Investigation of Metallurgical Residues from Ireland: Method Statement

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The investigation of metallurgical residue assemblages by GeoArch is normally a two-stage process of preliminary evaluation report including a provisional catalogue and interpretation with a statement of potential, followed by further detailed investigation and analysis separately commissioned by the client if appropriate. The balance of work between the two stages can be flexible; for instance some clients may occasionally wish for the evaluation report to be a quick summary without the production of a full catalogue (i.e. the equivalent of a MAP2 evaluation of potential). A full range of analytical techniques are available for application to the investigation of the materials where appropriate.

1. Materials and Procedures

All materials submitted to GeoArch should be accompanied by a copy of the appropriate ***Licence to Export***. A ***Licence to Export*** will normally be required for all material at the evaluation stage, although some larger projects may entail the practical component of the evaluation being undertaken at the client's premises in Ireland. In such cases the exporting of materials will only occur for the second stage of the project. A ***Licence to Alter*** specific specimens has previously formed part of the formalities for the exportation of material for the second stage of a project, but guidelines agreed with the NMI allow the ***Licence to Alter*** application not to be accompanied by lists of specific specimens for detailed analysis of archaeometallurgical residues, but instead to cover the **same list of material** as the ***Licence to Export***. The licence application **must** be accompanied by a ***Method Statement for archaeometallurgical analysis (this document)***. The details of the actual affected specimens and relevant analytical procedures will be confirmed by direct agreement between GeoArch and the NMI after the initial evaluation and before the commencement of any destructive analysis.

Materials submitted for evaluation will be retained pending any potential commissioning of second-stage work. Material employed in stage two investigations will be retained pending client acceptance of the report and confirmation there are no additional questions to be asked of the collection. All material will be returned, with the exception of material destroyed during analysis (and covered by a ***Licence to Alter***) and any material lodged, by prior agreement with the NMI, in reference collections maintained by GeoArch (such material will be held on loan on an extended, but finite export licence). The ultimate fate of returned materials will be subject to consultation by the client with the NMI, but recommendations may be made in either/both of the evaluation and full reports. As a minimum it is to be hoped that the archived pieces of sampled materials, together with SEM polished mounts, would ultimately be deposited in the collections of NMI (although such materials may, in the short term, form part of the GeoArch reference collections).

If clients submit material to GeoArch by courier or post, they should not underestimate the difficulty in ensuring suitable packaging for dense slag materials. Archaeometallurgical ceramics (tuyères, crucibles, moulds, hearth lining...) should not be submitted in the same package as bulk slag

collections. Several small packages generally survive the rigours of travel much better than a small number of large ones.

2. The Evaluation report

Aim: the excavator will receive a report outlining the assemblage, a provisional interpretation, an assessment of its significance and potential for yielding more data upon further investigations.

The evaluation report includes production of a catalogue (normally including short descriptive notes and weights) listing all macroscopic items in the assemblage. Wherever possible, excavators are urged to submit their entire residue assemblage for evaluation, rather than a subsample. Each specimen is examined using a low-powered binocular microscope or a handlens as appropriate. Wherever possible, identifications are made. Any non-archaeometallurgical finds material identified during this process will be returned to the excavator for incorporation within the site's finds. In cases where archaeometallurgical artefacts (non-slag material such as tuyères, moulds or crucibles) are identified in the collection, these will be retained for study, but the site director notified of this material which may require incorporation within finds registers following normal protocols. Where the material includes small quantities of micro-residues these will be described, counted and weighed (where possible) using low-powered optical microscopy. If the assemblage includes large quantities of microresidues their time-consuming detailed cataloguing is usually held over to the full report stage. The evaluation report will usually contain a summary provisional interpretation of the assemblage (and of its distribution and structural context, if context/geographic data are supplied by the excavator). The evaluation will assess the significance of the assemblage, and its potential for further investigation. Recommendations for further investigations may be made where appropriate. Such recommendations may be based on the potential of the material to enhance interpretation of the site, or of the potential of the material to enhance broader archaeometallurgical understanding.

3. Further investigations:

Aim: further investigations may provide detailed information on the nature of processes and technology. They may, where appropriate, supply additional information on likely source materials, technological details, or information allowing detailed comparison with similar sites.

The further investigations may include traditional approaches complementary to, and building upon, those of the evaluation report. Thus additional morphological studies of residues may be indicated, or typological investigations on, for instance, crucible material. More scientific studies may also be proposed, such as using chemical techniques to model furnace reactions, or to determine provenance of raw materials. Where detailed analysis is proposed, a full range of potential investigative techniques are available, including chemical analysis (XRF for major elements, WD-XRF for major elements, ICP-MS for trace elements), petrographic studies using optical (reflected or transmitted light) or electron-optical (analytical SEM) techniques, investigation of crucible residues (ED-XRF) and mineralogical investigation (XRD). These facilities are available through standing relationships with Cardiff University, the Open University and English Heritage. GeoArch can also act as intermediary to source and interpret other sorts of specialist investigations (e.g. coal petrography and provenancing). Sample preparation to support these investigations (cutting, grinding, polishing, thin-section preparation and crushing) is normally undertaken in the University's laboratories by their technicians.

Where destructive analysis of materials classifiable as artefacts is proposed, full details, including images of the specimen(s) will be supplied to the NMI for approval before commencement of the analysis.

