CHAPTER 3

Geochemical Methodology

3.1 Aims and scope of geochemical site investigations

The aims of the geochemical site investigations undertaken for the HMS-IRC project were:

(1) To provide a basic chemical characterisation of each site, with the added aim of identifying issues of concern for human and animal health and the environment, and

(2) To provide sufficient data to allow scoring of each site using the HMS-IRC scoring system.

Initially, the scope of the site investigations included **solid waste**, **surface water**, **groundwater**, **stream sediments** and **soil**. Later, **leachate** testing was incorporated into the geochemical programme while soil was excluded. A geochemical soil survey around each of the sites would be a substantial undertaking and would require significant resources and would be time consuming. For this reason, the soil geochemical survey is more appropriate to site-specific investigations of individual sites rather than to a national survey of the kind conducted under the HMS-IRC project.

3.2 Solid waste analyses

3.2.1 Types of solid mine waste

For the purpose of the HMS-IRC project, solid waste means any solid matter on mine sites that is a by-product of mining or of the processing of mined material. This includes spoil, whether in deliberately created spoil heaps or in casually dumped material, tailings, processing waste and stripping waste. It also includes a thin layer of fines or dust that is dispersed at most mine sites as a consequence of action on partially or fully processed material. This dispersal may occur as a result of human or mechanical activity, wind or rain. This is largely confined to former processing areas and a short distance from them. On some of the older sites, revegetation has taken place leaving a thin layer of **soil** on top of mine waste. This soil is generally a mixture of organic material, mine waste and introduced soil. It can be heavily contaminated by heavy metals and it constitutes a particular type of soil in the context of Irish mine sites, not to be confused with soil on land surrounding but never a part of a mine site.

Spoil *sensu stricto* is mined ore that has become diluted in the course of mining by its largely unmineralised host rock or gangue. In consequence, its concentration of ore material is diluted to the point of making it uneconomic to process further. In Ireland, extensive spoil heaps are characteristic of 18th and 19th century mine sites, e.g. Avoca and Glendasan. Before the large-scale, mechanised mining of the 20th century and the efficient extraction techniques that accompanied it, miners focused on high-grade zones within relatively narrow ore zones or *lodes*. Blasting of such zones caused dilution by the host rock. The mined material was usually tipped close to the entrance to shafts or adits and picked over by hand to extract the best ore. This inefficient winnowing process has created many spoil heaps with significant metal contents.

In contrast to the relatively inefficient mining of high-grade ore in the 19th century, mining in the 20th and 21st centuries has involved mechanical mining of large volumes of ore material and relatively efficient extraction of the ore material using sophisticated techniques in purpose-built processing plants. Ore is generally crushed in the mine itself and then passed to the processing plant for grinding, typically to sand- or silt-sized particles. Froth flotation has been employed in most modern Irish metal mines to separate the ore minerals from the gangue material and it is particularly useful because it can be used to process polymetallic ores. Surfactants are added to the slurry that binds preferentially to specific metals to make them hydrophobic. When air is passed through, a froth forms to which the hydrophobic metals bind. This froth or scum is removed from the surface of the slurry. The waste slurry left after completion of this process is called tailings. The tailings material is commonly disposed of in purpose-built lagoons called tailings ponds. Tailings are also placed underground as backfill providing storage for the tailings and support for the underground workings. Backfilling of underground workings is commonplace in modern operating underground mines in Ireland but was not extensively employed as a disposal method in the closed mines studied in the HMS-IRC project, with the exception of Avoca.

The four abandoned large-scale 20th century mines in Ireland (Tynagh, Gortdrum, Silvermines and Avoca) are, therefore, characterised by large tailings ponds. Smaller-scale deposits of similar material are found on 19th century sites also but these tailings are generally by-products of gravity separation methods. In addition to tailings ponds, the large 20th century mines studied also have waste heaps created

from low-grade material stripped from the surface during excavation of open pits. These waste heaps, not spoil heaps in the narrow meaning of the term, are generally very large-scale accumulations that typically contain a high proportion of very coarse blocks.

Siltation ponds are used on mine sites to separate material from process water. Solid siltation wastes are found, for example, at Gortdrum and Tynagh in the remains of dried-out ponds. Other waste found on the sites of processing plants is generally a product of a specific process.

