

Rapid on-site screening for historic contamination at mine sites

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Abstract

GHD and Newcrest Mining Limited (Newcrest) have carried out a large scale assessment of rapid on-site screening (ROSS) technology using a portable x-ray fluorescence (XRF) analyser (model type: Niton XL3T) as part of the Newcrest contaminated land assessment programme for expansion of a mine site. The XRF analyser was used to determine concentrations of metals across a number of old workshop and plant areas of the site to seek to delineate any potential impact in near surface soils and aid management decisions regarding both the scale of potential impact and the requirements for materials management. A dual assessment was undertaken in which traditional soil sampling and laboratory analysis was carried out in conjunction with in situ XRF sampling to allow a direct comparison between the two techniques.

As would be expected the ROSS survey carried out proved to be significantly quicker than taking soil samples and dispatching to Perth for laboratory analysis, with an average sampling time of two minutes per sample location. This reduced sampling time allowed GHD to significantly increase the sampling density in comparison to conventional soil sampling. In addition, the XRF technology utilises global positioning system (GPS) information which, when used with a portable computer, allows the immediate download of data to geographical information software (GIS) and presentation of results on a geo-referenced map in the field. The turnaround time from data collection to data presentation using this technology is therefore reduced to a single day, allowing 'real-time' review and modification of the sampling strategy which would not otherwise have been possible using traditional laboratory based analysis.

A robust understanding of the distribution of contamination on a given site is critically important when calculating volumes of material as part of materials management to avoid overestimating quantities of impacted material that may require separation or special treatment. The increased sampling density that can be achieved using ROSS when compared to traditional investigation techniques results in a more detailed understanding of the distribution of contamination both at the micro (or intra sample) and macro (or inter sample) scale, which will improve confidence levels with respect to calculating volumes of potentially impacted material.

The study carried out by GHD and Newcrest indicates that in situ screening using ROSS for characterisation of contamination on a large scale mine site is valid and is cost and time effective at the investigation stage, particularly at remote site locations. ROSS offers potentially significant cost and time savings when carrying out works to delineate areas of impacted materials and will aid operational decision making with respect to efficient materials handling and waste management. In addition, the large sampling densities that can be achieved using the ROSS technique allows a more robust estimation of the distribution of contamination than can be achieved with a traditional laboratory based sampling programme of comparable cost.

1 Introduction

Virtually all soil analysis carried out in the Australia for the purposes of environmental studies takes place in laboratories far from sites being investigated, which imposes a significant cost and time burden. This is particularly true for mine sites in Western Australia (WA), which are commonly very remote from laboratory locations. On-site field analysis techniques have been available as an alternative to laboratory studies for a number of years however they are not widely used in environmental studies. There are a number of reasons why this has previously been the case, such as cost, accuracy, acceptability by regulators and the requirement for skilled operators. However, technology has been rapidly advancing in this arena such that in situ screening is now a viable option.

As part of the contaminated land assessment programme for open pit expansion Newcrest Mining Ltd (Newcrest) contracted GHD to assess a number of areas to determine the distribution of metals (including copper) present in near surface soils. The initial phase of the contaminated sites investigation was achieved via shallow boreholes using an RC drilling rig and the collection of laboratory samples for analysis in Perth. However, due to the remote location of the site this investigation was logistically complex and proved to be a costly exercise. The initial phase of work identified a requirement for further sampling to delineate the presence of certain metals, particularly copper. For the additional delineation work, GHD proposed to use on-site field based analysis using an XRF analyser to overcome logistical and cost constraints of investigation.

2 On-site analysis in context

On-site analysis techniques have been used successfully for many years to give 'real-time' information about the presence of contaminants during site investigations. Gas and vapour detection is one area in which analysis is dominated by on-site methods such as the photo ionisation detector (PID) and flame ionisation detector (FID) equipment which are routinely used for delineation and remediation activities. Because of the wide acceptance of using these portable vapour detection devices the technology has advanced at a fast pace. Gas and vapour detection devices as a consequence are now highly sophisticated, accurate, relatively cheap, and are accepted by regulatory bodies as an acceptable analytical method.

