

Appendix 4

XRF Analyser

Assessment of analytical performance of Niton XLt 792Y field-portable XRF analyser

In order to provide independent assessment of the quality of analyses carried out using the field-portable XRF analyser, 221 samples, or approximately 15% of the total of material analysed *in situ* for the project, were reanalysed by both the Niton XRF in the GSI laboratory and by Emission Spectrography (ES) at OMAC Laboratories in Loughrea, Co. Galway. Prior to laboratory analysis, the samples were air-dried and ground in an agate mill to a nominal grain size of <150 µm. Direct comparison of the results obtained for these 221 samples by XRF and ES allows an assessment of the accuracy of the laboratory-based XRF analyses if it is assumed that the ES analyses are essentially accurate and that samples are completely homogenized. In addition, the results of analyses of several standards, completed during the course of laboratory-based XRF analyses, provide further control on the accuracy of the XRF data.

A limitation to this approach is that the upper calibration limit for both the XRF and ES is around 2% for elements of interest such as Cu, Pb and Zn. *In-situ* XRF analyses indicated that many mine waste samples have metal concentrations well in excess of this limit and this was supported by laboratory-based XRF analysis and ES. In order to assess the performance of the XRF at high (>2%) metal concentrations, a limited number of prepared samples were subjected to assay analysis at OMAC Laboratories. .

The results of all of these comparative analyses are outlined below for the following elements: Ag, As, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Th, U, V, W, Zn. Other elements analysed routinely by XRF have not been included in the comparative analysis either because they are not of particular importance in mine waste samples (e.g. Rb and Sr) or because very high XRF detection limits prevented detection in most cases (e.g. sulphur and phosphorus).

1. Ag - silver

Table 1.1 Ag statistics (mg/kg)

Ag, n=221	OMAC	GSI
Min	0.3	<DL
Max	200	649
Median	3.3	<DL

Most GSI analyses of samples recorded Ag values below the limit of detection (Table 1.1). In 53 out of the 60 cases where it was detected in GSI, the measured Ag was higher in the GSI analysis than in the OMAC analysis, indicating a clear relative bias to higher values for the XRF analyser (Figure 1.1). Ag is reported for three standards analysed in GSI: NIST 2710 (35 mg/kg), NIST 2780 (27 mg/kg) and RCRA (500 mg/kg). Mean values for XRF analyses of these standards were, respectively, 29 mg/kg, 21 mg/kg and 432 mg/kg. OMAC ran two lab standards, SY-4 (<0.5 mg/kg) and ICP-4 (28 mg/kg): measured values for the latter were within 0.2 of 28 and below the limit of detection for the former. The upper calibration limit for Ag on the OMAC ES is 500 mg/kg. Data for GSI standard analyses do not suggest significant problems with XRF analyses for Ag at high, or indeed low, concentrations and there are no peak overlaps in the XRF spectrum that could give rise to falsely high Ag results.

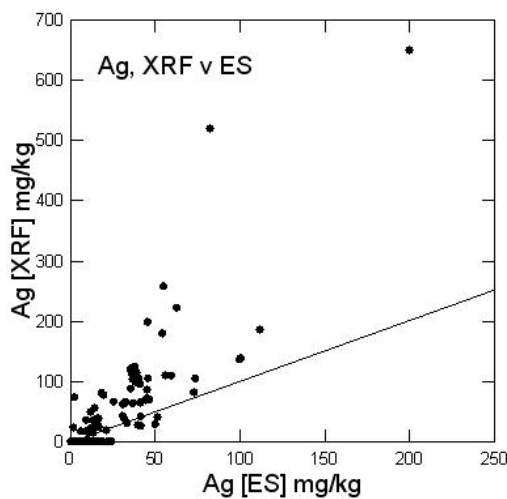


Figure 1.1 Ag XRF (GSI) v ES (OMAC)

2. As - arsenic

Table 2.1 As statistics (mg/kg)

As, n=221	OMAC	GSI
Min	<5	<DL
Max	6605	55277
Median	58	70

The As results reveal that the GSI analyser shows a similar and even more pronounced bias towards higher values compared to the OMAC analyses. In this case, the OMAC ES system has an upper calibration limit of 20,000 mg/kg, the same as the GSI XRF so this should not be a factor. Moreover, the deviation between GSI and OMAC results can be very high even at low measured OMAC values. Sample heterogeneity does not explain the

differences as one would expect a range of high and low values for both instruments rather than a bias for one.

The most obvious potential analytical problem in respect of As lies with the XRF because of almost complete overlap in the XRF spectrum between the main As and Pb peaks. The K_{α} peak for As is 10.53 keV while the main (L_{α}) peak for Pb is 10.55 keV. Where there is significant Pb in the sample, as is the case for many of the mine waste samples analysed, the subsidiary peaks, K_{β} for As (11.73 keV) and L_{β} for Pb (12.61 keV), provide some discrimination. The K_{β} peak for As has much lower intensity than the K_{α} peak and this may have an impact on precision and accuracy levels, especially at low concentrations. However, the most dramatic differences between the GSI XRF data and the OMAC data generally involve high measured XRF concentrations of As and low measured ES concentrations, coinciding with high Pb values as measured by both methods. This is particularly notable in samples from Glendalough and other Pb mines, such as Keeldrum. A plot of the difference in As concentrations as measured by each method and total Pb concentrations, as measured by XRF, shows good agreement between OMAC and GSI As concentrations where Pb concentration does not exceed 1%. Above this level, the measured OMAC and GSI As concentrations diverge sharply. A partial spectrum of one Keeldrum sample (KLD-07-SP01.4 bot) is reproduced below. Measured As values for this sample are 67 mg/kg (OMAC) and 6734 mg/kg (GSI). The Pb values are > 20,000 mg/kg (OMAC) and 233,568 mg/kg (GSI). Despite such a high apparent As value for the XRF analysis, there is no obvious peak for the As K_{β} line. A similar situation can be observed for other samples with very high Pb concentrations where the As XRF value far exceeds the ES value. It would appear, therefore, that the correction routines for the XRF analyser cannot deal adequately with very high concentrations of Pb and generate falsely high As results.

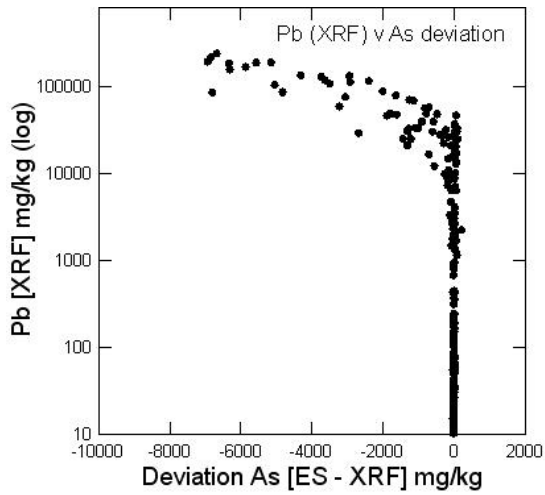


Figure 2.1 AS OMAC v GSI deviation

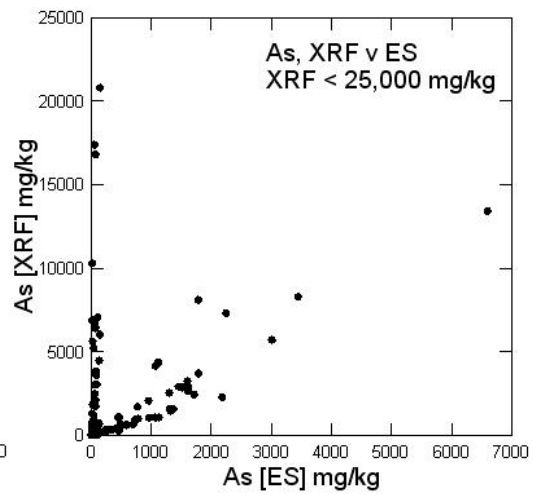


Figure 2.2 Pb v As

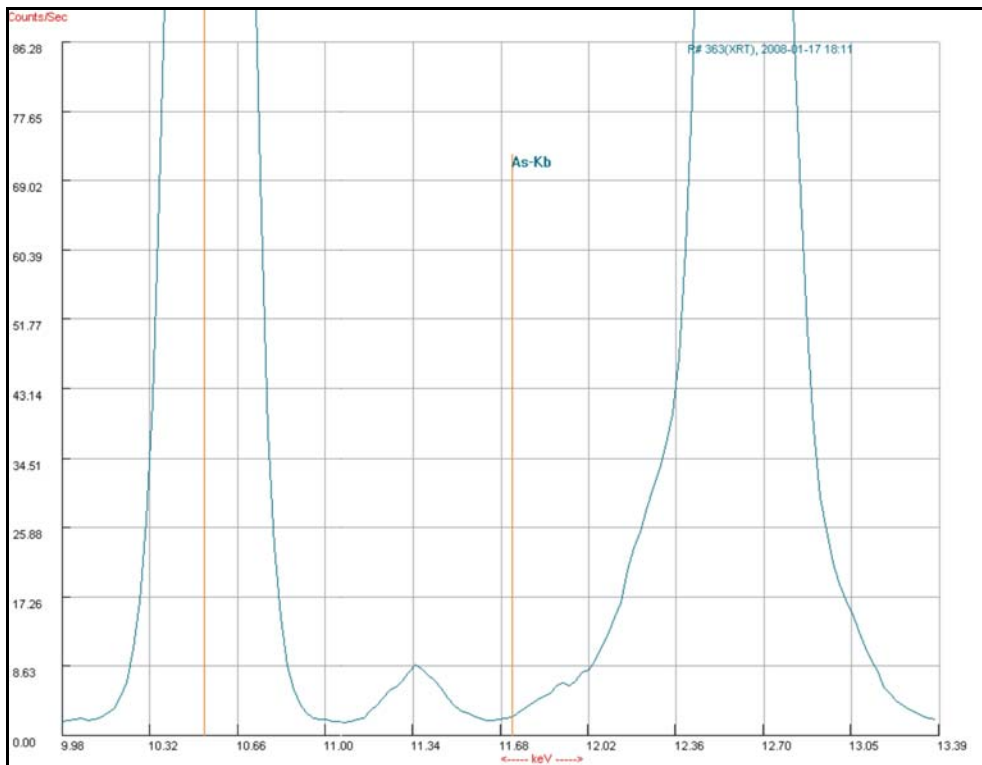


Figure 2.3 As spectrum, GSI XRF (measured As = 233,568 mg/kg)

3. Ba - barium

Table 3.1 Ba statistics (mg/kg)

Ba, n=221	OMAC	GSI
Min	21	<DL
Max	7901	98484
Median	421	646

Ba results again show a bias toward higher data for the GSI XRF analyses relative to the OMAC ES analyses (Table 1.1). This is most pronounced for measured GSI values above 1% (10,000 mg/kg) (Figure 3.1) but is also apparent even at lower values, e.g. below 2000 mg/kg (Figure 3.2). Thus, excluding both ES and XRF data above 2000 mg/kg as well as XRF data below the detection limit, the median value for the GSI XRF is 610 mg/kg, that for OMAC ES analyses 374 mg/kg. Despite the bias toward higher Ba in the GSI analyses, the data below 2000 mg/kg do show a reasonable spread across the 1:1 line (Figure 3.2). When data <10,000 mg/kg are plotted, it is clear that at least some of the ES data are also biased toward higher values, with a distinct grouping of values between 3000 and 8000 mg/kg corresponding to XRF values below 3000 mg/kg (Figure 3.3). Most of these analyses are from Gortdrum and Ballycorus mines. There is also a distinct group of points for which GSI XRF results range up to c. 10% (100,000 mg/kg) and for which OMAC ES results are around 3000 mg/kg or less. These samples are all from Tynagh mine, the one site sampled where barite was a major component of the ore.

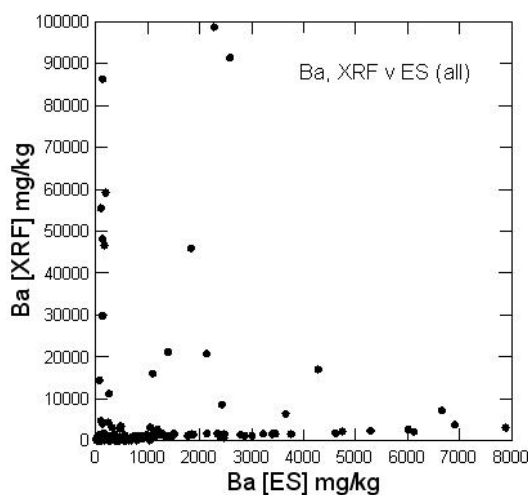


Fig. 3.1 Ba, OMAC v GSI (all) 2000mg/kg

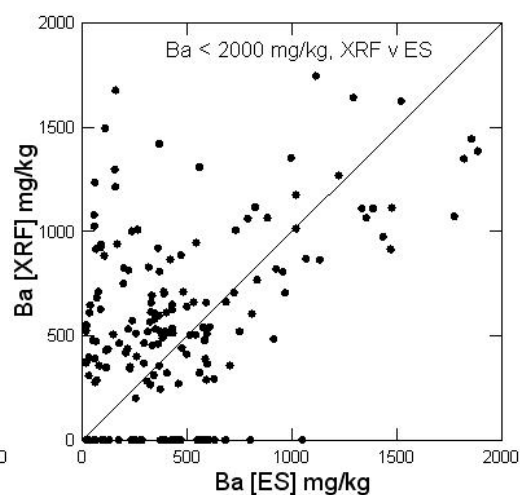


Fig. 3.2 Ba OMAC v GSI, < 2000mg/kg

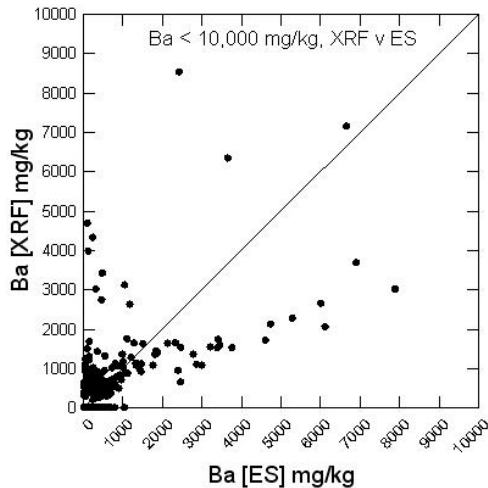


Figure 3.3 Ba, OMAC v GSI, <10,000 mg/kg

Standard analyses (Table 3.2) tend to confirm that there is a general bias toward high values for the GSI XRF. OMAC standard data are too limited to allow firm conclusions but results reported were within ranges defined for the standards employed. The upper calibration limit for the OMAC ES is 5000 mg/kg. In the absence of standards with concentrations of Ba exceeding 1000 mg/kg it is difficult to draw firm conclusions about the overall performance of the XRF given that so many mine waste samples return analyses well in excess of 5000 mg/kg. As with all elements, XRF analyses exceeding 1 – 2% Ba must be considered semi-quantitative.

