R^2$; in that case, $R^2$ should be more than 0.8 and the correlation should be positive.

## 6.8 Completeness

As with all investigation methodologies, all potential contaminant sources and all contaminants of concern must be investigated.

Conventional sampling and analysis may be needed to supplement XRF results to assess any contaminants of concern to which XRF is not applicable.

This is especially relevant to cadmium, chromium, organic contaminants, and any element where chemical speciation is necessary.

## 6.9 Comparability

Field XRF does not necessarily measure the same thing as conventional sampling and analysis. **For semiquantitative applications, field XRF measurements must be corrected using the best-fit relationship** determined via regression analysis (see section 6.6). Uncorrected data must always be clearly identified as such when tabulated or plotted.

Conventionally, contaminant elements would be assessed via a strong acid digestion of the less than 2 mm particle size fraction. Therefore, laboratory analysis does not capture elemental content in gravel fraction. This is further reason to sieve soils containing coarse material for XRF purposes (see section 7.7).

In rare circumstances, where a contaminant element is also present within the silicate matrix (and therefore not extracted by the laboratory digestion), XRF measurements could be systematically higher than chemical analyses. This would be revealed in the regression analysis (carried out as described in section 6.6) as a large negative intercept.

Currently, SCSs for contaminant elements are set for inorganic compounds of elements only. Field XRF measurements are totals and cannot distinguish between organic compounds, inorganic compounds and metallic forms. If the contaminant is likely to be present in organic or metallic forms to any significant extent, XRF data cannot be compared to SCSs.

XRF data must never be directly compared to criteria for leachable fractions, such as toxicity characteristic leaching protocol or synthetic precipitation leaching protocol, both of which relate to liquid and are reported in milligrams per litre (mg/l).

Field XRF results cannot be used to determine the extractable fraction of a contaminant.

## 6.10 Sensitivity

Sensitivity refers to the ability of a method to detect a contaminant. To conclude that a contaminant element is below an assessment criterion, **the instrument detection limit must be less than one-third of the criterion**. This can usually be demonstrated simply by having some measurements sufficiently distant from source for concentrations to fall below this minimum requirement. Detection limits may be inferred at a lower level of confidence by plotting reported concentrations against measurement errors and deducing that the measurement error would be less than 30 per cent at the desired detection limit (meaning the instrument would be expected to report a detection).

Manufacturers often supply indicative detection limits for their instruments. Although these are useful for planning purchases and investigations, do not use these limits for QA/QC purposes. Actual detection limits may be higher due to matrix effects, moisture content and interferents (see section 6.6).

# 7 In the field

## 7.1 Before setting out

Check that the battery (and spare) is charged, you have enough sample bags or cups and a supply of spare windows. Reference materials for field calibration and checks should accompany the instrument.

It is useful to carry appropriate cleaning materials for the instrument window, to ensure accurate results and avoid damaging the instrument.

## 7.2 Instrument settings

Ensure the instrument is set for **soil** analysis. Some instruments also have settings for rock, paint, alloys and so on. These will probably give inaccurate results when applied to soils.

Most modern XRF instruments perform two or three scans at different primary beam energies at each measurement. The investigator may decide which scans to undertake, as long as **at least one scan has a primary beam energy in the 20 keV to 40 keV range** that is effective for the elements shortlisted in section 4.2.

Set an appropriate measurement duration. For modern instruments, the **minimum requirement is 15 seconds per beam**; this may reduce with further improvements in technology.

## 7.3 Safety

Before beginning to scan, check that the XRF housing is undamaged, dosimeters are being worn and the controlled area is clear.

## 7.4 Reference scans

Always **scan an SRM and a blank** at the start and end of a field XRF session and at any change of battery, to ensure the instrument is functioning correctly. If undertaking *ex situ* sampling using bags, place the standards and/or blanks in a representative bag before scanning. (Some bags can contain traces of elements of interest, such as zinc.)

Check results against previous results for the same instrument and the same materials. If a substantial difference is evident between consecutive reference scans, all intervening data may have been compromised and **must be reviewed to determine whether they are still usable**. A review of data should be done in such a way that it will reveal any inconsistency in results or long-term change in performance of the XRF.

Users should do reference scans frequently. This minimises the risk of having to redo work and detects early indications of instrument drift that may require user recalibration of the instrument or servicing by the agent.

Blanks should contain no detectable elemental content (trace iron is tolerable); detects may indicate the blank and/or window needs cleaning or replacing. If this is ineffective, the instrument needs servicing.

## 7.5 Soil logging

Because soil heterogeneity and moisture can have substantial effects on XRF measurements, **all soils must be logged in accordance with the New Zealand Geotechnical Society's guidelines** (NZGS, 2005), with particular attention to:

- presence of coarse material
- presence of anthropogenic material (including concrete and wastes)
- colour, especially the distribution of colour (mottled, banded and so on)
- organic soil, especially if evidently heterogeneous with rootlets or carbonaceous material
- moisture content.