The analysis of soil/rock samples for contaminants commands a much more lucrative market than for gas detection and so it would make economic sense that on-site analytical techniques in this field would be in a further state of advancement than that of gas detection. However, the reverse is true, virtually all soil analysis carried out in Australia takes place in laboratories off site. On-site techniques are used very rarely, and when they are, they have been used only as part of remediation projects for validation purposes. The reasons for the slow uptake of on-site analysis appear to be centred on two main aspects as summarised below.

2.1 Use of emerging technology

Like any emerging technology, early field-based techniques were generally not user friendly, required skilled operators and were not very accurate. For example, up until recently, heavy and base metal detection required analysers that contained highly radioactive sources; had unacceptably high detection limits, and required a very skilled operator. Field analysis for hydrocarbons in contrast has been possible for a number of years though the use of volatile organic carbon (VOC) detectors and field testing kits. However, despite being used successfully by companies such as Shell, widespread adoption has still not occurred.

In the last five years, significant advances have occurred in the development of portable x-ray fluorescence (XRF) analysers that use an x-ray tube which, only produce radiation when activated. The simultaneous analysis of 20+ metals has been made possible with this technology, and detection limits have dropped considerably. The main reason for this breakthrough has been down to economics in the uptake of the technology by other business sectors, and the miniaturisation of computing technology. These new XRF analysers are now being widely used in the mining industry for exploration, in the materials testing industry for analysing alloys, and as part of quality control in the metals industry. Capital gains from the adoption of these devices by other sectors have focussed significant resources into R&D of miniaturised XRF, and this is expected to continue.

2.2 Acceptability

Acceptability by the regulatory bodies responsible for administering and enforcing environmental acts (e.g. Department of Environment and Conservation (DEC), Environmental Protection Agency (EPA), Department of Mines and Petroleum (DMP) in Western Australia) is the single biggest hurdle to be overcome in Australia and other countries with a strict regulatory system, and an adopted set of rigid guidance documents. It is interesting to note that gas and vapour detection devices overcame this hurdle long ago, although the inherent difficulties in collecting gas and vapour samples may suggest why this is the case (gas and vapour samples are difficult to extract, store and transport, which stimulated early development of the technology). Soil samples are in comparison easy to extract, store and transport and so a culture of off-site laboratory analysis is prevalent in the environmental business sector. This culture has been underpinned by a

widespread (and potentially misguided) mindset that any analysis not carried out in the laboratory is of an unacceptable quality. However, the new breed of XRF devices have technical specifications that operate very close to the performance achieved by laboratories using inter-coupled plasma spectrometry (ICP) methods of analysis. The situation in the United States of America is comparatively less polarised than in other developed countries as the United States Environmental Protection Agency (USEPA) has validated many on-site techniques including XRF devices and a published standard has been developed for the use of these devices (Method 6200 – USEPA, 2007).

3 Characterisation of contamination in context

The characterisation of contamination at a given site is a process that is affected by many variables, all of which add a degree of error to the final assessment. The characterisation of contamination is generally expressed in terms of concentration, distribution and volume. These factors are the key drivers in assessment of environmental risk, and ultimately the requirement for capital expenditure on intervention such as remediation. Although a key part of the site assessment process, characterisation of contamination is one of the least understood and poorly defined aspects of site assessments carried out by environmental practitioners.

The distribution of contamination at a site is the most important factor to be defined when assessing potential environmental risks and the scope for any intervention that may be required (e.g. remediation). Distributions can generally be described as localised (point source), or diffuse (present across large areas of the site), and can vary in three dimensions, i.e. laterally and vertically. If nothing is known about the nature of the distribution of contamination prior to sampling, then (statistically) intense sampling is required to determine the true nature of the contamination distribution. If insufficient sampling is carried out then it will be difficult to determine if an individual high sample result represents a localised point source, or simply represents ‘higher end’ concentrations from a diffuse source. Poor characterisation of materials can result in unnecessary capital expenditure, waste of resources, and in the worst case, environmental degradation. Factors affecting the characterisation of contamination are outlined as summarised below.

3.1 Sampling frequency

Generally, the more samples that are analysed from a given site (or location), the greater the confidence in the overall assessment. The direct relationship between increasing levels of confidence with sample numbers is related to the inherent variability (heterogeneity) of the composition of soil materials at both the micro and macro scale.