On 19th century sites such processes including cobbing or hand-dressing of ore with hammers, coarse crushing, stamping, i.e. fine crushing and gravity separation into buddles.

In the case of 20th century sites, the processing equipment and buildings have, in general, been dismantled and removed after mine closure. Remains of processed or concentrated ore are therefore not widespread or voluminous. Nevertheless, most of the sites have some examples of processing waste. Such waste, because of its nature, can contain very high levels of metals or other elements.

3.2.2 General overview of solid waste analyses

Solid waste analyses were carried out using an FP-XRF analyser. The analyser allowed semi-quantitative *in-situ* analysis of mine waste and quantitative laboratory-based analysis of prepared samples. The field analytical method is outlined in Appendix 2. Approximately 10% of sites analysed in the field were sampled for follow-up analysis by XRF in the GSI laboratory. Most of these samples were also sent to a certified commercial laboratory where they were analysed by inductively coupled plasma – atomic emission spectrometry (ICP-AES) after multi-acid digestion. Comparison of these samples with those analysed by XRF has allowed a detailed assessment of the XRF analyser's performance to be carried out (Appendix 4). The FP-XRF has proved to be an extremely useful tool that has enabled completion of many more analyses than would have been possible using traditional laboratory-based methods. As described in Appendix 4, the analyser's performance, both *in situ* and in the laboratory, has more than met the project's requirements.

Table 3.1 provides a breakdown of the numbers of solid waste analyses completed for the HMS-IRC project, excluding check samples sent to the external laboratory.

The 1,432 *in-situ* analyses form the basis for the scores assigned to waste heaps in the HMS-IRC scoring system and comprise over 87% of all solid waste analyses. The bulk of these analyses were on spoil. Of the 208 samples analysed by XRF in the GSI laboratory, 37 were not previously analysed in the field. These were mostly siltation pond samples from Gortdrum that were too wet for *in-situ* analysis. The remaining 171 samples were from the 1,432 sites analysed in the field and, of these, 165 were sent to OMAC Laboratories for comparative analysis by ICP-AES. These 165 samples constitute 11.5% of the 1,432 *in-situ* analyses.

Waste Type	Field	Lab	Totals
Spoil	906	94	1,000
Tailings	341	55	396
Processing Waste	148	49	197
Soil	25	3	28
Other	12	7	19
Totals	**1,432**	**208**	**1,640**

Table 3.1 Numbers of solid analyses carried out during the HMS-IRC project.
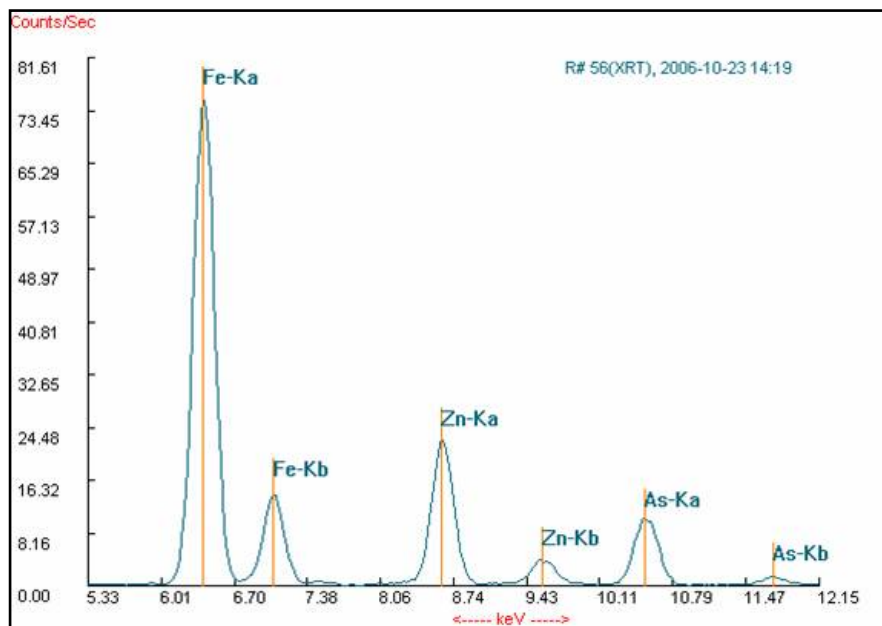
3.2.3 XRF analysis