Table 3.2 Ba XRF standard analyses

Instrument	Standard	n	Analysis χ	Accepted values
GSI XRF	NIST 2710	77	819	707
GSI XRF	NIST 2780	47	638	993
GSI XRF	NCS 73308	42	529	42
GSI XRF	CCRMP TILL-4	5	792	395
OMAC ES	SY-4	3	304 -336	340
OMAC ES	ICP-4	4	224 - 526	250 - 600

The Ba peaks in the XRF spectrum are K_{α} (32.19 keV), K_{β} (36.38), L_{α} (4.47) and L_{β} (4.83). Both K peaks are at the high-energy end of the spectrum where background counts are high. The Ba L peaks are substantially overlapped by Ti K_{α} (4.51) and Ti K_{β} (4.93). At relatively low concentrations of Ba (< 5-800 mg/kg depending on sample type), analysis appears to depend on the L peaks as the K peaks do not exceed background at this level.

4. Bi - bismuth

Table 4.1 Bi statistics, mg/kg

Bi, n=221	OMAC	GSI
Min	<5	<DL
Max	221	10982
Median	<5	<DL

The median values for both GSI XRF and OMAC ES analyses are below the limit of detection (5 mg/kg for ES analyses, set at 2.5 mg/kg), indicating that Bi was not detected by either method in most samples analysed (Table 4.1). Samples where Bi was detected fall mainly into two quite distinct groups: those detected at relatively high levels by both instruments and those detected at high levels by the GSI XRF and at low levels or not detected at all by the ES technique (Figure 4.1 & 4.2). The first group includes Avoca spoil and tailings and the second group includes spoil from Ballyvergin and Glendalough.

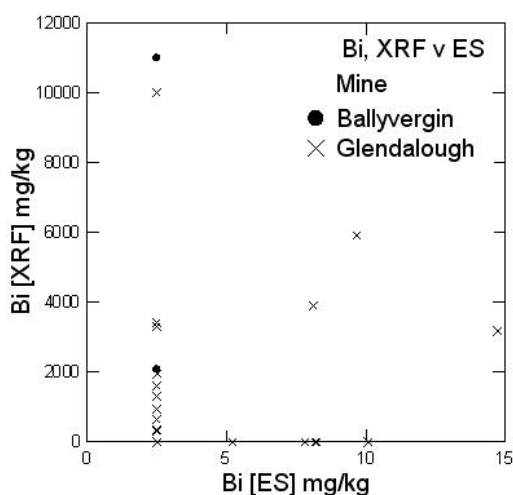


Fig. 4.1 Bi, XRF v ES (all)

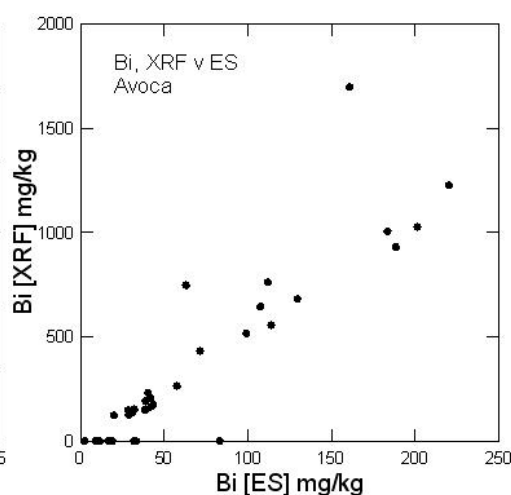


Fig. 4.2 Bi, XRF (high) v ES

The crustal abundance of Bi is < 0.02 mg/kg and consequently it does not occur in significant quantities outside of ore deposits. Some of the values (1000s mg/kg) recorded for Bi by the GSI XRF are greatly in excess of what might be expected for Bi even in Bi-enriched deposits and are suggestive of analytical artefacts. The most obvious source of such artefacts is the overlap between Bi and Pb peaks on the X-ray spectrum. A plot of Bi v Pb shows a broad linear relationship between these elements for GSI analyses but no such relationship for OMAC analyses (Figure 4.3 & 4.4). Nevertheless, some Bi enrichment may be expected in Pb-rich ores because the main Bi species, Bi^{3+} , is isoelectronic with Pb^{2+} and Bi substitutes for Pb, notably in galena.

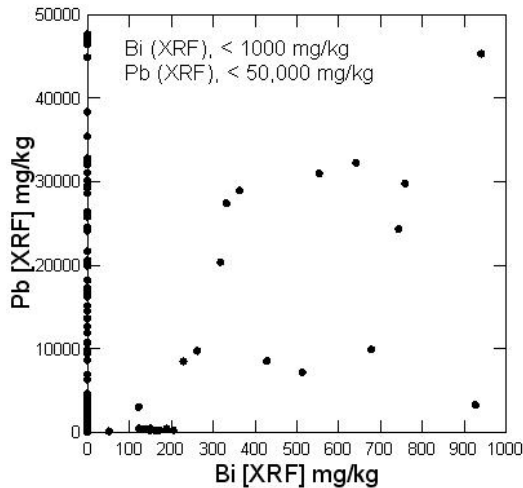


Figure 4.3 Bi v Pb GSI

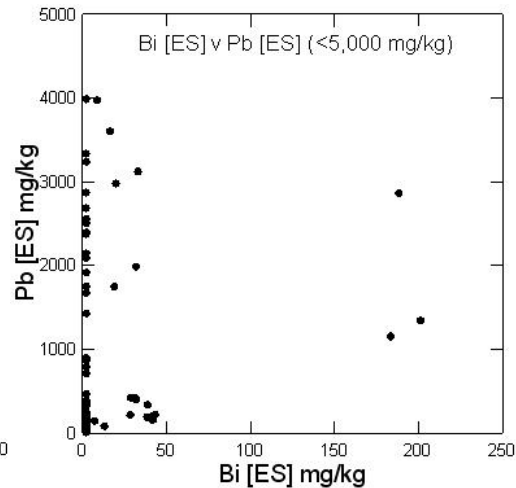


Figure 4.4 Bi v Pb OMAC

Most standards available in GSI do not have recorded Bi values. Exceptions are RCRA (0.88 mg/kg – too low for detection by GSI XRF) and CCRMP TILL-4 (40 mg/kg). The mean Bi value of analyses performed on CCRMP TILL-4 by the GSI XRF was 188 mg/kg, suggesting significant positive bias for Bi XRF analyses. The TILL-4 sample has only 50 mg/kg Pb yet its spectrum suggests that measured Bi concentration may be influenced by overlap from both Pb L_{α} and Rb K_{α} peaks. The difference in count data for the Pb L_{α} and Bi L_{α} suggests that measured concentration of Bi (= 187 mg/kg in this analysis) should be much less than that of Pb (= 65 mg/kg), yet the reverse is the case. Overlap alone does not seem to explain the very high Bi value returned for the TILL-4 standard and poor calibration is another possibility. One OMAC standard (ICP-4) has 30 mg/kg Bi and results during the ES analysis of GSI samples were, 24, 24, 27 and 30 mg/kg.

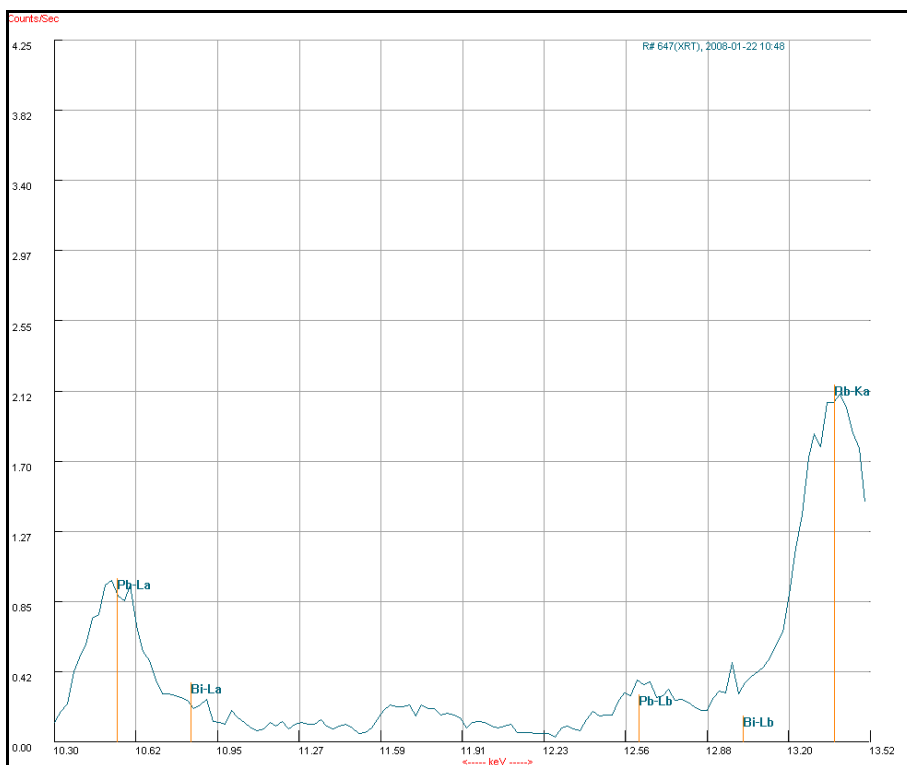


Figure 4.5 Bi spectrum for CCRMP TILL-4 standard

In the case of mine waste samples with high levels of Pb, it appears that overlap between the Pb and Bi peaks has led to false high values for Bi. One of the highest Bi values recorded by the GSI XRF was for a Ballyvergin spoil sample, with measured Bi of 2072 +/- 914 (1 σ) mg/kg and over 15% Pb. The OMAC analysis indicated Bi was below the detection limit. In the spectrum extract below the Bi peaks appear to be completely overlapped by the tails of the Pb peaks which have very high counts owing to the high Pb concentration. Additionally, the error on the Bi analysis is very high. For 95% certainty that the element has been detected the measured value should exceed 3 σ , so in this case and, indeed all other similar cases of very high Bi XRF values, the analysis cannot be relied upon.

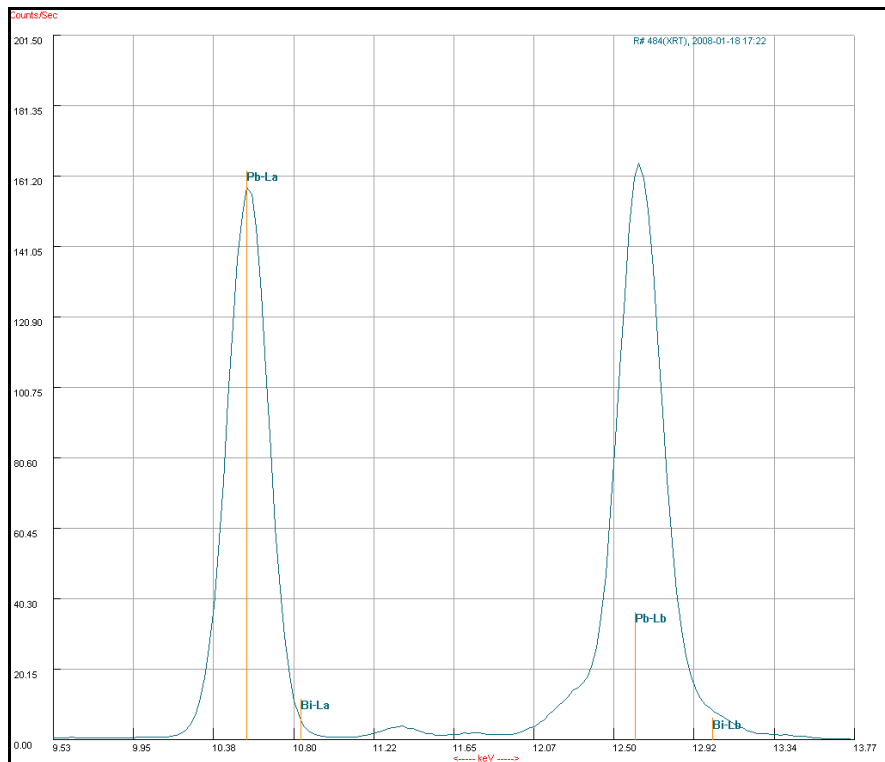


Figure 4.6 Bi spectrum for BVG-07-SP01.9

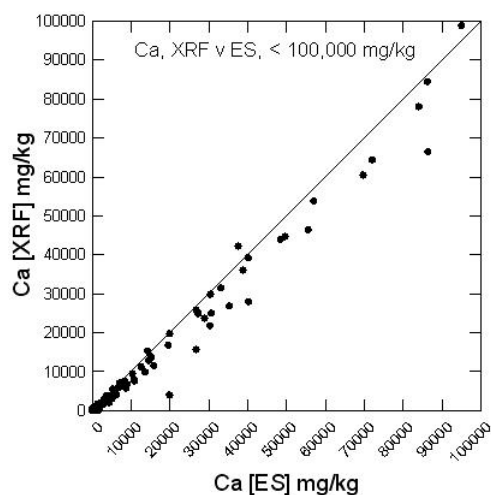
In summary, Bi XRF analyses are not generally reliable. Where samples have high Pb concentrations, false high Bi values may be recorded. Even where Bi is present in quite significant concentrations up to 200 mg/kg or more, as measured by OMAC ES analysis, the XRF values are generally overstated. Poor or limited XRF calibration as well as high Pb values may be a factor.