A given site (or location) will have a given population distribution with respect to, e.g. copper concentrations in soil. The ‘true’ sample population distribution for copper concentration within material present on the site can never be known as this would theoretically require testing of every gram of material present. Given the economic limitations of sampling to this level, the common solution to the problem is to approximate the sample population utilising the basic descriptive statistics of a maximum, minimum, median, mode and true mean value. However, as we can never know the ‘true’ sample population, then the number of samples used to estimate these descriptive statistics is the controlling factor in how close these statistical estimations are to defining the true population. On this basis as the number of samples taken from the site increases, the closer the assessor will come to defining the ‘true’ population descriptive statistics, for example the mean concentration that is measured is more likely to approach the actual mean (assuming no systematic error).

Guidance on the number of samples to be taken on a site for the purposes of contaminated sites assessment in Western Australia is provided by the DEC in published guidance documentation (Contaminated Site Management Series publications), however, the assumptions on which the sampling requirements are based are very broad. The key assumption is that the population distribution of contamination on a site is described by normal distribution, and that hotspots of contamination present are of uniform size, shape and vertical profile. This is not commonly true for many sites and the actual sampling density required to characterise the distribution of contamination at the site (with respect to calculating a reliable estimate of true mean, range and standard deviation) will often be far in excess of the values indicated by the guidance. One of the main reasons for this flawed basis of determining sampling density being adopted by regulators in Australia is

economics. The regulators recognise that sampling using traditional soil sample collection and laboratory analysis can cost large amounts of money and so have factored this in when setting regulatory requirements.

Increasing sampling density is the single most effective method to yield a more accurate, statistically robust picture of contaminant distribution. However, the corresponding increase in cost involved is almost always commercially prohibitive when considering the standard procedure of sending staff to a remote site, physically taking samples by hand and dispatching them to a laboratory often hundreds to thousands of kilometres away. Rapid on-site screening techniques are much less vulnerable to such constraints making them a viable solution to the current economic barrier to increased sampling frequency.

3.2 Heterogeneity

Heterogeneity is simply a measure of the degree of variability of a parameter. This can vary on a number of scales from micro to macro levels. In the context of contamination assessments, important parameters are the degree of inter sample (macro scale) and intra sample (micro scale) heterogeneity.

With respect to intra sample heterogeneity, samples collected from a site for laboratory analysis commonly comprise a bulk 500–1,000 g of material per sample. The heterogeneity of the sample with respect to physical and chemical properties may be significant, for example grain size may vary between silt to gravel, and various mineral phases may be present and unequally distributed (for example localised pyrite crystals, or surface crusts of oxy-hydroxides). The degree of variation in the concentration of contaminants within the sample will therefore depend primarily upon the nature of the material. Typically, for ICP analysis a laboratory will extract a small 1–10 g sub sample of the 1,000 g parent sample on which to complete analysis and the selection of the sub sample may take place after sieving or crushing of the parent sample. Therefore, if intra sample heterogeneity is significant then clearly it will be unlikely that a single 1–10 g sub sample will be representative (chemically or mineralogically) of the sample as a whole.

With respect to inter sample heterogeneity, samples are collected from a number of locations within a sampling area on a random or targeted basis. Contamination may be concentrated within a particular material (for example an secondary mineral such as an oxy-hydroxide surface crust), at a particular location, or at a particular depth. If random sampling is being employed then it is clear that inter sample heterogeneity will have a potentially significant impact on the ability of the sampling programme to characterise the distribution of contamination on-site. In addition if intra sample heterogeneity is also high, then the density of sampling will need to be correspondingly high to ensure intra as well as inter sample variability is accounted for. It is important to realise in this context that the degree of inter as well as intra sample heterogeneity is not commonly known when the sampling program is being developed, consequently there is a significant risk that too few samples will end up being taken to account for inter sample heterogeneity.

3.3 Accuracy of sampling and analytical method

No analytical technique is 100% accurate and so random and systematic errors will affect the final result. In addition, if untrained site personal carry out sampling then error may be introduced in the sampling process such as cross contamination between samples using unclean equipment, and poor sample selection, which may result in highly contaminated materials being left unsampled. Quality control procedures can be used to reduce these errors, however, in reality they cannot be excluded.