X-ray fluorescence (XRF) analysis is a long-established and well-understood analytical technique. The analyser used for the HMS-IRC project (right) uses a battery-powered cathode tube to generate a beam of X-rays. This beam is focused through a 20-mm diameter aperture onto the sample. The X-rays then collide with atoms of elements within the sample. The excitation of, or transfer of energy to, an atom results in the emission of X-rays by that atom. The emitted X-rays each have an energy that is characteristic of the atom that emits it. Thus, iron emits two principal X-rays, called Kα and Kβ, with characteristic energies of 6.40 and 7.06 KeV, respectively (Fig. 3.1). The X-rays emitted from the sample are in turn detected by the XRF analyser. The relative concentration of any element in a sample is proportional to the number of its characteristic X-rays emitted.

The XRF analyser is equipped with two filters, one for detection of elements of atomic number ≥23 (vanadium) and one for elements with atomic number between

15 (phosphorus) and 22 (titanium). Each filter allows better detection and resolution of elements within the ranges specified.

Figure 3.1 Typical X-ray spectrum for portable XRF analyser.

As the analysis is carried out, the X-ray count data are processed by the analyser using an in-built programme that utilises standard correction factors and calibration data for each element. The analyser is calibrated at the factory prior to delivery. Different calibrations can be used depending on the nature of the material to be analysed. In the case of the HMS-IRC instrument, an 'environmental' calibration was selected as most appropriate as it allowed for a wide range of sample types. The calibration was carried out using well-characterised soil and sediment standards containing variable amounts of metals and other elements of interest.   Further details are contained in Appendix 4.

The analyser is calibrated to analyse 30 elements (Table 3.2).   Inter-element interference and peak overlap can make accurate calibration of some element combinations difficult.   The elements were selected for calibration on the basis of what were considered to be the most useful in the context of Irish mine sites.

The detection limits listed in Table 3.2 are those supplied by the manufacturer of the analyser, NITON, for prepared samples analysed under optimum conditions. Detection limits have not been determined for all elements, especially relatively rare elements such as (Bi) and (Tl). The standards used in determining the detection limits were soils and sediments.

Where sample preparation and analytical conditions are consistent, variation in detection limit for any given element will depend primarily on sample matrix composition. For example, in a sample with a high concentration of heavy elements such as iron and lead, X-rays emitted by various elements in the sample, and especially the lighter elements, will not easily escape the sample matrix owing to interference by atoms of the heavy elements. Thus the detection limit for any element will be higher than in a sample with a low or lower concentration of heavy elements.

Trials conducted by the US EPA on the NITON portable XRF analyser (US EPA 2006) gave detection limits of 1 to 20 mg/kg for As, Pb, Hg, Se and V, 20 to 50 mg/kg for Cu, Ag and Zn, 50 to 100 mg/kg for Cr and Ni and >100 mg/kg for Sb and Cd. The detection limits for Sb and Cd may have been biased toward high values as a consequence of high concentrations of other metals in the matrices of the standards analysed. Otherwise, the US EPA tests are in good agreement with the detection limits reported by NITON.

Accuracy in XRF analyses depends upon the correction programme used and, principally, the calibration. Correction programmes take account of the physics of X-ray excitation and emission and are relatively standard. Calibration is the greatest influence on accuracy. The greater the difference in composition between the sample being analysed and the standards used in the calibration the greater the potential inaccuracy in the results. The HMS-IRC analyser was calibrated using soil and sediment standards. The matrix in such standards comprises mainly silicates.

The matrix in mine waste samples will have, in addition to silicates, high concentrations of metal sulphides, oxides and hydroxides that will influence X-ray behaviour during analysis. Such influences will not necessarily be accounted for by the correction programme and the result can be a significant departure from accuracy. Comparison of the certified composition of the National Institute of Standards and Technology (NIST) mine waste standard (NIST 2780) with the results of analyses by the HMS-IRC analyser (Appendix 4) show a consistent bias towards lower measured element concentrations than those certified by NIST.