5. Ca - calcium

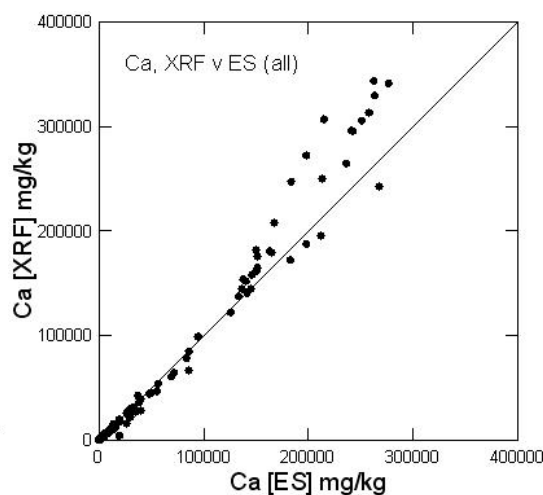
Table 5.1 Ca statistics (mg/kg)

Ca, n=221	OMAC	GSI
Min	50	<DL
Max	277104	342883
Median	2810	1966

Median values of Ca for ES and XRF data suggest a bias towards higher values among the ES analyses and this is borne out by the scatterplot for values below 100,000 mg/kg (10%) (Figure 5.1). Above 100,000 mg/kg (Figure 5.2), however, most GSI XRF analyses show a strong bias towards higher values compared to the ES data. Ca is one of the lighter elements analysed by XRF and, without a vacuum, detection limits, accuracy and precision are not expected to be as good as for heavier elements. Mean values for GSI XRF analyses of standards are 9837 mg/kg for NIST 2710 (certified value = 12500 mg/kg), 1795 mg/kg for NIST 2780 (1950 mg/kg), 4083 mg/kg for NCS 73308 (2800 mg/kg) and 6987 mg/kg for TILL-4 (8925 mg/kg). The low concentration of Ca in these standards prevents any realistic conclusions being drawn from the standard data other than that reasonable Ca results have been attained at relatively low element concentrations. The upper limit for the OMAC ES calibration is 12.5% and standard analyses showed very good agreement with accepted values (5.75% for SY-4 and 15.5% for ICP-4).



**Figure 5.1 Ca, OMAC v GSI [$< 10\%$]
[all]**



**Figure 5.2 Ca, OMAC v GSI
[all]**

There is no overlap between Ca and any other likely major peak so the variable quality of the analytical performance of the XRF could reflect the calibration, the lightness of the element or matrix effects. The latter may play a significant role, particularly in combination with the lightness of the element, since samples with high concentrations of heavy elements will have

a matrix that will impede lower-energy X-rays such as those emitted by lighter elements. This might help explain the general bias to lower values for GSI XRF analyses among samples with < 10% Ca. Those samples with Ca exceeding 10% generally have low concentrations of metals such as Pb and Zn (Figure 5.3 & 5.4).

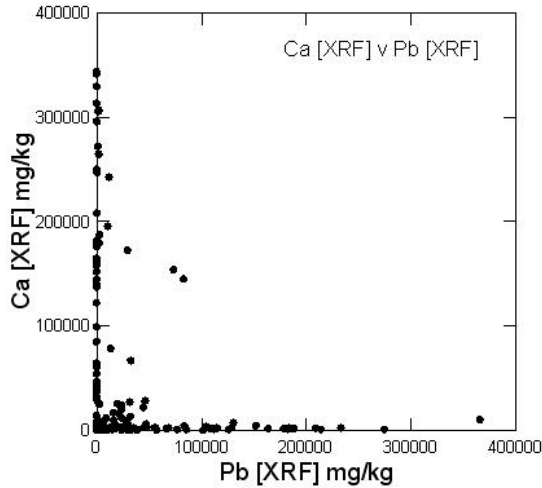


Figure 5.3 Ca v Pb [GSI]

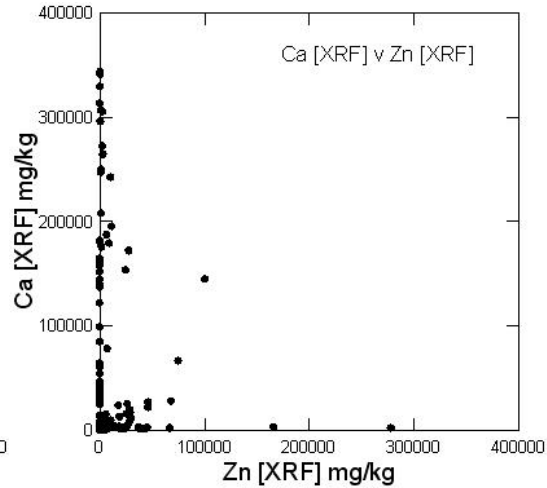


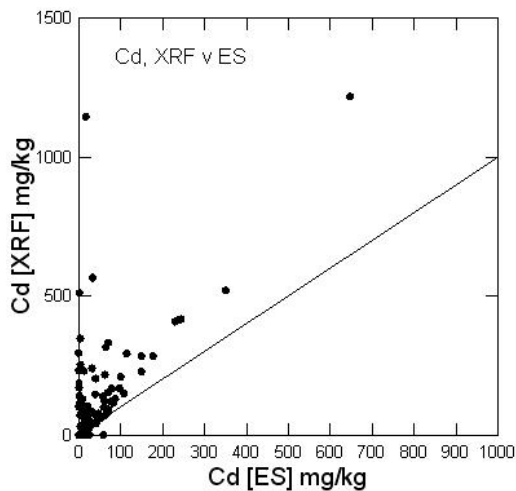
Figure 5.4 Ca v Zn [GSI]

6. Cd - cadmium

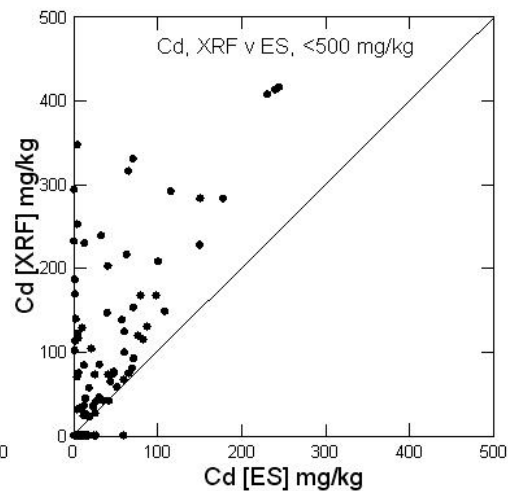
Table 6.1 Cd statistics (mg/kg)

Cd, n=221	OMAC	GSI
Min	<1	<DL
Max	648	1215
Median	1.5	<DL

Two thirds of Cd XRF analyses (146 out of 221) were below the limit of detection, giving a median value of 0.0. The minimum measured detected value was 22.5 mg/kg. Most OMAC results (118 out of 221) were \leq 2mg/kg, close to the limit of detection of 1 mg/kg. For those samples in which the XRF detected Cd (Fig 6.1, 6.2), there is a clear bias towards higher values in the XRF results when compared to the ES results.



**Figure 6.1 Cd, OMAC v GSI
500ppm**



**Figure 6.2 Cd, OMAC v GSI <
500ppm**

Examples of this bias include spoil from Ballyvergin and Keeldrum, where measured XRF values of 1142 and 294 mg/kg contrast with ES values of 18 and 1 mg/kg, respectively. Comparison of the XRF spectra for the Ballyvergin sample, BVG-07-SP01.9, and the standard RCRA, analysed in the same run, provides striking evidence of this bias toward high values (Fig 6.3). The RCRA standard is a spiked soil with c. 500 mg/kg Cd and 500 mg/kg Ag. Its spectrum shows two strong K α peaks for Ag and Cd and measured values were 456 and 464 mg/kg, respectively, close to the accepted values. The Ballyvergin sample analysis, with measured Ag and Cd concentrations of 519 and 1142 mg/kg, respectively, shows much smaller peaks for these elements than the standard. Errors on the count data are low and there are no peak overlaps that could explain high measured XRF values for the Ballyvergin sample. Similar spectra can be observed for other samples where measured XRF values greatly exceed those of the ES analyses.

Only the RCRA (500 mg/kg) and NIST HIGH 2710 (21.8 mg/kg) standards have Cd at levels detectable by XRF. Mean Cd value for the RCRA standard (n = 13) was 496 mg/kg (range 466 – 524 mg/kg); for NIST 2710 (n = 77) the mean was 15 mg/kg (range 0.0 – 39 mg/kg). Neither is indicative of major problems with XRF Cd analyses. A possible reason for the bias in analysed samples is that the main Cd X-ray peaks lie at the high-energy end of the X-ray spectrum (K α = 23.11 keV), where background count data are relatively high. One may speculate that poor correlation of background count data in samples and the standards used to calibrate the XRF contributes to the discrepancies observed.

The preliminary conclusion is that XRF Cd analyses are generally unreliable and show bias to higher values compared to those obtained by ES analysis. Deviations from values obtained by ES analysis increase as apparent concentrations increase. Unsatisfactory calibration of the XRF at the high-energy end of the spectrum may contribute to this but the reason for the bias is not known with any certainty.

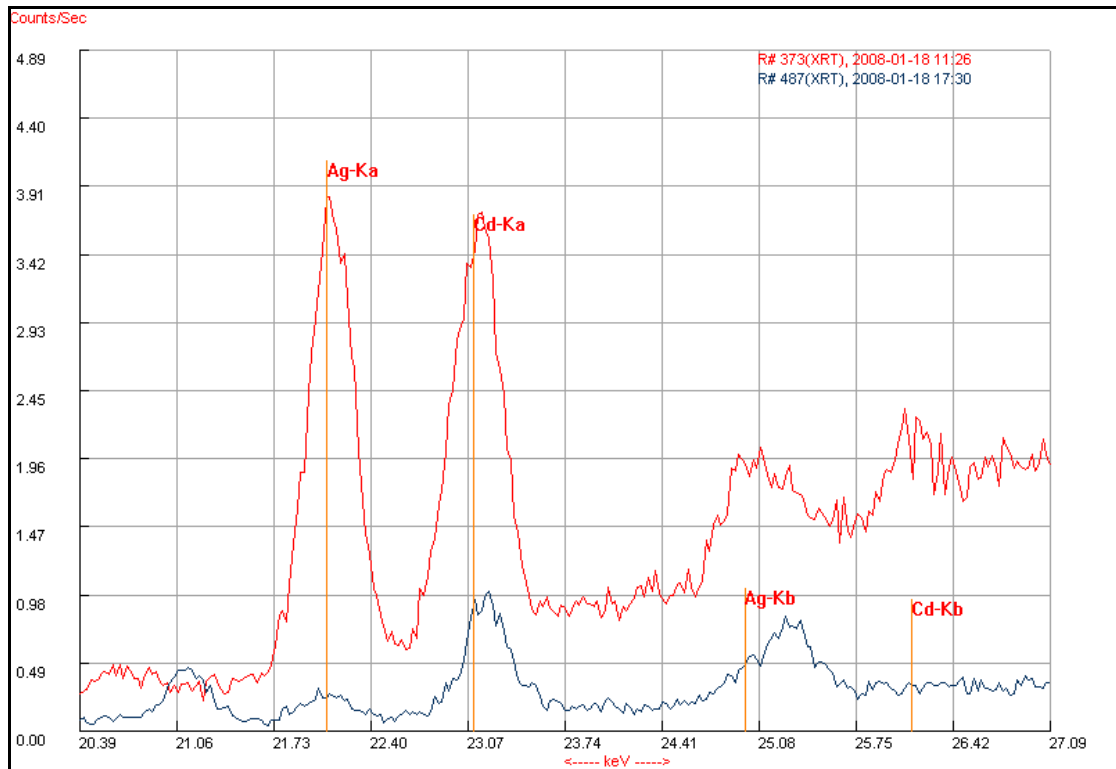


Figure 6.3 RCRA Standard spectrum (red) and Ballyvergin spoil sample spectrum (blue) for Ag and Cd Ka lines

7. Co - cobalt

Table 7.1 Co statistics (mg/kg)

Co, n=221	OMAC	GSI
Min	<1	<DL
Max	156	2062
Median	10	<DL

Comparison of XRF and ES analyses for Co reveal similar trends as for Cd. Only 40 XRF analyses detected Co and of these 39 had values ≥ 180 mg/kg. Figure 7.1 shows extreme bias toward higher values among XRF analyses compared to ES analyses. This bias is confirmed by standard analyses (Table 7.2).

The $K\alpha$ and $K\beta$ XRF peaks for Co have energies of 6.93 and 7.65 keV, respectively. The $K\beta$ peak for Fe is very close to the $K\alpha$ peak for Co and, where Fe is present in high concentrations, its $K\beta$ peak may overlap the Co $K\alpha$ peak. This overlap appears to provide a reasonable explanation for the behaviour of Co in XRF analyses and can be illustrated by comparison of two samples, AVO-07-SP01.2 and TYN-07-SP01.7, from Avoca and Tynagh, respectively (Figure 7.2).

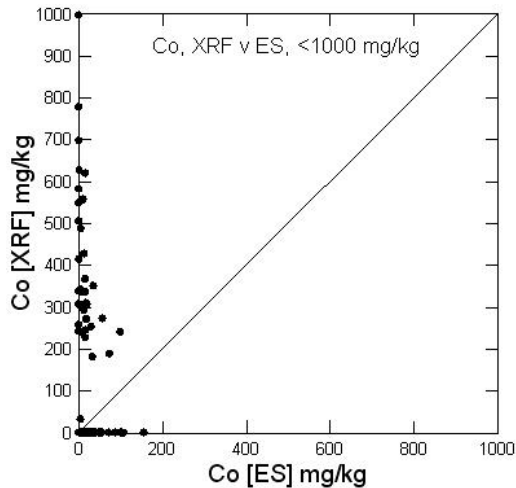


Figure 7.1 Co, OMAC v GSI (<1000 mg/kg)

Table 7.2 Co XRF standard analyses

Standard	n	Range	\bar{x}	Accepted values
NIST 2710	77	0 - 0	0	10
NIST 2780	47	0 - 379	88	2.2
NCS 73308	42	0 - 287	94	15
CCRMP TILL-4	5	0 - 261	198	8

The Avoca sample has measured XRF values of 2061 mg/kg Co and 31.7% Fe. The Tynagh sample has measured XRF values of 0 mg/kg Co and 46.9% Fe. The Tynagh sample has high Cu and Pb and the metal-rich matrix probably accounts for the relatively small size of the Fe peaks when compared to the Avoca sample which has much lower concentrations of other metals. The smaller Fe K β peak for the Tynagh sample only partly overlaps the Co K α peak energy. In contrast, the Avoca sample K β peak has a much greater overlap with the Co K α peak. This could explain why the Avoca sample has a measured XRF Co value of 2061 mg/kg, while Co for the Tynagh sample is below the detection limit, i.e. the large Fe K β peak has raised the count rate in the region of the Co K α peak, giving rise to a false Co measurement.