Generally, the error introduced by modern analytical instrumentation as analytical bias is likely to be relatively low. It is expressed as the bias of the method, and is the difference between the mean of a number of measurements by a given method and the 'true' value of the concentration. The bias of a given analytical method is usually estimated using a certified reference material (CRM) which has a known concentration of the substance being measured.

A study carried out in Europe (CLAIRE, 2004) indicates that for a particular case study sampling was by far the greatest cause of uncertainty rather than analysis. Precision was estimated at 83% of the concentration value for the sampling method, but was much lower at 7.5% for analytical method. The overall random component of uncertainty was estimated as being 83.6%, that is to say, the value of any concentration for an individual location was reproduced to within $\pm 83.6\%$ of the quoted value (at 95% confidence). Given that sampling precision was 83%, then clearly the majority of the overall variability was related to sampling

rather than analytical factors. Therefore, to reduce uncertainty the most effective solution must be to increase sample numbers and for mine sites (particularly remote sites) to do this cost effectively.

4 Field application of ROSS

In 2009, GHD completed a phase of traditional site investigation works in areas of old workshops and plant at a Newcrest mine site as part of mine expansion pre-works. One of these areas is approximately 4.5 ha in size and was developed historically as an ore processing plant. The main historical operational areas included: Ore processing, run of mine loader, copper concentrating plant, mixing tanks, chemical storage (including copper concentrate storage); and a power substation. It was suspected that as a result of past use, copper compounds may be present within near surface soils at potentially elevated levels.

The investigation carried out by GHD indicated that copper was found at elevated levels within surface soils in some localities, however due to the limited sampling carried out (with respect to the size of the site) the full distribution of the copper in surface soils at the site was uncertain. GHD consequently recommended further assessment be carried out on-site in the form of a delineation survey utilising ROSS to better define the distribution of copper in this area of the site.

The decision to use an XRF analyser as part of the ROSS survey to complete the assessment rather than traditional sampling and laboratory based techniques was made for the following reasons:

- The speed of analysis using ROSS is a significant factor in deciding to adopt this method. The average sampling time per location using the XRF on-site was estimated as being approximately three minutes (sampling can theoretically be completed even more rapidly than this however the precision of the technique can become compromised by electing to run a short sample analysis run time).
- The size of the site meant that delineation works based on a 50 m nominal sampling grid would require around 80 samples to be collected. Taking physical samples at the site for laboratory analysis in Perth was anticipated to be time consuming as the ground conditions were hard lateritic soil making recovery of representative physical samples difficult. In addition the costs of freight and analysis associated with laboratory analysis would be significant.
- Given the site's historical use it was determined that inter sample heterogeneity was likely to be high requiring a greater the number of samples to be taken to improve the characterisation of material. Use of ROSS allowed an increased sampling density strategy to be developed.
- Intra sample variability was also thought to be potentially high. Use of XRF analyser was therefore considered to be advantageous as intra sample variability could be estimated in real time in the field. Traditional laboratory based assessments do not offer this real time data and so the field assessor is essentially blind to potential intra sample variability issues.
- The XRF analyser could be linked to a GPS unit using a Bluetooth link. This meant that all sample results could automatically be allocated location coordinates. This reduces the possibility of human error compared to traditional techniques of using a separate hand held GPS unit and manually recording coordinates or waypoints.
- Data from the XRF analyser including GPS coordinates can be downloaded in real time onto a site laptop or palmtop running GIS software to provide real time visualisation of data. This cuts the data processing time to produce contaminant distribution maps from a matter of weeks to hours.
- As excavation or ground penetration permits are required at mine sites under the Mines Safety and Inspection Act (1995) to excavate into the ground (even for shallow sampling) this can add an additional logistical problem to sampling as sample locations are required to be marked out and then approved by site engineers. The advantage of the XRF in this case is that sampling can be carried out directly onto the ground surface and so permits are not required to recover physical samples.
- The sampling programme was to be carried out during the summer, in which daytime temperatures at the site were around 45°C making physical activity a health and safety concern. By using on-site

analysis techniques the sampling would be quicker and less physically demanding, and so would reduce potential health and safety risks.