4. Destructive analytical techniques - details:

Initial Preparation: Material to be the subject of destructive analysis is first cut by diamond saw. Wherever possible the material is cut in half, with half of the sample retained for the archive (although for smaller samples this may not be practical). The extraction of material for SEM mounts will be focussed on particular parts of the sliced sample. The samples for bulk elemental composition may be selected from small areas of the sliced material, or complete slices may be selected to provide bulk compositions of the material. Initial cutting of small samples may be undertaken in-house, but larger samples are cut on the rock saws in the School of Earth, Ocean and Planetary Science, Cardiff University, Cardiff, Wales.

X-Ray Fluorescence (XRF) for major elements: this technique involves crushing a sample of material to obtain a bulk analysis. The actual sample required is only a few grams, but larger amounts of material are desirable in order to ensure the analysis is truly representative and to improve the accuracy of the measurement of weight change on ignition. The sample is dried (typically 100C overnight) and powered. A c4g subsample is then weighed, heated (typically at 900C overnight), and reweighed to calculate loss on ignition (LOI). Approximately 0.9g of the ignited powder is then fused with a lithium borate/lithium tetraborate flux in a platinum crucible to obtain a fused glass bead, upon which the XRF analysis is made. This analysis is usually undertaken for GeoArch in the laboratories of the Department of Earth Sciences, The Open University, Milton Keynes, England, equipped with an Applied Research Laboratories 8420 with dual-goniometer wavelength-dispersive X-Ray spectrometer. Elements typically included in the analysis will be Si, Al, Fe, Mn, Mg, Ca, Na, K, P, and Ti. All sample batches are run with internationally certified standards.

Inductively-coupled plasma mass spectrometry (ICP-MS) for minor and trace elements: ICP-MS is a technique for obtaining trace and minor elemental compositions of samples ranging down to the parts-per-billion (ppb) level. 200mg of powdered sample (either prepared specially, or ideally using a subsample of the powder already produced for the XRF analysis) is put into solution (typically using nitric and hydrofluoric acids) for the analysis on the ThermoElemental X-series ICP-MS in the School of Earth, Ocean and Planetary Science, Cardiff University, Cardiff, Wales. Elements typically included in the analysis will be Be, Ti, V, Cr, Mn, Fe, Co, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Sn, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Pb, Th and U. All sample batches are run with internationally certified standards.

Analytical Scanning Electron Microscope: Most routine high-magnification microscopy is undertaken using an electron microscope, since this permits simultaneous textural (using backscattered electron imagery) and microanalytical (Energy dispersive X-Ray analysis) investigation. The samples need to be highly polished, whether they are based on cut blocks of macroscopic material or strew mounts of microscopic material. The specimens are mounted in resin for polishing, which is undertaken in the laboratories of the Department of Earth Sciences, The Open University, Milton Keynes, England. The actual investigation is undertaken in the School of Earth, Ocean and Planetary Science, Cardiff University, Cardiff, Wales. The Analytical SEM is based on a Cambridge Instruments (LEO) S360 with a secondary electron detector for surface imaging, a 4-quadrant back-scatter electron detector for density imaging, and a cathodoluminescence detector. The analytical instrumentation comprises an Oxford Instruments INCA ENERGY (EDX) energy dispersive X-Ray analysis system and INCA WAVE (WDX) wavelength dispersive X-Ray spectrometer. The EDX system

is normally used for residue investigation, although the more sensitive WDS facility is available, for instance, for alloy analysis. Image recording is usually undertaken digitally via the OI INCA system. Detection limits for EDX analysis are variable but typically 0.02-0.05%. The software also allows for multi-element x-ray mapping and line scanning.

***X-Ray diffraction*:** XRD on powdered samples allows mineralogical/phase determination. It is of particular use in characterising clay minerals, using oriented slides. This can be undertaken at the School of Earth, Ocean and Planetary Science, Cardiff University, Cardiff, Wales, where the X-Ray Diffraction Laboratory contains two Philips automated powder diffractometers, models PW1710 and PW1840. The diffractometers give compound or mineral names, as opposed to a list of elements as in other analytical methods. Solid and powdered samples can be analysed and matched against a database of 70,000 recorded phases, thereby identifying and quantifying the unknown phases that are contained within a sample. XRD is used only rarely by GeoArch in archaeometallurgical projects.

***Optical Petrography*:** Optical microscopy may be undertaken on thin sections or polished blocks. These can be examined in-house using an Olympus BH2 polarising microscope with both reflected and transmitted illumination. The slides are prepared in the School of Earth, Ocean and Planetary Science, Cardiff University, Cardiff, Wales. Optical petrography is used only rarely by GeoArch in archaeometallurgical projects, but may be important where rock samples, including some types of ore, are involved.

5. Non-destructive analytical techniques - details:

Energy dispersive X-Ray Fluorescence: ED-XRF is a technique for obtaining semi-quantitative or qualitative chemical analysis from the surface of specimens in a non-destructive manner. This technique is particularly useful for the appraisal of metal residues on crucibles, moulds and other archaeometallurgical samples, without causing any damage to the artefacts. This work is normally undertaken using the Eagle II ED-XRF system at English Heritage's laboratories at Fort Cumberland, Portsmouth, England.

6. Reporting

GeoArch reports are normally supplied to clients in both Adobe Acrobat (.pdf) and Microsoft Word (.doc) formats. Illustrations may be supplied as separate files if required. Hard copy reports are now not normally issued unless specifically requested by the client.

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