	NIST Standard Reference Material (Soil matrix)	
Element	60 s	120 s
P	2.5%	
S	1.5%	
K	500	
Ca	400	
Sc	200	
Ti	200	
V	175	
Cr	60	
Ag		50
As		15
Ba	1,000	
Cd		65
Co		150
Cu		60
Fe		175
Hg		12
Mn		175
Ni		90
Pb		20
Rb		15
Sb		175
Se		150
Sn		150
Sr		30
Zn		40

Table 3.2 Elements calibrated for XRF analysis with detection limits (mg/kg).

The analysis time is controlled by the user. For HMS-IRC analyses, analysis time was 90 s for *in-situ* analyses and 180 s for laboratory analyses. In each case, two-thirds of the analysis time (60 and 120 s, respectively) were apportioned to the heavy-element filter and one-third (30 and 60 s, respectively) to the light-element filter. All HMS-IRC samples analysed in the laboratory were run at least twice and the average of the two results was taken as the final result.

Quality control (QC)/quality assurance (QA) procedures for XRF analysis included:

1. Routine calibration of the X-ray beam at 1- to 2-h intervals;
2. Regular analyses of a range of standard material during laboratory-based analyses of prepared samples;
3. Re-analysis of prepared samples by a certified external laboratory using ICP-AES and other standard analytical techniques.

Appendix 4 contains a detailed account of the performance of the XRF analyser, based on analysis of standards and comparison of results for samples analysed both by XRF and ICP-AES in an external laboratory.

3.2.4 Spoil analyses

Most solid waste analysed in the course of the project was spoil. The analysis method followed the sampling protocol in Appendix 2. In general, the aim of the *in-situ* analyses was to provide an estimate of minimum, maximum and median concentrations in any given spoil heap and on mine sites. The median value has been adopted in the HMS-IRC scoring system. Typically, five-, six- or nine-point grids with 5- to 10-m spacings were employed. However, modifications to this ideal approach were made depending on heap shape, size and chemical variability.

Chemical variability can be implied by visible colour or mineralogical variation. The real-time analysis afforded by the portable XRF analyser also allowed judgements to be made in the field regarding changes to sampling plans. Such modifications included reducing the number of analyses where low levels of elements of interest were detected and increasing the number where 'hot spots', i.e. zones with unusually high concentrations of elements of interest, were detected. While the inclusion of hot-spot analyses may serve to bias the median value towards higher concentrations, recognition and analysis of such zones are important aspects of the characterisation of mine sites and the determination of issues of concern.

The general approach to *in-situ* analysis is to mark out a 20 x 20 cm area in which the top 5 cm approximately of spoil are raked over and larger clasts removed. The spoil is then compressed and smoothed to form a suitable flat, compacted surface with minimal pore space, thus reducing the influence of air on the analysis (right). Three separate

spots within the 20 x 20 cm area were covered within the 90 s of XRF analysis in order to counteract the effects of the chemical variability inherent in many samples of mine spoil. High moisture contents also posed some difficulties for *in-situ* analyses at some sites. Moisture is a potential problem because, like air, it dilutes the proportion of solid material in any given sample and it also interferes with and attenuates the X-rays. The result is a lower apparent concentration of elements of interest in a sample. However, analyses of fine or compacted material, such as tailings or siltation deposits, are more likely to be affected by moisture than those of spoil which is typically relatively coarse-grained and less retentive of water than fine waste.

3.2.5 Tailings analyses

The 20th century mines studied for the HMS-IRC project all have large tailings impoundments that store the waste material following mineral processing. Some 19th century mines also have tailings deposits, though they are much smaller in scale and typically less well impounded.

The general approach to tailings analysis was similar to that adopted for spoil analysis. The aim was to obtain an estimate of the minimum, maximum and median concentrations of elements of interest in the tailings. A grid was defined for each deposit. Because of the typically much greater surface area, grids on tailings deposits tended to be much larger than those on individual spoil heaps, with the number of individual sites exceeding 30 in some cases. In addition to the composition at the surface of the deposit, vertical compositional variation was also assessed. At Avoca and Gortdrum, a trailer-mounted mechanical drill was used to retrieve samples up to 6 m below the surface of the tailings pond. At other sites (Tynagh, Abbeytown, Glendalough), a combination of manual digging and augering was used to analyse samples at depths of up to 1.5 m below the surface.