- Although copper was the target species, the presence of other metals could not be ruled out. Because the XRF technology has been validated using USEPA (2007) Method 6200 for 26 metal species then a broad range of metals could be determined. Laboratory analysis for all 26 species in comparison would be a costly exercise. Additional species of interest that were also analysed included nickel, arsenic and zinc.

5 XRF field testing methodology

The United States Environmental Protection Agency (USEPA) has developed a standard method (6200) for the use of XRF analysers in the field. USEPA (2007) Method 6200 is now incorporated into SW-846, the Office of Solid Waste's official compendium of analytical and sampling methods, as part of the library of standard methods. This method covers in situ and ex situ analysis of 26 analytes of general interest using field-portable x-ray fluorescence.

5.1 Field method

Thermo-Fisher Scientific has used the basis of the 6200 methodology to prepare a field methodology for the use of the Niton brand of XRF analysers (used by GHD in this study). This is outlined as follows:

5.1.1 Summary of method 6200 testing protocol

The summary below lists the steps for in situ sample testing following USEPA (2007) Method 6200 specific for Thermo Scientific NITON XLt and XL3t analysers.

- Step 1: Identify data quality objectives.
- Step 2: Ensure soil is not saturated (no standing water).
- Step 3: Remove any large, non representative debris.
- Step 4: Create smooth, flat surface.
- Step 5: Select target analytes and appropriate excitation sources.
- Step 6: Select instrument parameters based on data quality objectives (DQOs).
- Step 7: Perform energy calibration.
- Step 8: Analyse instrument blank.
- Step 9: Perform calibration verification.
- Step 10: Analyse samples.
- Step 11: Analyse method blanks, calibration verification samples, and energy calibration checks.
- Step 12: Perform precision measurement.
- Step 13: Report concentrations consistent with precision.
- Step 14: Submit at least 5% samples for confirmatory analysis.

GHD adhered to this methodology when completing the ROSS survey to ensure that the quality of the data gathered was as robust as practically possible. Some additional sampling considerations that were taken in account were:

- The depth of x-ray penetration is approximately 0.17 mm at its greatest. This is important when considering the influence that surface dust can have on cross contamination. In addition the roughness of the surface of the sample can have an impact on results as the air voids can have a negative impact on the precision. As a result GHD ensured that the analyser window was cleaned between each sample, and that sampling was completed on sand or finer size particles.

- The moisture content of a sample when in excess of 20% can have a negative impact on sample precision. Sampling was therefore scheduled on dry materials only.

6 ROSS field results

GHD used a Niton XL3T XRF analyser linked to a Bluetooth GPS unit to carry out the site assessment in accordance with the field methodology outlined in Section 5. Seventy-eight sample locations were selected and analysed based on nominal 50 m grid spacing. Sampling was carried out over a period of two days, in addition to other works on the site. Quality control procedures included the use of a reference sample to ensure that the device was performing to an acceptable level of precision and that cross contamination as a result of dust impact was not occurring. The reference sample was analysed 11 times over the duration of the sampling programme.

The data gathered from the ROSS survey was analysed using spatial analysis software (Surfer by Golden Software), and copper concentration contours were plotted onto the base map of the site. The contouring indicated that elevated levels of copper are directly related to areas of the site where copper fines were handled or processed. The contouring also indicated that copper bearing materials appear to have been spread away from the original source zone; although there is a clear inverse correlation between concentration and with distance from the main sources. The contour plots prepared are therefore useful as part of interpretation of the distribution of copper present on-site as there are clearly several point source localities, along with a general diffuse level of copper contamination across the site. In addition the boundaries of the areas of material with potentially significant copper impact appear to be relatively well constrained with sampling density carried out. This level of interpretation would not have been possible with a lower sampling density that would otherwise have been obtained in a conventional laboratory based assessment. There is always the danger using lower sampling densities that large areas of a site may be categorised incorrectly with respect to contamination impact.

6.1 Quality control

Calibration testing against a certified standard reference material supplied with the XRF analyser was carried out on-site as part of quality control testing to determine the relative level of precision. The reference material had a certified copper concentration of 237 mg/kg.

