‘Slag_Fun’ – A New Tool for Archaeometallurgy: Development of an Analytical (P)ED-XRF Method for Iron-Rich Materials

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This paper describes the development of a new analytical tool for bulk chemical analysis of iron-rich archaeometallurgical remains by Polarising Energy Dispersive X-ray Fluorescence ((P)ED-XRF). Prompted by the ongoing archaeological and archaeometric analyses of early first millennium BC iron smelting and smithing finds from Tell Hammeh (az-Zarqa), Jordan, the creation of this tool has already benefited several studies on iron-rich slag, of widely varying provenance as well as age (Anguilano 2002; Chirikure 2002; Ige and Rehren 2003; Stanway 2003). Following an explanation of the archaeological background and importance of the Hammeh finds, the paper describes the technical foundations of XRF analysis and the design, development and application of the “slag_fun” calibration method.

Archaeological Background

Excavations in 1996, 1997 and 2000 at Tell Hammeh (az-Zarqa), Jordan (Fig. 1), the last directed by the author, uncovered extensive remains of iron smelting and smithing, dating back to approximately 1000-750 BC (van der Steen 1997, 2001, 2003; Veldhuijzen 1998, 2000; Veldhuijzen and van der Steen 1999, 2000). In addition to tuyères, charcoal and vitrified furnace remains, large quantities of various types of slag were found, forming an unprecedented assemblage of iron production remains. All of the material was found in clear stratigraphic contexts and within what is evidently an area strictly used for metallurgy.

Figure 1. Tell Hammeh (az-Zarqa) seen from the south.

The Hammeh finds are significant for at least four reasons: age, quantity combined with variety, location and elemental composition. Dating from no later than 750 BC, possibly starting around 1000/950 BC, the finds are chronologically early when compared to the remarkably few other archaeological finds of regular iron production activity in southwest Asia. In Europe, the vast majority of 'early' iron smelting is Imperial Roman in age; very few smelting sites elsewhere predate 500 BC (Pleiner 2000: 7-8,13; Waldbaum 1999).

The finds at Hammeh are furthermore characterised by their quantity: 400 to 500kg of slag and some 350 tuyère fragments were excavated from approximately 9% of the estimated area involved in production. This should be seen in combination with the variety of the assemblage: tapped and non-tapped smelting slag, primary smithing slag, vitrified technical ceramics (tuyère and furnace wall), 'intermediate' slag consisting of vitrified technical ceramics 'mixing' with slag, tuyère nozzles and rear ends, olive wood charcoal and furnace base structure(s). This puts Hammeh in stark contrast to the paucity of other production related finds of comparable date in the Near East. Generally, these comprise only a handful of slag, and are most likely related to iron working rather than smelting (Ingo *et al.* 1992a, 1992b; Luciani *et al.* forthcoming; Luciani pers. comm.).

The Hammeh material is also quite remarkable in a geographical sense, as it is almost the only early first millennium BC evidence of iron production activities across southwest Asia. Most of the aforementioned finds of younger or similar age are from northern Syria and Anatolia, and the only other large area featuring significant remains is the Colchis region within Transcaucasian Georgia, on the borders of the Black Sea, but almost no archaeometric data is available from these sites (Khakutaishvili 1976, 2001; Pleiner 2000: 36-37, 58).

Finally, the Hammeh slag is microscopically different from most other known early iron production slag, in that it is much glassier, indicating a different bulk composition. Chemical analysis, using the calibration method described in this paper, shows that the Hammeh slag samples have a peculiar elemental composition, which clearly sets it apart from 'common' bloomery slag (Ingo *et al.* 1992a: 273-275; Luciani *et al.* forthcoming; Luciani pers. comm.). With a high lime and low iron oxide content, they resemble slag resulting from a technological process that was not in use until a millennium and a half later, *i.e.* the blast furnace process (Pleiner 2000: 251-252, 255-256), even though the Hammeh slag is the result of a regular bloomery smelting operation.

All in all, the Hammeh material provides a unique example of early iron metallurgy in the Near East, and analysis of this material will contribute significantly to the current understanding of the early technological developments that form the 'coming of iron' (Craddock 1995; Muhly and Wertime 1980; Pleiner 2000; Tylecote 1992). Hence, the Hammeh material is significant for both the archaeology of the region and the study of technology in general.