Tailings analysed for the HMS-IRC project are typically sand to silt grade. On the surface of deposits they are relatively dry and easily analysed *in situ* by portable XRF. At depth, however, owing to the effects of retained water and the pressure of overlying tailings, they become increasingly plastic and less viscous (right). Below approximately 1 m at Gortdrum and Avoca, the tailings have the

consistency of wet mud. This material was placed in plastic bags prior to analysis through the bag.

3.2.6 Processing waste

On 19th century mine sites scored for HMS-IRC, processing waste includes waste from crushers, stamps batteries, gravity-separation equipment, such as buddles, and furnaces. Processing waste observed on 20th century mine sites included siltation pond sediment, furnace residue and thickener waste. Apart from waste derived from specific processes, a thin layer of waste typically covers the sites of former processing plants. This is material that has been spread around the vicinity of the processing plant by human and mechanical activity, as well as by wind and rain and it is relatively thin.

With the exception of siltation pond residue and the thin coating referred to above, processing waste tends to occur in very localised areas on the sites of former processing plants, e.g. in and around particular buildings and structures. Analysis of such waste for the HMS-IRC project was typically opportunistic and directed towards ascertaining the range of elements and their concentrations present in the waste. It followed no preconceived pattern of analysis, e.g. a grid.

3.2.7 Soil and other waste

Soil in this context refers to soil overlying mine sites, particularly 19th century sites that have undergone revegetation over a long period of time. On such sites the establishment of a soil cover appears to follow from a gradual colonisation of the mine surface by invading species from the immediate surrounding land and the establishment of an organic substrate on top of the residual mine waste. On some sites, grassland has been established, presumably through intensive amelioration efforts by landowners. Where grass is established, the base of the root zone is typically at or just above the buried mine waste. The soil is inevitably mixed to some degree with residual mine waste from the surface of the mine site. Analysis of this soil was generally accomplished by turning over the sod and analysing the soil at the base of the root zone, with a grid-based approach similar to that adopted for spoil.

Other waste analysed included granite blocks and mortar in a smelter chimney in Ballycorus and mortar in the remains of an engine house in Ballyhickey. Aggregate derived from waste piles at Gortdrum was also analysed. Again, these were opportunistic analyses and followed no specified pattern.

3.3 Water analyses

Surface water analyses were carried out on and around mine sites to assess the potential for downstream contamination of local watercourses by mine water discharges via adits or shafts, by leachate generated within solid waste heaps or by surface run-off from the site. In general, water from rivers and streams was sampled upstream and downstream of the mine site. Mine discharges and leachate were also sampled. Active surface run-off was sampled in only one instance but ponding of run-off is common on mine sites and this water can give an indication of the chemistry of run-off.

Groundwater was sampled from field wells and springs where available. Wells bored for water supply to private homes were not sampled because the time required to locate wells, secure permission and sample them was considered excessive. In addition, many such wells are equipped with treatment cells that inevitably alter the chemistry of the water.

Water was sampled in both summer and winter in order to determine the effect on water chemistry as a result of the variation in flow rates of water in rivers, streams and mine discharges. Winter sampling took place between November 2006 and early March 2007, summer sampling between June and September 2007. Not all sites were sampled in both periods – smaller sites with only minor or even no mine water discharges were sampled only once. Flow rates were measured using a portable cut-throat flume. This was suitable for small-channelled discharges less than 1 m wide, i.e. adit discharges and small streams. Some flows too large to be measured with the flume were estimated by measuring the depth of water at intervals across the stream and measuring the speed of flow with a float. Table 3.3 provides a summary of the number and type of samples collected for the project.

A description of the sampling methodology is contained in Appendix 2. Samples were analysed by Alcontrol Ltd. Table 3.4 lists the parameters analysed and the analytical method employed. Some parameters analysed in the first period, winter 2006–2007, were not analysed in summer 2007. These included biological oxygen demand (BOD) and chemical oxygen demand (COD). The exclusion of these parameters reflected the fact that they are largely indicative of contamination of water by organic sources and not mine waste. Moreover, the requirement that BOD and COD analyses be carried out within 48 h of sampling placed significant

constraints on the sampling programme, particularly in remote areas where it was not always possible to arrange rapid delivery of samples to the laboratory.