Table 1 Quality control testing

Sample Index	Copper Concentration (mg/kg)	Error (mg/kg)	Relative Percent Difference (RPD)
109	208.66	23.55	12.72
139	199.44	23.15	17.21
174	202.67	23.5	15.62
211	201.16	23.22	16.36
212	202.24	23.22	15.83
213	187.21	22.62	23.47
214	220.51	23.76	7.21
215	217.19	23.6	8.72
286	239.99	24.55	1.25
287	213.21	23.43	10.57
288	211.4	23.78	11.42
Mean	209.43	23.49	12.76

The quality control testing indicated that the device was performing with an adequate degree of analytical bias as the mean value for relative percent difference (RPD) for 11 analysis runs of the standard was 12.76%.

Method blanks were also analysed as part of quality control testing, 24 analysis runs were completed with the device reporting a non detect in all circumstances. The average level of detection was reported as being 15.8 mg/kg.

6.1.1 Inter sample variability

The results for copper concentration from the XRF analysis completed are given in Figure 1. It is clear that the distribution of copper concentrations within the sample population is closer to a uniform type than a normal type. This indicates that statistical analysis of the results to determine 95% confidence interval, or to estimate the true mean value on this data set is not appropriate.

The distribution shown in the data set indicates that the inter sample variability is inherently high at the site, and that the true maximum range of the population probably has not been established (i.e. the true maximum value has not been established). This being said the range established was deemed to be adequate given that a spatial correlation was established with respect to sample concentrations. Therefore although the true maximum value was not established, the location of the true maximum can be estimated with a sufficient level of confidence.

This observation of the wide range in the data set highlights the importance of sampling frequency as if fewer samples were taken at the site (as would have been the case using traditional sampling and analysis techniques) then the estimate of the range would have been significantly less accurate. To provide an accurate estimate of the true mean value at the site and to estimate the true scale of inter sample variability, a significant number of additional samples would be required to be taken at the site. Given the limitations of the traditional sample collection and laboratory analysis technique, further XRF sampling would be the most effective way to carry this out.

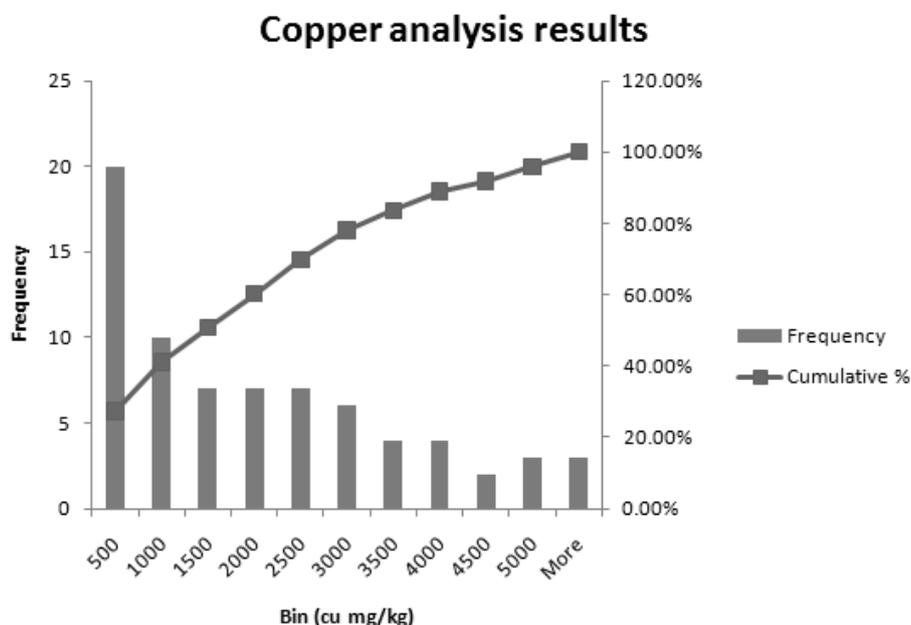


Figure 1 Distribution of copper results

6.1.2 Intra sample variability

To assess the degree of potential intra sample variability inherent within material from the site, repeat analysis was completed on a selected sample from the site. The procedure for this was as follows:

- The sample of material was analysed using the XRF five times (analysis being completed on different parts of the sample on each occasion).