Geological information, such as dominant minerals or parent rock type, should be supplied.

Soil photographs, at sufficient scale and resolution for the reader to make out the details of interest, may be helpful and should be supplied as part of the report (where relevant).

## 7.6 *In situ* measurement

*In situ* measurement means that the XRF instrument is placed directly onto the ground, or onto a large undisturbed sample, such as a split core. When measuring *in situ*, the following steps should be taken.

- Re-evaluate whether *in situ* analysis is applicable. If soils are visually heterogeneous, coarse or wet, do not proceed; collect samples for *ex situ* measurement and/or conventional soil sampling and analysis.
- Make the soil surfaces to be scanned as smooth and flat as possible. Remove all grass cover, any smearing from excavation and so on. Avoid clean gravel, shell, roots and other inert particulate material, or remove using a clean gloved hand or non-metal spoon.
- Check the instrument window is clean and intact.
- Place the window directly in contact with the soil, perpendicular to the surface, and keep the instrument still during the scan. An instrument stand or 'soil foot' may be helpful.
- Record sample depth accurately, as a single value not an interval.
- Make replicate scans in accordance with the SAP.
- Collect soil samples for laboratory analysis in accordance with the SAP, from as close to the scan point as possible.
- Do not let the instrument overheat; a sunshade may be helpful.

## 7.7 *Ex situ* measurement

*Ex situ* measurement involves collecting a soil sample for which the investigator must take the following steps.

- Re-evaluate whether *ex situ* analysis is applicable. If soils contain any particulate contaminant or are predominantly coarse sand and gravel, do not proceed; collect samples for conventional soil sampling and analysis.
- Avoid or remove all grass cover, smearing from excavation, clean gravel, shell, roots and other inert particulate material. Collect representative soil samples from as narrow a depth interval as possible and place into a clean bag (thin plastic or paper) or laboratory-supplied container. If the soil contains more than minor coarse sand or gravel-sized material, pass through a clean 0.6 mm (US No. 30) stainless steel mesh sieve.
- Record sample depth intervals accurately.
- Split soil samples for laboratory analysis in accordance with the SAP.
- Air-dry wet samples. When air-drying samples, avoid airflows that generate dust, which may cross-contaminate samples and create a health and safety hazard by entraining contaminant particles in air.
- Mix each individual sample thoroughly. Do not composite samples.
- Transfer the samples to proprietary sample cups (optional).
- Compress the samples by shaking or pressing to reduce voids. After compression, the samples must be at least 15 mm thick.
- Check the instrument window is clean and intact.
- Place the window directly in contact with the sample, completely covering the window and perpendicular to the surface, and keep the instrument still during the scan. A plastic clamp, instrument stand or proprietary support or workbench may be helpful.
- Make replicate scans (either at different points or after remixing) as required by the SAP.

# 8 Reporting

Ensure that the investigation report includes the following.

- ☐ All information specified for the investigation being undertaken, as set out in the *Contaminated land management guidelines No. 1 – Reporting on contaminated sites in New Zealand* (Ministry for the Environment, 2021a) (CLMG 1).
- ☐ The make and model of the XRF instrument.
- ☐ The calibration used, scan energies and scan duration.
- ☐ Sampling and analysis plan (SAP), in sufficient detail for a capable reader to be able to replicate the investigation, including any changes to the SAP made during the investigation.
- ☐ Soil logs covering the matters highlighted in section 7.5.
- ☐ Unprocessed concentrations and errors for all contaminants of interest and all identified interferents for all scans, including reference scans (any compromised data, such as incomplete scans, may be omitted so long as this is clearly stated in the report, along with the reason).
- ☐ All laboratory analytical results, clearly matched to field XRF measurements.
- ☐ All QA/QC information, including a PARCCS assessment of the XRF dataset.

  This part of the site investigation report should be written with sufficient clarity to demonstrate the reliability and/or uncertainty in the data, and should cover:

  - calibration records
  - variation between replicate XRF measurements
  - potential interferents and their apparent effect on the data
  - detection limits for contaminants of interest
  - reference scans, including consistency against SRMs and detections in blanks
  - for semiquantitative applications, regression slopes, intercepts and correlation coefficients, identification and discussion of any issues, such as outliers in the matched data, unbalanced data, nonlinearity and so on
  - details of any IANZ accreditation held (copies if requested)
  - training records and operator licence details (if requested).
- ☐ Summary data for the corrected dataset.

Ensure that any plotted data are clearly identified as unprocessed or corrected.

The full XRF dataset, and the reference scan results log, do not have to be appended but must be made available to reviewers on request, preferably in a format that enables easy interrogation of the data.

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