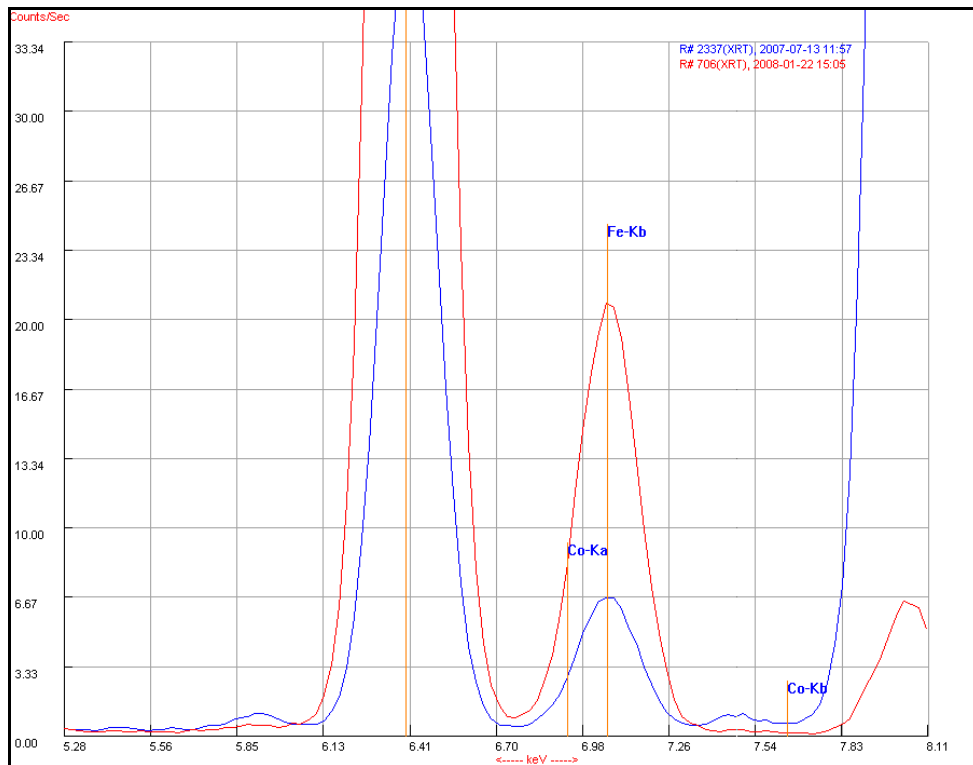


Figure 7.2 Partial spectra for Avoca (red) and Tynagh (blue) samples showing relationship between Co and Fe peaks

8. Cr - chromium

Table 8.1 Cr statistics (mg/kg)

Cr, n=221	OMAC	GSI
Min	1.0	<DL
Max	157	667
Median	34	0

Analyses of Cr reveal a similar relationship between XRF and ES analyses as observed for Cd and Co: high detection limits and an apparent bias towards higher values for XRF analyses compared to ES analyses (Figure 8.1). Of 221 analyses in the comparison study, Cr was below the detection limit in 139 of the XRF analyses. The lowest recorded measured value for XRF was 26 mg/kg. Table 8.2 summarizes the standard data for the XRF and they suggest a detection limit in excess of 50 mg/kg is more realistic. Analyses of two standards with 136 and 500 mg/kg Cr, respectively, yielded generally good results.

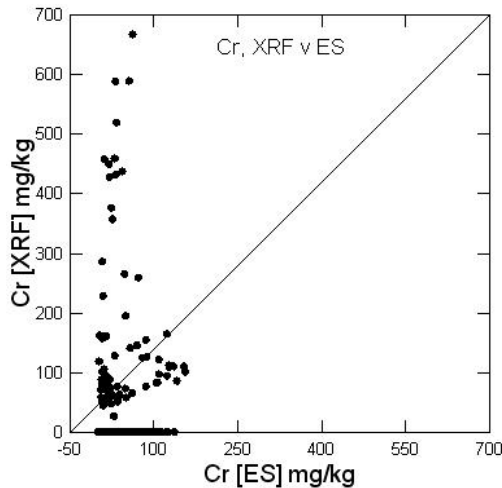


Figure 8.1 Cr, OMAC v GSI

Table 8.2 Cr XRF standard analyses

Standard	n	Range	<i>x</i>	Accepted values
NIST 2710	77	0 - 0	0	39
NIST 2780	47	0 - 69	3	44
RCRA	13	432 - 538	461	500
NCS 73308	42	107 - 195	146	136
CCRMP TILL-4	5	0 - 0	0	53

As with other elements that show a bias toward higher values in the XRF analyses, an obvious potential source of spurious high Cr values may be overlap of X-ray peaks. Figure 8.2 shows spectra for the RCRA standard (measured Cr = 454 mg/kg) and a sample of spoil from Letter mine in West Cork (measured Cr = 258 mg/kg). The RCRA standard shows an identifiable Cr K α peak but there is no clear peak for the Letter mine sample, although apparent background count levels at this point are higher than those in the standard analysis, possibly as a result of interference from the L α peak of Nd and the L β peak of Ce. The Cr K β peak location is overlapped by the Mn K α peak. Whether the latter has any influence on computed XRF values for Cr is unclear. It may be that the relatively high background level of the count data at the Cr K α peak is sufficient to give rise to measured Cr. The lack of any identifiable peak at this point for the Letter sample suggests that the 258 mg/kg recorded may be spurious. Examination of the spectra for other samples with high Cr in XRF analyses relative to ES analyses indicates a similar situation.

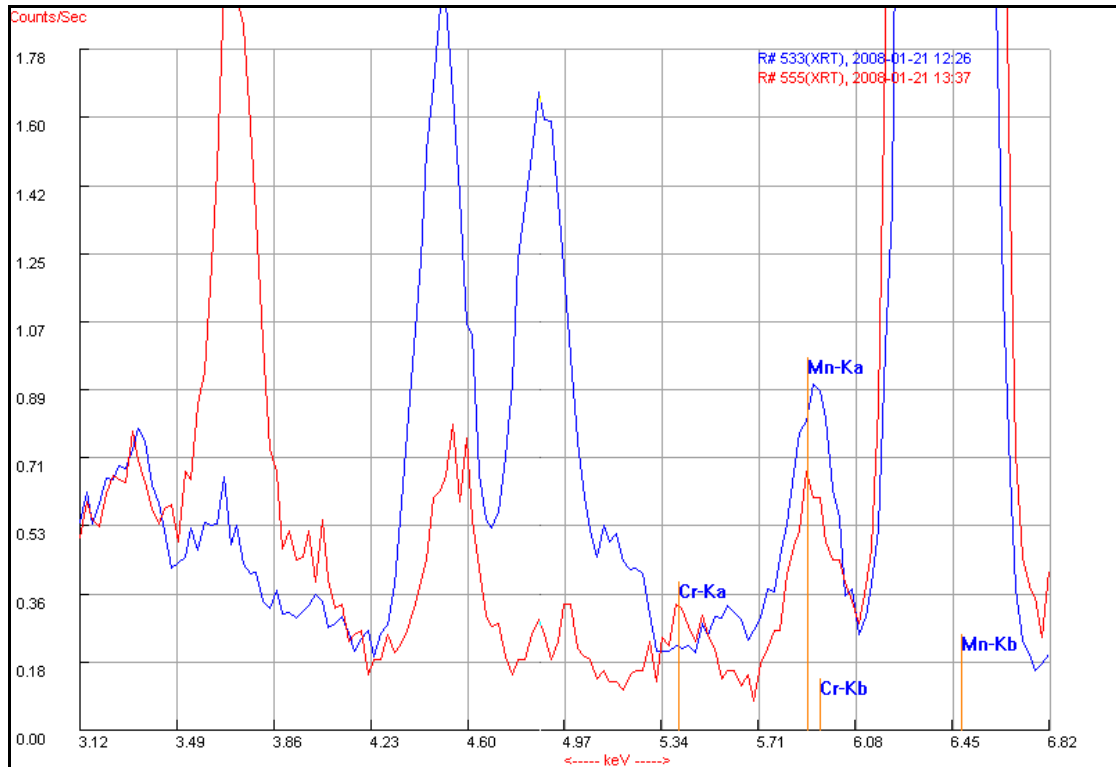


Figure 8.2 Partial spectra for RCRA standard (red) and Letter sample (blue) showing relationship between Cr and Mn peaks

9. Cu - copper

Table 9.1 Cu statistics (mg/kg)

Cu, n=221	OMAC	GSI
Min	6.1	<DL
Max	73531	102361
Median	453	405

Cu values for XRF and ES analyses show broad agreement across the range of data (Figure 9.1 - 9.3). For values below 10,000 mg/kg the correlation coefficient, r , is 0.85 and for those below 1000 it is 0.95. Below 1000 mg/kg there is a bias towards higher values among ES analyses; between 1000 and 5000 mg/kg, XRF values tend to be higher than ES analyses. These biases reflect different sample compositions: samples from Pb-Zn mines such as Glendalough, Ballycorus, Tynagh, Ballyhickey and Caim tend to give higher Cu results for XRF analyses while samples from Cu mines such as Allihies, Gortdrum and Avoca tend to have higher Cu in ES analyses. In general, however, the biases observed are proportionately much less than those seen for some other elements.

Table 9.2 Cu XRF standard analyses

Standard	n	Range	\bar{x}	Accepted values
NIST 2710	77	2836 - 3100	2993	2950
NIST 2780	47	144 - 206	175	215
NCS 73308	42	0 - 36	23	23
CCRMP TILL-4	5	226 - 242	234	237

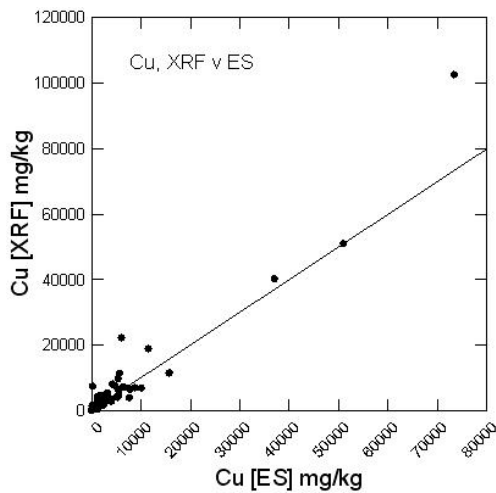


Fig. 9.1 Cr, OMAC v GSI mg/kg

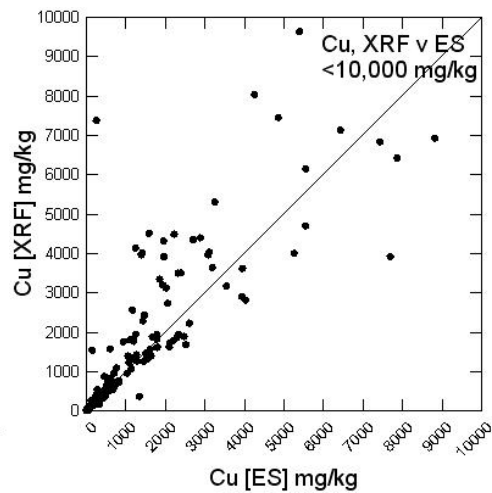


Fig. 9.2 Cr, OMAC v GSI, <10,000 mg/kg

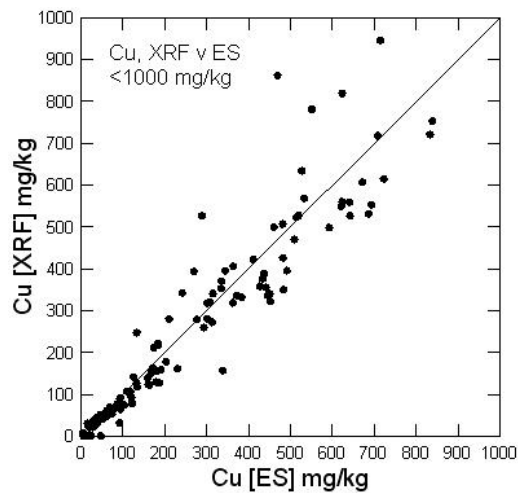


Figure 9.3 Cu, OMAC v GSI, < 1000 mg/kg

Cu was detected in all but 13 samples out of the 221 analysed in the comparison study. The median values for both ES and XRF analyses are in reasonable agreement, as expected from scatterplot distributions. Data for standards (Table 9.2) indicate very good accuracy for XRF data across a range of values. Detection limit for Cu appears to be around 20 mg/kg. An exception to the generally good accuracy obtained for standard analyses is the NIST 2780 mine waste standard. XRF analyses of this standard generally return lower values than expected for a range of metallic elements. This may be interpreted as a reflection of the difference in matrix composition between the mine waste standard and the soil standards used to calibrate the XRF. One might expect similar effects to be observed in the mine waste samples analysed, i.e. a systematic bias towards low values in XRF analyses. If one assumes the ES analyses are accurate, then no such bias is apparent.

10. Fe - iron

Table 10.1 Fe statistics (mg/kg)

Fe, n=221	OMAC	GSI
Min	1477	2335
Max	490,947	1,851,542
Median	35885	32169

XRF analyses of Fe show a significant bias towards higher values when compared to ES analyses, especially at high concentrations (> 10,000 mg/kg) (Fig 10.1). Below 10,000 mg/kg there is much better agreement between OMAC ES and GSI XRF analyses, with a bias in many cases toward higher values among ES analyses. As with other elements, the XRF is calibrated to 2% (20,000 mg/kg) Fe for a soil matrix, whereas the ES analyses are calibrated to 12.5%.