- The sample was sieved through a 1 mm sieve to separate the fine and coarse fractions.
- Analysis of the fine fractions was then carried out five times, and a sample of this fraction sent to a laboratory for ICP determination.
- Analysis of the coarse fraction was carried out five times, and a sample of this fraction sent to a laboratory for ICP determination.

It is important to note that the laboratory analysis is completed on approximately 10 g of homogenised sample, whereas the XRF analyser typically will report concentrations from about 1 g of sample or less.

The results of this analysis are given below in Figure 2.

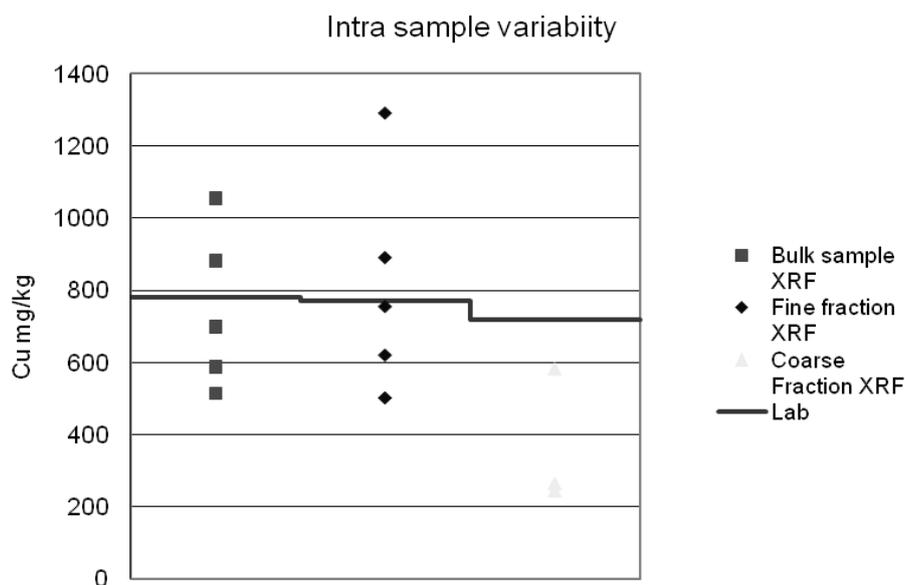


Figure 2 Intra sample variability

A number of findings can be drawn from the results shown in Figure 2. It is clear that intra sample variability as indicated by the XRF results is relatively high as the range of values for the five different analyses runs for bulk and fine fractions vary by more than 600 mg/kg (or 100% in relative terms) within each population.

When compared to inter sample variability indicated on Figure 1, the degree of intra sample variability shown in Figure 2 is very significant as a deviation of 600 mg/kg is sufficient to shift a result between three of the bin ranges used for categorisation of inter sample variability. For example, a duplicate analysis carried out of a single analysis result of 800 mg/kg may result in value that ranges between 500–1,100 mg/kg and could therefore plot in the 0–500, 500–1,000 or 1,000–1,500 mg/kg bin ranges. On this basis, a point source sample from a single location could belong to any one of three adjacent 500 mg/kg bin ranges depending on which part of the sample is analysed. To account for this level of intra sample variability, the inter sample variability distribution could therefore be reassessed using larger bins (of 1,000 mg/kg or greater) to reflect the fact that a difference of less than 600 mg/kg may be difficult to attribute to inter or intra sample variability due to the variability. However, this would reduce the number of bins used to five, which would reduce the resolution of any statistical analysis of the population distribution carried out.

The degree of variability and the range of sample results appear to vary between the three different grain size fractions analysed. The coarse fraction appears to report a generally lower value for copper (a lower minimum value), and the fine fraction reports a generally higher value (a higher maximum value). The result of this analysis is that there appears to be an apparent variability in copper concentration between grain size fractions, and within each population, however as highlighted in Section 5 air voids can have a negative impact on the accuracy of the analyser, which may explain the apparent variability between grain sizes.