Sample Type	Winter 2006–2007	Summer 2007
Upstream of Mine Site	33	28
Downstream of Mine Site	86	80
Adit/Shaft Discharge	54	38
Ponding/Surface Run-off/Seepage	53	26
Open Pit Lake	9	10
Spring/Well	15	12
Total	**250**	**194**

Table 3.3 Water samples by source and season, HMS-IRC project.

Analysis	Method	Elements
Total Metals	ICP MS	Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sn, U, V, Zn (Detection limits: <1–2 µg/l)
Dissolved Metals	ICP MS	Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sn, U, V, Zn (Detection limits: 1–2 µg/l)
Total Mercury (Hg)	ICP IRIS	Hg (Detection limit: 50 µg/l)
Dissolved Mercury (Hg)	CV AA	Hg (Detection limit: 0.05 µg/l)
Major Cations (Total)	ICP-MS	Ca (Detection limit: 120 µg/l) Mg (Detection limit: 100 µg/l)
Major Cations (Total)	Flame Photo	Na, K (Detection limit: 200 µg/l)
Anions	KONE	PO_4 (Detection limit: 30 µg/l) SO_4 (Detection limit: 3,000 µg/l)
Oxygen Demand	5-day ATU	BOD (Detection limit: 2,000 µg/l)
Oxygen Demand	Photometry	COD (Detection limit: 15,000 µg/l)
Solids	Meter	TDS (Detection limit: 5,000 µg/l)
Solids	Gravimetric	TSS (Detection limit: 10,000 µg/l)

Table 3.4 HMS-IRC water analyses: parameters and methods.

3.4 Stream sediment analysis

Stream sediments upstream and downstream of mine sites were sampled to assess the degree of contamination, if any, arising from mine water discharges and

transport of solid waste into watercourses. Elements in mine water discharges are either in the dissolved state or in solid matter in suspension. Precipitation of dissolved chemical elements from mine discharges onto the stream bed occurs when the solubility of these elements decreases as the mine water mixes with stream water. Elements in suspension can be deposited on the stream bed in response to changes in flow velocity or other physical parameters.

A total of 107 samples were collected at 16 mine sites. At each site, sediment was collected from a number of sub-sites over a stream length of 5–10 m where feasible. Not all mine sites are in proximity to streams and not all streams near mine sites contained sufficient sediment for sampling. Each sample was passed through a 2-mm and then a 150-µm polypropylene mesh sieve in the field and the fine fraction was stored in a sealed bucket. After drying in the GSI laboratory, the samples were analysed by XRF. Analysis procedure was the same as that for laboratory-analysed solid waste samples: 120 s for the heavy-element filter, 60 s for the light-element filter, each sample analysed at least twice with the average concentrations taken as the result. Appendix 2 contains a full description of the sampling methodology and analytical procedure employed.

Sampling of the 150-µm fraction as opposed to, say, the total sediment fraction has a number of advantages. Metals tend to partition into the finer fraction in stream sediments and as a consequence detection of metal contamination of stream sediments is more likely using the 150-µm fraction than a coarser or total fraction. Aquatic organisms that feed on the river or stream bed may more readily ingest the finer than the coarser sediment fraction so that the former is a more relevant measure of environmental impact. Finally, analysis of the fine fraction allows comparison of HMS-IRC data with those of the GSI's Regional Geochemistry Programme and the use of the latter to augment the data for selected areas.

3.5 Leachate analyses

Leachate analyses were carried out on solid waste samples to provide a proxy analysis for contaminated groundwater in the vicinity of waste heaps. The HMS-IRC scoring system requires an indication of the potential of any waste heap to contaminate groundwater. In the absence of specific groundwater data around sites, the leachate analysis was used to model the extreme case where groundwater is contaminated to the extent that its composition is essentially that of leachate.

Leachate testing is described in detail in Appendix 2. Analyses of dissolved elements were carried out by Alcontrol Ltd. using ICP-MS, as outlined for water analyses (Section 3.3). Samples were selected as far as possible from among those already collected as part of the solid waste analysis programme. A total of 64 samples, covering 23 mine districts or sites, were analysed. For most sites, composite samples were created from several individual samples in an attempt to make the leachate sample as 'representative' as possible and the results were applied to all waste heaps in that site.