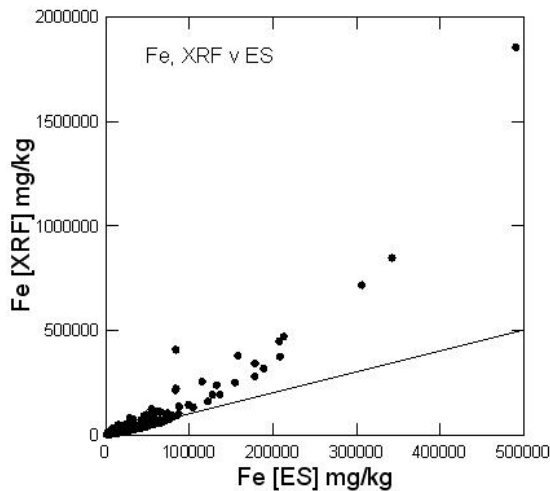


Figure 10.1 Fe, OMAC v GSI mg/kg

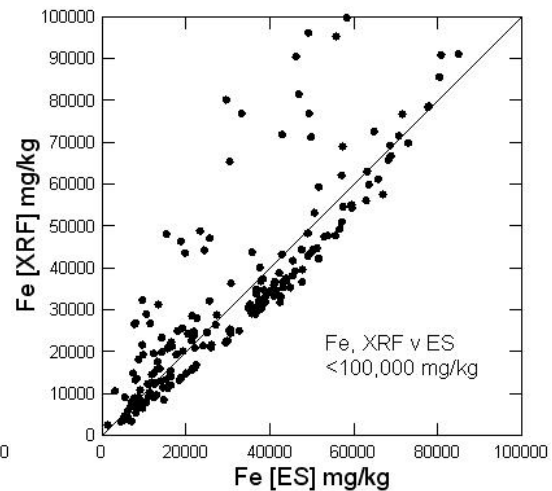


Figure 10.2 Fe, OMAC v GSI, <100,000 mg/kg

Table 10.2 Fe XRF standard analyses

Standard	n	Range	\bar{x}	Accepted values
NIST 2710	77	32694 - 35644	34136	33800
NIST 2780	47	22374 - 23924	23130	27840
NCS 73308	39	18846 - 20304	19660	27000
CCRMP TILL-4	5	32614 - 33813	33008	39700

The two standards (Fe = 5.3% and 4.3%) analysed by ES during sample runs gave acceptable results. Standards (2.7 – 3.97 % Fe) analysed by XRF gave less satisfactory results (Table 10.2), with most returning significantly *lower* values than expected. This is consistent with observed results for most samples in the comparison study below 40,000 mg/kg (4%) Fe (OMAC): at this level, most samples gave higher values in ES analyses compared to XRF analyses (Fig. 10.2, 10.3). Exceptions are samples from, mainly, Glendalough which are significantly biased toward higher Fe values in this range. At higher Fe concentrations, samples from other mines such as Avoca, Caim, Ballyvergin and Tynagh also show bias toward higher XRF values compared to ES analyses (Fig 10.4).

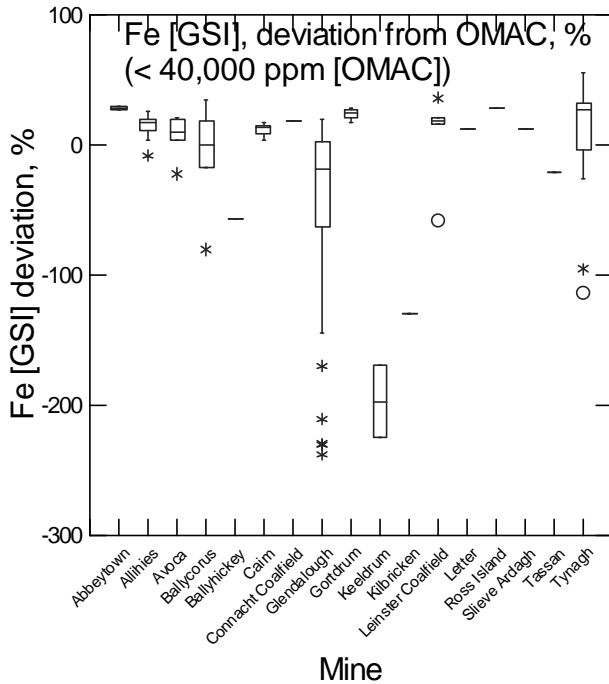


Figure 10.3 Fe deviation, %, < 40,000 mg/kg

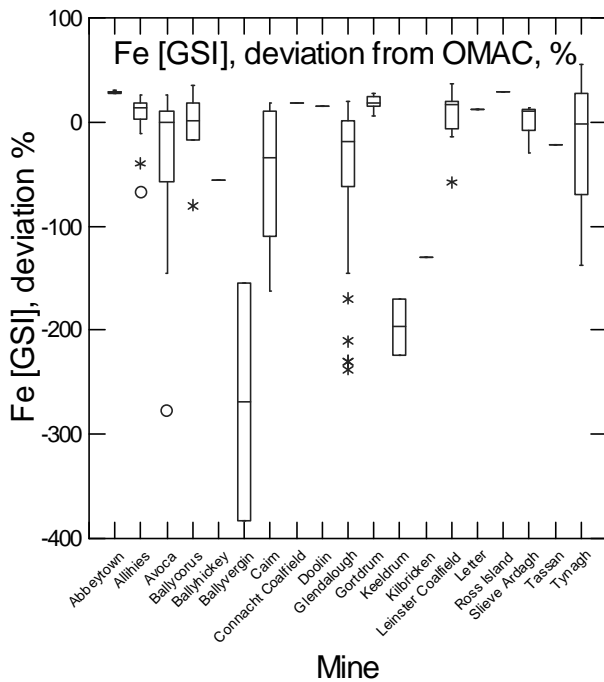


Figure 10.4 Fe deviation %, all

Because Fe is typically present in samples in relatively high (%) concentrations, the main K α XRF peak (6.40 keV) is generally very well defined and not overlapped by any other peak. Consequently inaccuracies in analysis are likely to reflect uncertainties in either the XRF calibration or correction programme. The XRF is calibrated for soils with metal concentrations below 2% and the complex, metal-rich matrices presented by mine waste will inevitably affect the accuracy of analyses. Fig 10.3 and 10.4 show that the deviations of XRF analyses from those of OMAC ES analyses

vary in a coherent way according to mine site, i.e. waste from the same mine site, with a broadly similar composition, tends to produce analyses with similar inaccuracies.

In conclusion, XRF analyses show a bias toward higher Fe compared to ES analyses at high Fe concentrations. At lower concentrations, i.e. below approximately 5%, most XRF Fe analyses are quite close to or even lower than those of ES. Exceptions are samples from specific mines that have much higher XRF values. The correlation of high values with specific mine sites suggests that the deviations observed can best be explained by uncertainties in calibration and correction factors arising from the particular composition of waste on those sites.

11. Hg - mercury

Table 11.1 Hg statistics (mg/kg)

Hg, n=221	OMAC	GSI
Min	0.5	0
Max	3.8	391
Median	0.5	0

Hg was detected by XRF in only 23 samples and by ES in 7. Only in 4 samples, all from Gortdrum, was Hg detected by both methods. In these samples the XRF returned values between 10 and 20 whereas the ES analyses yielded values between 1 and 4. These ES analysis involved multi-acid digestion and this is detrimental to Hg analysis as it causes volatilization and loss of the metal at the preparation stage. The effect of this can be seen in Fig 11.1, where results for samples from Tynagh, Gortdrum and Silvermines, prepared using both multi-acid digestion (MA-ES) and aqua regia (AR-ES), are compared. It is clear that the multi-acid digestion technique causes severe loss of Hg from samples prior to analysis. Comparison of the aqua regia-based analyses with XRF analyses of the same samples show reasonable agreement for most samples across the range of values (Fig 11.2), though there are clearly large deviations in two cases where Hg was measured at very low concentrations in the AR-ES analysis. As all Hg analyses in this comparison study were done by MA-ES it is therefore not possible to make valid comparisons between the GSI XRF and OMAC ES analyses.

Hg occurs in very low concentrations in most soils and for the most part even in mine waste. Only one XRF standard, NIST 2710, contains Hg at a level (33 mg/kg) measurable by XRF. The XRF detected Hg in 32 out of 77 analyses of NIST 2710. For the analyses where it detected Hg, the range was 23 to 44 mg/kg (mean 28.9). The analytical errors are large and 33 mg/kg is clearly very close to the limit of detection for the XRF in this standard. Nonetheless,

when the XRF detected Hg the measured value was close to the certified value.

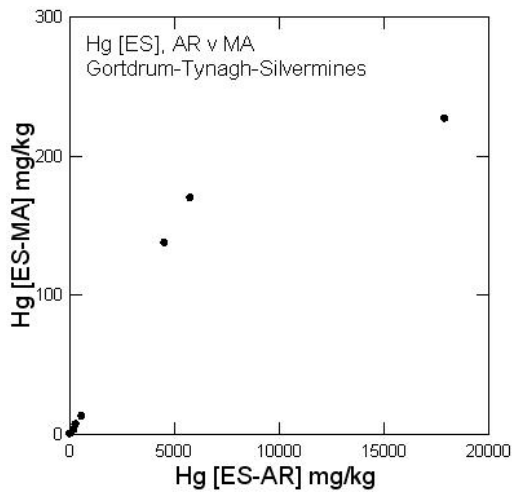


Figure 11.1 Hg, OMAC (AR v MA)

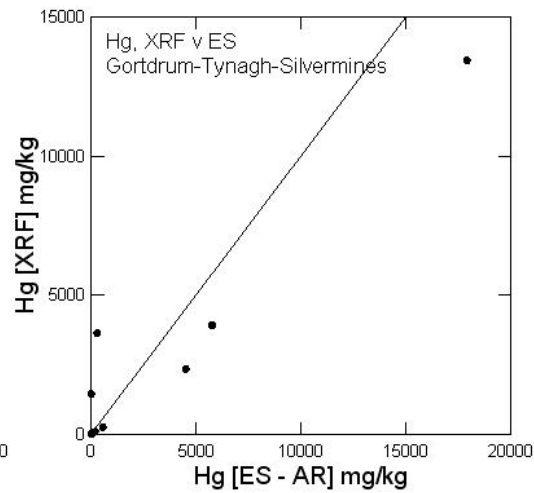


Figure 11.2 Hg, OMAC v GSI

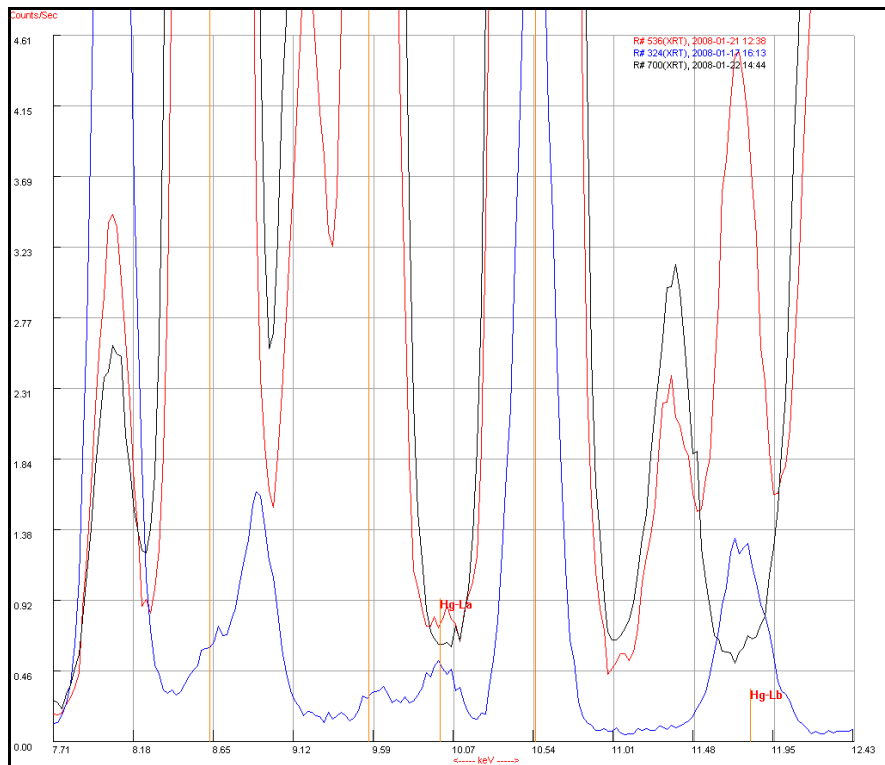


Figure 11.3 Partial spectra for samples from Gortdrum (blue), Kilbricken (red) and Glendalough (black). The peaks to either side of Hg La are Zn Kβ (left) and Pb Ka.

Peak overlap must be considered in assessing XRF results for Hg. The Hg La peak has energy 9.99 keV and is located between the Kβ peak of Zn and the Ka peak of Pb. In Zn-Pb mines these two peaks can be very strong, raising

the background count levels in the vicinity of the Hg peak and potentially giving rise to spurious Hg results. Fig 11.3 show partial spectra for three samples with apparently detected Hg, from Gortdrum (72 mg/kg), Kilbricken (348 mg/kg) and Glendalough (390 mg/kg). The Gortdrum sample has a well-defined peak for Hg but the Glendalough sample does not. The Kilbricken sample, despite having Zn and Pb peaks to either side similar in size to the Glendalough sample, also has a well-defined Hg peak. It is possible therefore that the Glendalough Hg analysis gives a spurious result. The peak close to the Hg $L\beta$ line is that of As $K\beta$.

Peak analysis of all 23 samples in which Hg was apparently detected by XRF suggests that in most cases a peak is present. Where high concentrations of Pb and Zn are recorded, as in Tynagh and Kilbricken samples, and some Glendalough samples, no peak can be distinguished and the measured Hg value is more likely spurious. In the case of samples of aggregate from Gortdrum with measured XRF values of 14 to 19 mg/kg Hg, a peak is observed (Fig. 11.4) and the ability of the XRF to detect Hg at such low apparent concentrations reflects the lack of any significant Zn and Pb in these samples.