It is relevant to note that in the case of the bulk and fine fraction the laboratory results are very close to the mean value of the XRF analysis. The relative percent difference between the laboratory result and the mean

value of the XRF results is very low at 4.2% for the bulk sample and 5.3% for the fine fraction indicating a close correlation. The coarse sample results for the XRF are all below the laboratory analysis in comparison, it is possible that the presence of air voids could be negatively impacting on the accuracy of the analyser as the XRF is known to be less accurate when analysing coarse grain sizes as a result of poor reflection, which may explain this result).

The results indicate that there is significant intra sample variability within the samples of material taken from site with respect to copper concentrations. Variability appears to be high both within grain size populations and between grain size populations. The laboratory analysis appears to be reporting a copper concentration very close to the mean value of the distribution indicated by the XRF (this would be expected given the effective compositing that occurs during laboratory sample preparation, although the similarity is surprisingly close). The implications of this intra sample variability analysis are threefold:

- Because inter sample variability is high, an assessment of the validity of using single point analysis values would be required to determine how representative this may be with respect to the level of intra sample variability indicated by the results. With respect to laboratory results this is particularly valid as the sub sampling process is inherently vulnerable to the high level of intra sample variability.
- Whilst laboratory analysis appears to provide an accurate estimate of the mean value of the copper concentration within the samples analysed, it does not indicate what the potential maximum concentration within a sample may be. In addition, the degree of accuracy for calculating the mean value in other samples of material may not be as high as in the selected sample.
- When carrying out analysis using XRF as part of ROSS on materials such as those encountered it is important to complete intra sample variability analysis prior to defining test criteria for a particular area of the site. This is to ensure that the effects of intra and inter sample variability can be accounted for when making spatial correlations. For the site investigated as part of this study up to five samples may be required from some locations to account for the level of variability detected.

7 Conclusions

An XRF analyser was used by GHD as a tool to allow rapid onsite measurement of metal (primarily copper) concentrations within surface soils at a Newcrest mine site. The use of the technology has been proven to bring a number of advantages over standard sampling and laboratory techniques to include increased sampling density, decreased time on-site, extended analytical suite, integrated GPS data recording and provision of real time data for onsite review.

Inter and intra sample variability are parameters that are known to significantly impact the ability of the assessor to interpret data sets, and are parameters that are often poorly understood as a result of the limitations on sampling frequency imposed by traditional sampling and laboratory analysis techniques. As a result of using the XRF analyser, the inter and intra sample variability could be assessed in real time, and a better estimate of both could be derived relative to traditional sampling and laboratory analysis. Both inter and intra sample variability distributions were found to be large at the site, which indicates that copper concentrations are likely to vary considerably both at the micro, and macro scale (although spatial correlation of the higher end values of the data set was still possible based on strong relationship between point sources of contamination). This discovery would not have been possible using a traditional sample collection and laboratory based analysis testing program. The implications of this finding are that accurate estimates of the true mean value, or of the sample population range of the material present on-site is likely to require a large number of samples, but this is made achievable and cost effective by the continued use of XRF field analysis techniques.

Comparison of laboratory and XRF data indicates that the laboratory results are very close to the mean value calculated from repeated analysis by the XRF of a particular sample. This indicates the analysis techniques are in good agreement with each other with respect to deducing a bulk value for copper concentration, however, the laboratory analysis technique does not allow intra sample variability to be calculated. This may be a significant factor when making decisions about spatial correlations as what may appear to be inter sample variability may in fact relate to intra sample variability. This also has implications for environmental

risk assessment as samples of material may contain significantly higher concentrations of contaminants than may be suggested by composited laboratory sample results.

The results indicate that for the sample material analysed, laboratory analysis is an appropriate method of verifying the mean of the intra sample population distribution defined by the XRF. Given the large intra sample range defined by the XRF for a given sample it is clear that the compositing technique employed by the laboratory may be prone to error however and it should not be assumed that this technique can always provide a reliable estimate of the mean value of intra sample variability. This is because its success in determining the true mean value of the intra sample population range is dependent upon broad inclusion of sample matrix across the population distribution range (within the sub sample) to achieve an accurate estimate of the sample mean. This cannot be assumed as selection of material for the sub sample in the laboratory is in reality arbitrary. The XRF analysis has therefore proved to be of additional value in identifying the limitation of the compositing technique so that this can be addressed in future planned work.

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