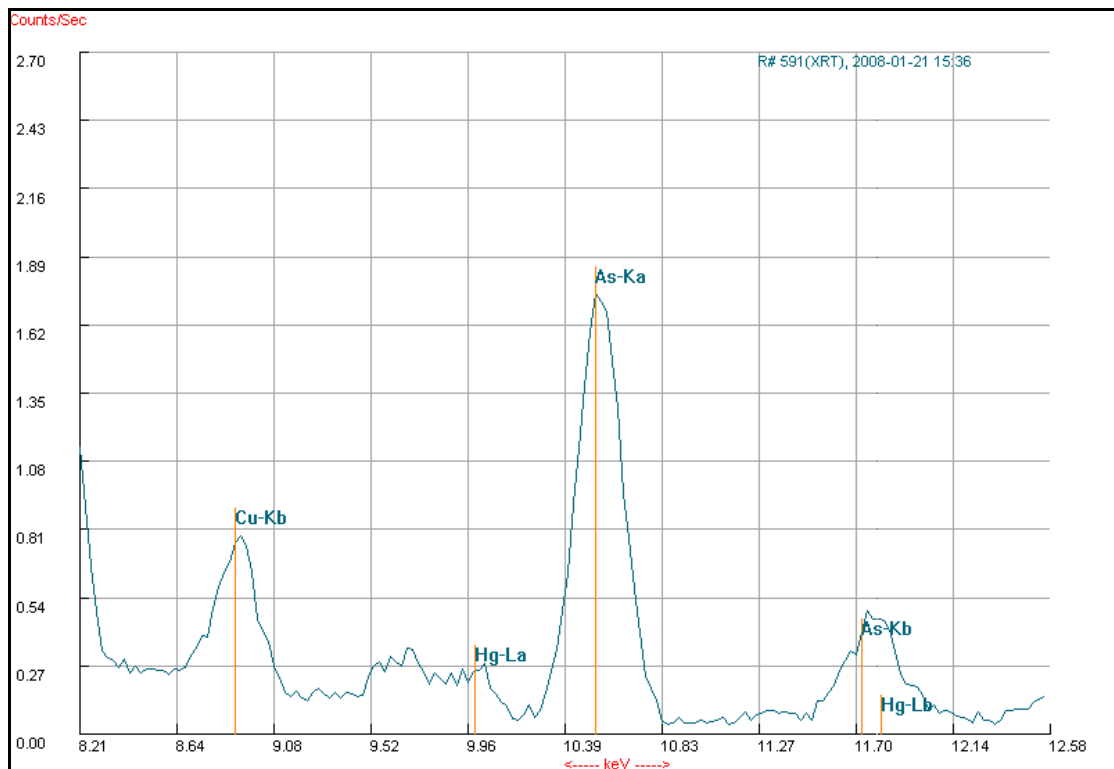


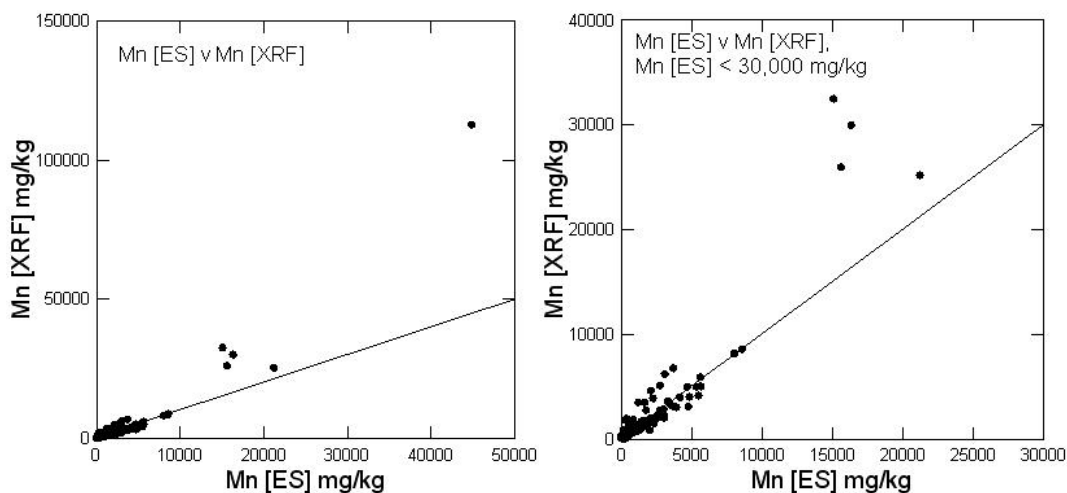
Figure 11.4 Partial spectra for aggregate sample from Gortdrum (measured Hg = 18 mg/kg) showing Hg peaks and adjacent As and Cu peaks.

12. Mn - manganese

Table 12.1 Mn statistics (mg/kg)

Mn, n=221	OMAC	GSI
Min	<5	<DL
Max	44927	112526
Median	825	803

The median concentrations of Mn, measured by XRF and ES in the 221 samples analysed for the comparative study, are very similar (Table 12.1) and suggest good overall agreement between both techniques. For the five samples for which the measured concentration exceeds 10,000 mg/kg or 1%, there is considerable divergence, with measured XRF concentrations significantly higher than corresponding ES concentrations (Fig. 12.1). However, for the 216 samples with measured concentration below 10,000 mg/kg, the correlation coefficient (r) for the two techniques is 0.91 (Fig. 12.1). However, this strong correlation is accompanied by considerable scatter about the 1:1 line. This is particularly apparent above 3000 mg/kg Mn but is also present at lower concentrations (Fig. 12.1). Below 3000 mg/kg, measured ES concentrations tend to exceed measured XRF concentrations. For the 197 samples for which the Mn concentration measured by ES was <3000 mg/kg, the measured ES concentration exceeded the measured XRF concentration in 145 samples. For these 145 samples, the median deviation between the measured XRF and ES concentration was 182 mg/kg (range: 3 – 1257 mg/kg). For the 52 samples for which the measured XRF concentration exceeded that measured by ES, the median deviation was 253 mg/kg (range: 9 – 2443 mg/kg). Thus, although there is a generally strong correlation between Mn concentrations measured by ES and XRF, there are in many cases quite large deviations between results obtained by the two techniques for the same sample.



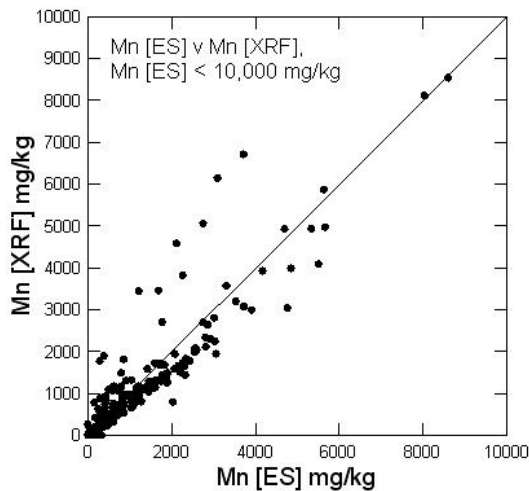


Fig. 12.1 Mn (XRF) v Mn (ES) for various concentration ranges

Certified Mn concentrations, ranging from 323 to 8530 mg/kg, are reported for four standards analysed during the course of the project (Table 12.1). XRF analyses of these standards demonstrate a general bias towards concentrations lower than those certified, with the exception of NIST 2710 for which the certified Mn concentration is relatively high (Table 12.2). These results are consistent with the deviations observed between XRF and ES analyses and confirm that the XRF analyser tends to underestimate the concentration of Mn, particularly for those samples in which the Mn concentration is below 3000 mg/kg.

Table 12.2 Mn XRF standard analyses

Standard	n	Range	\bar{x}	Accepted values
NIST 2710	77	9762 - 10633	10199	8530
NIST 2780	47	279 - 446	358	462
NCS 73308	39	647 - 768	706	1010
CCRMP TILL-4	5	283 - 367	323	490

13. Ni - nickel

Table 13.1 Ni statistics (mg/kg)

Ni, n=221	OMAC	GSI
Min	<1	<DL
Max	187	399
Median	17	<DL

Nickel was detected in only 29 of the 221 samples analysed by XRF for the comparative study. Comparison of XRF and ES data suggest that the XRF detection limit for these laboratory-prepared samples was typically around 40 to 60 mg/kg. Detection limits for *in-situ* analyses are likely to be significantly higher.

For those samples in which Ni was detected by XRF, there is a rough correlation (correlation coefficient $r = 0.51$) between concentrations measured by XRF and ES (Fig. 13.1). In 20 out of 29 analyses, the measured XRF concentration exceeds the measured ES concentration.

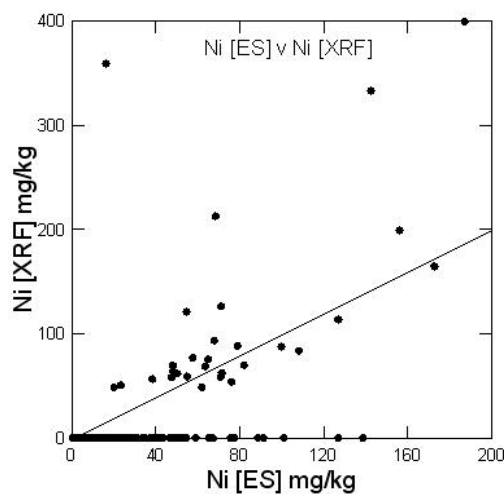


Fig. 13.1 Ni (XRF) v Ni (ES), all samples

A certified Ni concentration is reported for four of the five standards analysed over the course of the project, NIST 2710 (14 mg/kg), NIST 2780 (12 mg/kg), NCS 73308 (30 mg/kg) and CCRMP TILL-4 (17 mg/kg). Ni was detected in only two out of 39 analyses of NCS 73308 (51 and 59 mg/kg) and not at all in the other three standards. These results are generally consistent with the conclusions drawn from the comparative study regarding detection limits for Ni, clearly indicating that these limits are typically above 30 mg/kg.

In summary, XRF detection limits for Ni are typically around 40 – 60 mg/kg. There is a broad correlation between Ni concentrations measured by XRF and ES with a tendency for measured XRF concentrations to exceed those of ES.

14. Pb - lead

Table 14.1 Pb statistics (mg/kg)

Pb, n=221	OMAC	GSI	Pb, n=162	OMAC	GSI
Min	1.5	10	Min	2	10
Max	20000	773192	Max	19482	32774
Median	1745	1661	Median	171	169

The concentration of Pb in the 221 prepared samples measured in the laboratory by portable XRF ranged from 10 to 773,192 mg/kg (Table 14.1). The upper calibration limit for ES analyses was 20,000 mg/kg Pb and 59 of the samples analysed by ES had measured Pb concentrations in excess of this limit. Nevertheless, the similar median concentrations for each method (1661 and 1745 mg/kg, Table 14.1) indicate good agreement between the techniques. For the 162 samples with measured ES concentration below 20,000 mg/kg, the ES and XRF results are strongly correlated ($r = 0.94$) (Fig. 14.1), with the exception of a few samples for which the XRF results were much higher. For the 144 samples for which the measured ES concentration was below 10,000 mg/kg (1%), the correlation between XRF and ES data is almost identical ($r = 0.92$) (Fig. 14.1). The upper calibration limit for the XRF is 20,000 mg/kg (2 %) and these data suggest that, for the most part, XRF Pb analyses are generally quite accurate up to this limit.

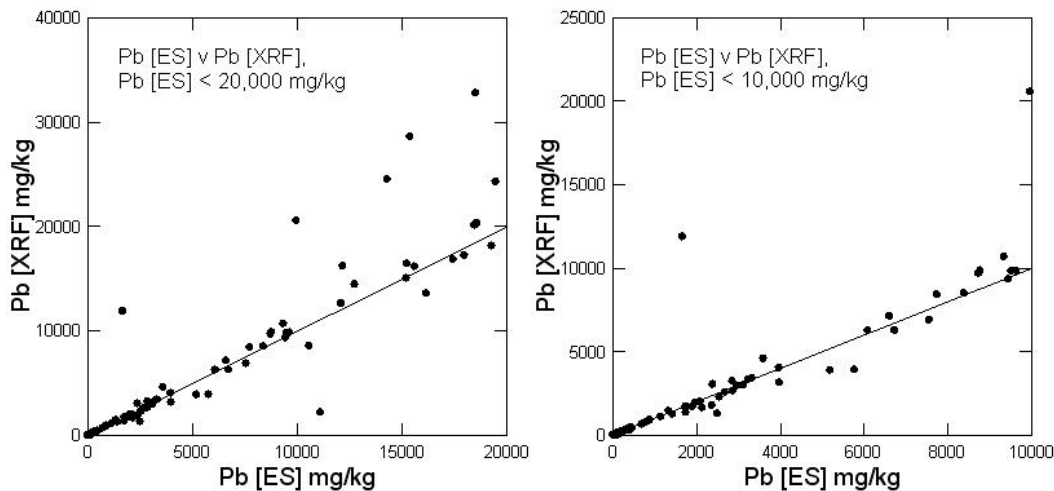


Fig. 14.1 Pb (XRF) v Pb (ES), various concentration ranges

The upper calibration limit for both the ES and XRF analyses is 20,000 mg/kg Pb (2%). Measured XRF concentrations exceeding this limit must be considered semi-quantitative. An attempt was made to assess the accuracy of XRF analyses of samples with very high measured metal concentrations by carrying out assays of the samples at OMAC laboratories. The assay analysis

included As, Cd, Cu, Fe, Pb and Zn. Comparison of results of Pb analyses for the 13 samples analysed by assay with those previously obtained by ES analysis at OMAC (Table 14.2) indicates good agreement for the most part between the two methods for concentrations below 20,000 mg/kg. Table 14.2 also compares the summary data for the assay and GSI analyses carried out in the laboratory and the field. In general, GSI XRF results for laboratory-analysed samples are somewhat higher than those obtained by assay, indicating a bias toward high measured values in samples with high concentrations (> 20,000 mg/kg) of Pb (Fig. 14.2). For samples analysed by XRF in the field, measured Pb concentrations tend to be lower than the corresponding assay value. Examples of high XRF results for Pb include (OMAC assay results in brackets) 9343 mg/kg (9149 mg/kg), 2.43 % (1.97%), 4.64% (3.54%), 10.19% (6.74%), 15.24% (9.77%) and 23.36% (15.79%).

Table 14.2 Pb assays

Pb, n=13	OMAC (ES)	OMAC (assay)	GSI XRF (lab)	GSI XRF (field)
Minimum	7744	7599	8427	4796
Maximum	>20000	309890	773192	142067
Median	>20000	67439	83294	39912
Mean	17604	78130	138960	53760

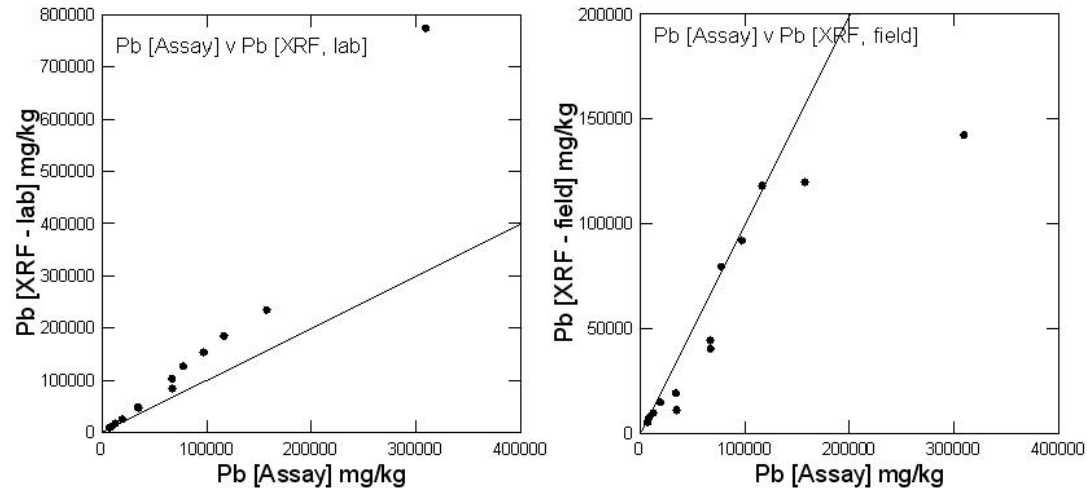


Fig. 14.2 Pb: assays v XRF analyses

Lead is reported for five standards analysed in GSI, NIST 2710 (5532 mg/kg), NIST 2780 (5770 mg/kg), RCRA (500 mg/kg), NCS 73308 (27 mg/kg) and CCRMP Till-4 (50 mg/kg). Mean values for XRF analyses of these standards were, respectively, 5609 mg/kg, 5078 mg/kg, 518 mg/kg, 29 mg/kg and 52 mg/kg. The results for the ICP-4 standard run by OMAC in December 2008 were 6327mg/kg and 6378mg/kg against an accepted value of 6350mg/kg. The SY-4 standard (accepted concentration: 93 mg/kg) gave results of 119 mg/kg and 107 mg/kg. The standard data suggest that the GSI XRF analyses give acceptable results at relatively high concentrations such as those in NIST

2710, a soil standard. The low mean recorded for NIST 2780, a mine waste standard, is typical of metal concentrations measured in this standard by XRF (compare data for other elements such as Zn and Cu). The metal-rich matrix present in this sample is quite different to that of the matrix in the soil samples used to calibrate the instrument and this difference is considered the likely reason for the consistently low metal concentrations measured by XRF in this sample, compared to the published accepted concentrations. In the case of the other three standards, the results are very good, suggesting accuracy in the XRF analyses at both low and high concentrations. Thus, data for GSI standard analyses do not suggest significant problems with XRF analyses for Pb at relatively high or low concentrations. There are no peak overlaps in the XRF spectrum that could, in a typical sample, give rise to falsely high Pb results. The exception is the peak overlap with As but this would represent a potential problem only in the unusual instance of a sample with high As concentration and low Pb concentration..

15. Sb – Antimony

Table 15.1 Sb Statistics

Sb, n=221	OMAC	GSI
Min	<5	<DL
Max	3504	5075
Median	20	<DL

Antimony was not detected in most GSI XRF analyses, giving a median concentration below the detection limit (Table 15.1). There is a broad correlation between XRF and OMAC ES analyses, with high concentrations measured by ES generally corresponding to high concentrations measured by XRF (Fig. 15.1). However, Sb concentrations measured by XRF tend to be significantly higher than those measured by ES analysis. Samples with low concentrations as measured by ES can have relatively high measured XRF concentrations. Peak overlap is not a factor in Sb XRF analyses. However, the K α peak for Sb lies at the high-energy end of the X-Ray spectrum (26.36 keV) where background count data are relatively high. This may contribute to spuriously high measured concentrations if there is a significant difference between count data for the sample background and that for the standards used to calibrate the XRF. The K α peak for Cd (23.11 keV) is also at the high-energy end of the spectrum and Cd concentrations measured by XRF are also biased toward high values relative to ES analyses.

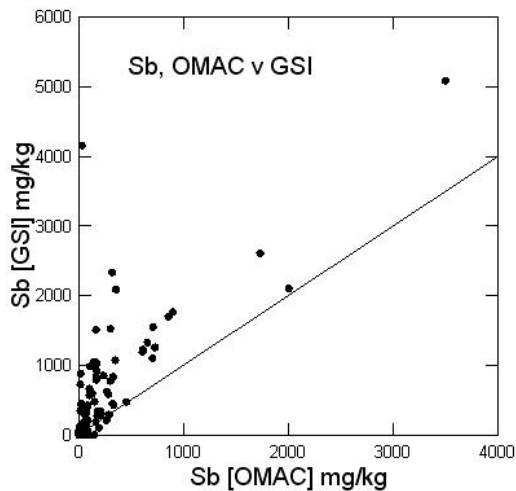


Figure 15.1 Sb OMAC v GSI

Analyses of standards by XRF also show a bias toward higher-than-certified concentrations. Antimony was consistently detected in two standards, NIST 2710 (certified concentration, 38 mg/kg) and NIST MW 2780 (160 mg/kg). The mean concentrations determined by XRF were 84 mg/kg and 216 mg/kg, respectively. Thus, analyses of standards confirm a bias toward high concentrations for analysis of Sb by the GSI XRF

16. Se – Selenium

Table 16.1 Se Statistics

Se, n=221	OMAC	GSI
Min	<10	<DL
Max	27	71
Median	<10	<DL

Selenium was detected in very few samples, whether analysed by ES (detected in six samples) or XRF (13 samples), and in consequence the median concentration of Se for both techniques was below the limit of detection (Table 16.1). The detection limit for Se by ES analysis was 10 mg/kg. In five cases where Se was detected by ES analysis, it was also detected by XRF analysis. There was good agreement between the results for four of these samples (Table 16.2), clearly indicating that the XRF is capable of detecting Se at relatively low concentrations, at least in laboratory-prepared samples. This largely reflects the position of the K α peak (11.21 keV) which is not overlapped by the peak of any other element commonly detected in mine waste samples. For seven of the eight samples in which Se was detected by XRF but not by ES, the measured XRF Se concentration was below 10 mg/kg. In all these cases the error on the count data was high,

indicating considerable uncertainty as to whether the element was detected or not.

Table 16.2 Measured Se concentrations in six samples: ES v XRF

Se mg/kg						
OMAC ES	27	24	23	15	11	9
GSI XRF	31	23	29	71	10	<DL

Selenium is reported only for one standard analysed by XRF in the GSI laboratory, RCRA, a spiked soil sample with a reported Se concentration of 500 mg/kg. The mean Se concentration for 13 XRF analyses was 422 mg/kg, a reasonable result that nevertheless suggests that the XRF is not particularly well calibrated for high Se concentrations. One of the two in-house standards run by OMAC, ICP-4, had a reported Se concentration of 15 mg/kg and four analyses gave concentrations of 13, 14, 16 and 18 mg/kg. This suggests that the ES analyses are accurate. The good agreement between XRF and ES analyses for the five samples in Table 16.2 suggests that the XRF is capable of measuring Se accurately at relatively low concentrations (down to 10 mg/kg).

17. Th – Thorium

Table 17.1 Th Statistics

Th, n=221	OMAC	GSI
Min	>5	<DL
Max	59	68
Median	6	<DL

Thorium was detected by the GSI XRF in only 20 out of the 221 samples analysed and its median concentration is, consequently, below the limit of detection (Table 17.1). The detection limit for the OMAC ES analyses was 5 mg/kg and the median for the 221 analyses was 6.4 mg/kg, with 168 analyses returning a value of 10 mg/kg or less. The concentration of Th in most of the samples analysed was, therefore, only slightly in excess of the 5 mg/kg detection limit. The generally low concentration of Th in most mine waste samples, as evidenced by the ES results, accounts for the low number of XRF detections. In the 20 samples in which Th was detected by the XRF, it was measured at concentrations that were typically around twice those of the corresponding OMAC ES analyses (Fig. 17.1; Table 17.2). Thus concentrations of Th measured by XRF appear to be exaggerated relative to ES analyses. One reason for this may be partial overlap of the main La Th peak (12.97 keV) by the L β peak of Pb (12.61 keV) (Fig. 17.2).

Table 17.2 Samples in which Th detected by XRF

Th (n = 20)	OMAC ES	GSI XRF
Min	5	18
Max	25	68
Median	12	27

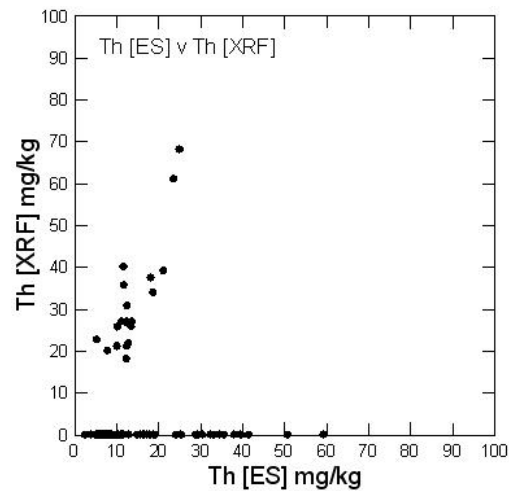


Figure 17.1 Th, OMAC v GSI

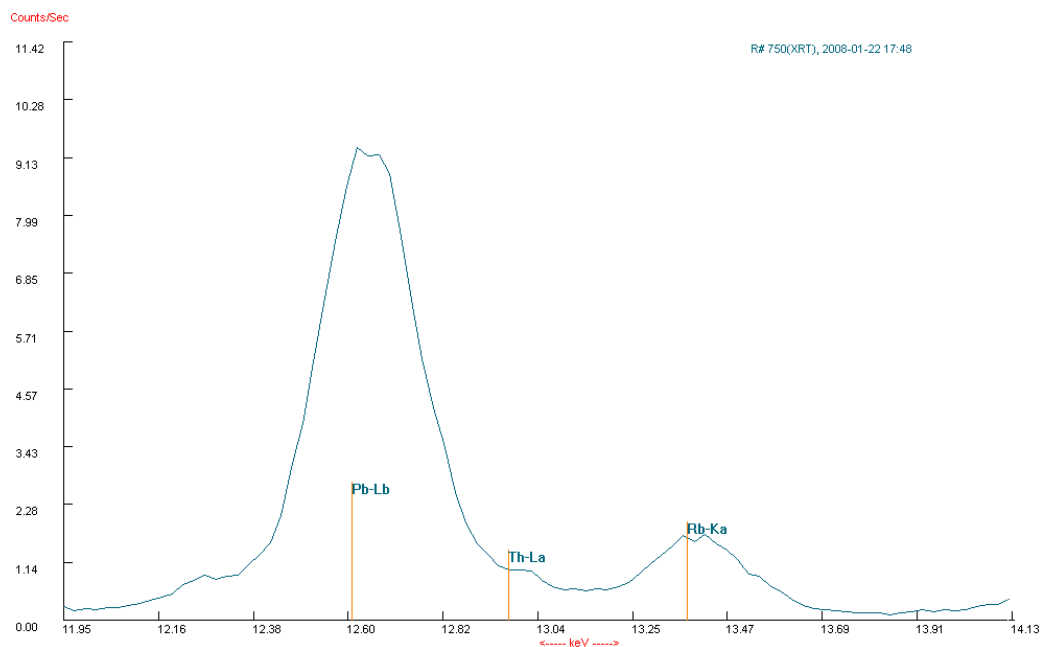


Fig. 17.2 Th La peak showing partial overlap by Pb Lβ peak

Of the five standards analysed by the GSI XRF, four have certified Th concentrations: NIST 2710 (13 mg/kg), NIST 2780 (12 mg/kg), NCS 73308 (5

mg/kg) and CCRMP TILL-4 (17.4 mg/kg). The XRF analyses did not detect Th in any of the 77 analyses of NIST 2710. For NIST 2780, only two XRF analyses returned concentrations above the detection limit but both were much higher (92 and 94 mg/kg) than the certified value. Similarly, only three out of 39 XRF analyses of NCS 73308 yielded measured concentrations above the detection limit (all between 15 and 16 mg/kg) and all three were well in excess of the certified concentration. Two out of five XRF analyses of CCRMP TILL-4 detected Th, giving concentrations of 32 and 37 mg/kg, approximately twice the certified concentration. Therefore, analysis of standards suggests that the GSI XRF detected Th at concentrations around 17 mg/kg but that measured concentrations were significantly exaggerated. This is consistent with the results of the analyses of the 221 samples by XRF and ES.

18. U-Uranium

Table 18.1 U Statistics

U, n=221	OMAC	GSI
Minimum	<5	<DL
Maximum	170	124
Median	<5	<DL

The GSI XRF detected U in only seven of the 221 samples analysed, with measured concentrations ranging from 23 to 124 mg/kg. Only in two samples did the measured U exceed 100 mg/kg. There was poor correlation with the corresponding OMAC ES analyses. For the remaining 214 samples in which the XRF did not detect U, the concentrations measured by OMAC ES ranged from <5 to 170 mg/kg, suggesting a relatively high detection limit for the XRF or else poor X-ray peak resolution owing to overlap by adjacent peaks. The most likely peak overlap is that of the U La peak with that of the Rb Ka peak.

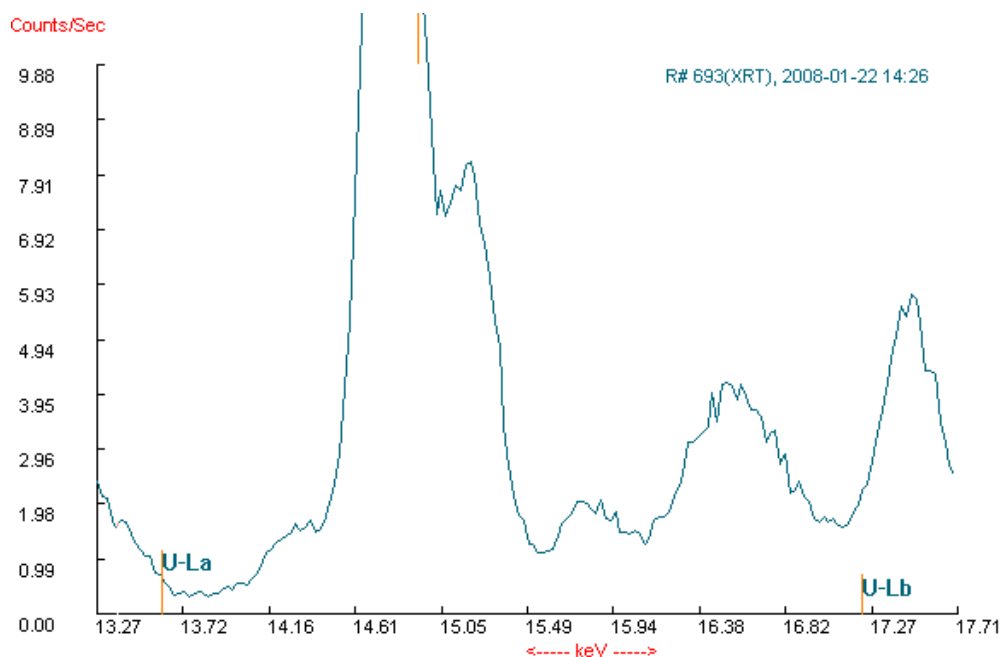


Figure 18.1 GLD-07-HEROPP8.2

Values for U are reported for several standards analysed for the HMS-IRC project but in most cases the reported concentration is 5 mg/kg or less, too low for detection by the XRF. An exception is NIST 2710, for which the accepted concentration is 25 mg/kg. The XRF detected U in 63 out of 77 analyses of this standard, returning a mean of 41 mg/kg. The Rb concentration of NIST 2710 is relatively low (120 mg/kg), indicating minimal potential for peak interference, and this may help explain the relatively successful results for XRF analysis of this standard.

19. V- Vanadium

Table 19.1 V Statistics

Zn, n=221	OMAC	GSI
Minimum	<2	0.0
Maximum	320	381
Median	49	0.0

Vanadium is one of the lighter elements analysed by the XRF and its detection limit is relatively high. Niton, the manufacturer of the XRF, has reported a detection limit in excess of 100 mg/kg V in soil matrix. The GSI XRF detected V in only 13 samples at concentrations ranging from 106 to 381 mg/kg. For the remaining 208 samples, the concentrations measured by OMAC using ES ranged from <2 to 156 mg/kg, with 10 samples exceeding 100 mg/kg. Fig. 19.1 shows the relationship between the OMAC and GSI measurements. For those analyses where V was detected by both techniques, there is a broad

linear trend with a tendency for GSI XRF concentrations to exceed the corresponding OMAC ES concentrations.

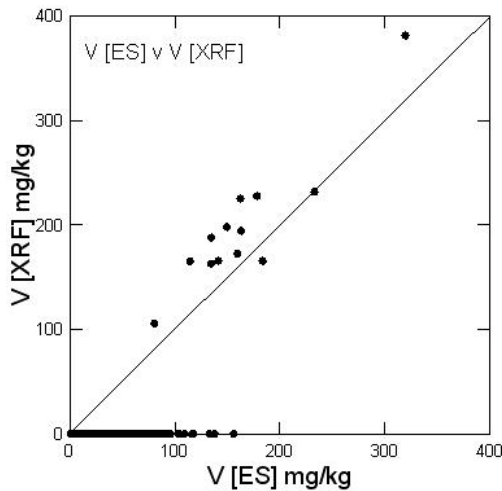


Fig. 19.1 V (ES v XRF)

The concentration of V is reported for four standards analysed in GSI, NIST 2710 (77 mg/kg), NIST 2780 (268 mg/kg), NCS 73308 (107 mg/kg) and CCRMP Till-4 (67 mg/kg). Mean values for GSI XRF analyses of these standards were, respectively, <DL (65 analyses), 277 mg/kg (48 analyses), 113 mg/kg (33 analyses) and <DL (5 analyses). Thus for the two standards in which V exceeds 100 mg/kg, the GSI XRF gave very good overall results.

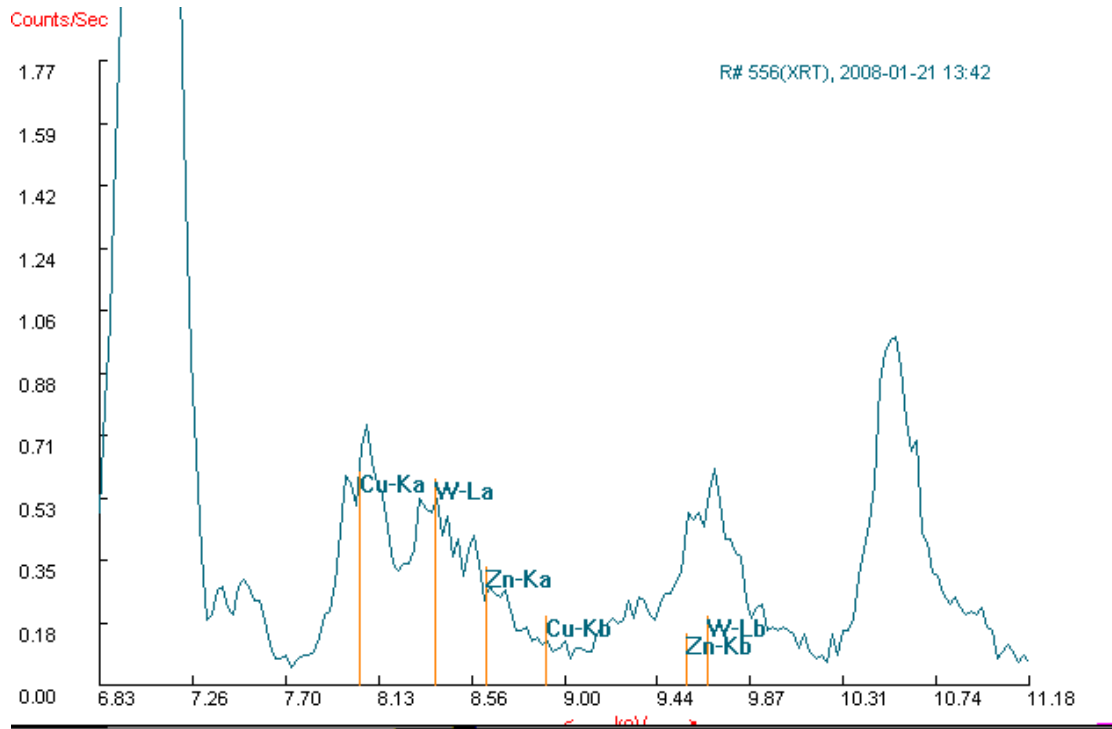
20. W – Tungsten

Table 20.1 W Statistics

W, n=221	OMAC	GSI
Minimum	<5	<DL
Maximum	28.6	<DL
Median	<5	<DL

The GSI XRF did not detect W in any of the 221 samples analysed for the comparative study. It is recorded as present in only one standard analysed, the CCRMP TILL-4, at a concentration of 204 mg/kg. The XRF gave a mean of 254 mg/kg for five analyses. Tungsten was below the detection limit of 5 mg/kg in 191 samples analysed by ES and the maximum concentration recorded in the remaining 30 samples was 29 mg/kg, suggesting a minimum detection limit for the XRF of around 30 mg/kg. In practice, the XRF detection limit for W in samples of typical mine waste is likely to be much higher in many cases, at least where the sample contains significant Zn. This is because the X-ray peaks for W that fall in the energy spectrum covered by

the XRF are the La and L β peaks with energies of 8.40 keV and 9.67 keV, respectively. These are very close to the two main Zn peaks, Ka (8.63 keV) and K β (9.57 keV). Thus W may only be detected unambiguously by the XRF where its concentration exceeds that of Zn, as in the standard CCRMP Till-4, in which the accepted W concentration is 204 mg/kg as opposed to 70 mg/kg for Zn. Fig. 20.1 shows the spectrum for this standard. In samples of mine waste from typical sulphide mines in Ireland, where Zn is one of the most



abundant elements, the XRF is likely to detect W only in exceptional circumstances where it is present in very high concentrations or Zn is present in very low concentrations.

Fig. 20.1 Partial XRF spectrum for CCRMP Till-4, showing W and Zn peaks

21. Zn-Zinc

Table 21.1 Zn Statistics

Zn, n=221	OMAC	GSI
Minimum	3	0.0
Maximum	104,549	278,319
Median	424	386

The measured Zn concentration in GSI XRF analyses exceeded that of the OMAC ES analyses in 77 out of 221 cases. For these 77 samples, the median Zn concentrations were 8578 mg/kg (GSI) and 5961 mg/kg (OMAC). For the 144 samples in which the measured OMAC concentrations exceeded those of

GSI, the median Zn concentrations were 119 mg/kg (GSI) and 168 mg/kg (OMAC). Of these 144 GSI analyses, 38 were below the detection limit. Thus, measured Zn concentrations in GSI analyses tend to be lower than those measured by OMAC ES for samples with relatively low Zn concentrations. Where the Zn concentration is high, i.e. > 1000 mg/kg in most cases, the GSI analyses tend to give higher measured Zn concentration than those of OMAC ES (Fig. 21.1). Overall, there is good agreement between GSI XRF and OMAC ES analyses, with similar median concentrations for all 221 analyses (386 and 424 mg/kg, respectively) (Table 21.1).

Zinc is reported for four standards analysed in GSI, NIST 2710 (6952 mg/kg), NIST 2780 (2570 mg/kg), NCS 73308 (46 mg/kg) and CCRMP Till-4 (70 mg/kg). Mean values for XRF analyses of these standards were, respectively, 6967 mg/kg, 1943 mg/kg, 29 mg/kg and 42 mg/kg. The results for the ICP-4 standard run by OMAC in December 2008 were 6327mg/kg and 6378mg/kg against an accepted value of 6350mg/kg. The SY-4 standard (accepted concentration: 93 mg/kg) gave results of 119 mg/kg and 107 mg/kg. The standard data suggest that the GSI XRF analyses are acceptable at relatively high concentrations such as those in NIST 2710, a soil standard. The low mean recorded for NIST 2780, a mine waste standard, is typical of metal concentrations measured in this standard by XRF (compare data for other elements such as Pb and Cu). The metal-rich matrix present in this sample is quite different to that of the matrix in the soil samples used to calibrate the instrument and this difference is considered the likely reason for the consistently low metal concentrations measured by XRF in this sample, compared to the published accepted concentrations. In the case of the other two standards, the results are reasonable, especially in the case of NCS 73308 where the accepted Zn concentration is not much greater than the expected detection limit for the XRF. Thus, data for GSI standard analyses do not suggest significant problems with XRF analyses for Zn at relatively high or low concentrations and there are no peak overlaps in the XRF spectrum that could give rise to falsely high Zn results.

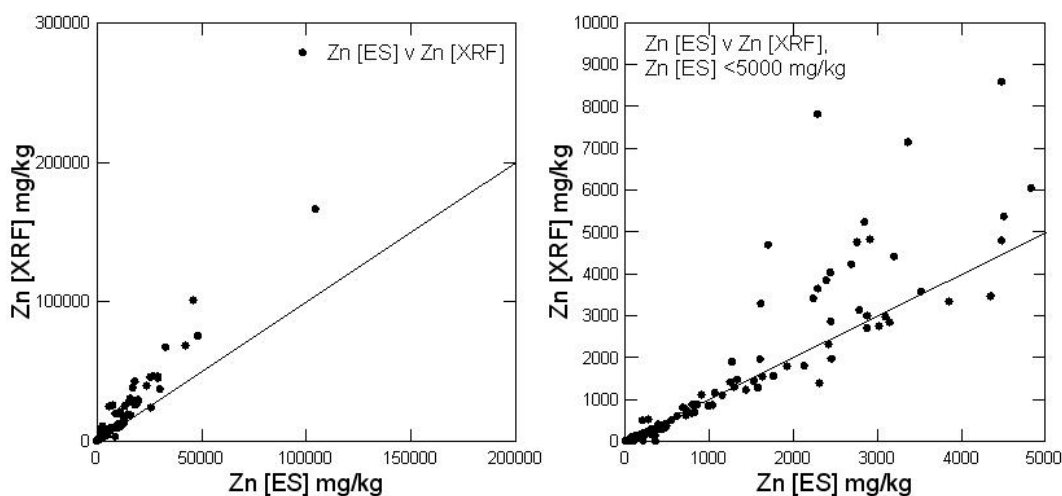


Fig. 21.1 Zn (XRF) v Zn (ES)

The upper calibration limit for the XRF is 20,000 mg/kg Zn (2%) and measured concentrations exceeding this must be considered semi-quantitative. An attempt was made to assess the accuracy of XRF analyses of samples with very high measured metal concentrations by carrying out assays of the samples at OMAC laboratories. The assay analysis included As, Cd, Cu, Fe, Pb and Zn. Comparison of results for the 13 samples analysed by assay with those previously obtained by ES analysis at OMAC indicates good agreement for the most part between the two methods. Table XX compares the summary data for the assay and GSI analyses. In general, GSI XRF results are significantly higher than those obtained by assay, indicating a bias toward high measured values in samples with high concentrations of Zn. Examples of high XRF results for Zn include (OMAC assay results in brackets) 2964 mg/kg (2866 mg/kg), 6.8% (4.1 %), 10.1% (4.6%) and 16.6% (9.6%).

Table 21.2 Zn assays

Zn, n=13	OMAC (ES)	OMAC (assay)	GSI XRF (lab)	GSI XRF (field)
Minimum	209	50	366	191
Maximum	104549	96294	278319	192785
Mean	25216	23790	52457	30494
Median	3102	2866	5230	2515