Introduction

The first step in the scientific study of slag is bulk chemical analysis. After slag has been tentatively interpreted and allocated to various parts of a production process according to its external appearance, its bulk composition is the first tool to confirm or deny these interpretations (Bachmann 1982: 8; Kronz 1998; Sperl 1980: 63).

Identical looking pieces of slag may have very different chemical compositions, possibly indicating different origins or processes. For example, the difference between copper and iron smelting slag can often only be determined by measuring its minute copper content. Other chemical elements, or ratios between elements, can help to determine the nature of the production process. The ratio between iron and lime, for example, can indicate whether a slag derives from a bloomery or a blast furnace, or may indicate the accidental or intentional use of fluxes (Morton and Wingrove 1969, 1972). Bulk chemical analysis is also necessary to assist the interpretation of microscopic examination of mineral phases within samples, and can be used to assess the need for, and nature of, further scientific analysis (Kronz 1998: 44-59). Different techniques exist to perform bulk chemical analysis. Only X-ray Fluorescence Spectrometry (XRF) will be discussed here.

X-ray Fluorescence Spectrometry (ED-XRF and WD-XRF)

A commonly used technique of bulk chemical analysis is X-ray Fluorescence Spectrometry (XRF), of which there are two kinds: energy dispersive (ED-XRF) and wavelength dispersive (WD-XRF). One main difference between ED-XRF and WD-XRF occurs at the last stage of energy determination. WD-XRF theoretically offers lower detection limits than ED-XRF, since it measures the emitted waves as sequential energy lines, with a much higher count rate per line. Measurement of energy in specific lines, as opposed to the entire spectrum, as in ED-XRF, avoids difficulties associated with overlapping element peaks (van Grieken and Markowicz 2002: 100-104).

Both XRF techniques can reach detection limits of a few parts per million (ppm), depending on the nature and preparation of the sample, as well as the particulars of the XRF instrument used. Each requires the measurement of standards of known composition, or certified reference materials (CRMs), against which the results of an unknown sample are compared. At the Institute of Archaeology, UCL, the available XRF technique is polarising ED-XRF ((P)ED-XRF), on a Spectro X-Lab Pro 2000 machine.

Polarising Energy Dispersive X-ray Fluorescence ((P)ED-XRF)

In (P)ED-XRF, an X-ray beam is directed at the surface of the sample under study. The interaction of this beam with the sample generates secondary (fluorescent) X-rays. Each chemical element produces characteristic secondary X-rays with different energies. These ‘dispersed’ energies are then detected and displayed as a spectrum, where intensity is set against energy. The resulting peaks shown in the spectrum indicate two things: the position of the peak indicates what element is present, and the peak height identifies how much of that element is present.

The primary X-ray beam can be aimed directly at the sample, but it is generally directed at a so-called ‘secondary target’ first. The primary beam is unpolarised, *i.e.* the photons are directed, but their amplitude has no preferred orientation. This causes extensive scattering effects, which generate significant background noise in the detection. The primary purpose of some of the secondary targets is therefore to polarise the primary beam, so only waves with parallel amplitude orientation will hit the sample (the principle of polarisation of the beam using targets is shown in Fig. 2).

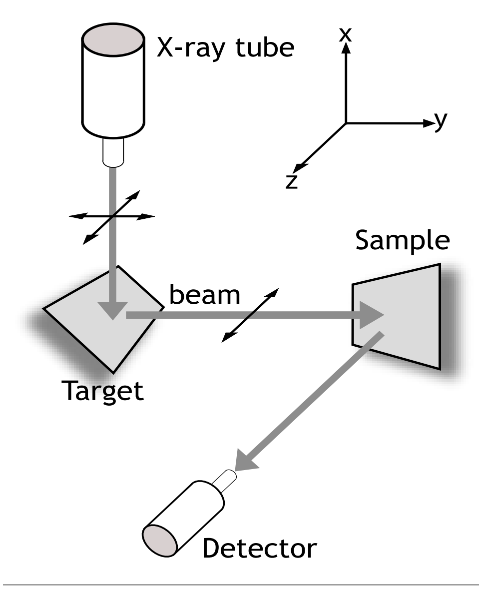


Figure 2. The principle of polarisation (P)ED-XRF, showing the orientation of target and sample in relation to the beam.

In this way the peak to background ratio is considerably enhanced, bringing the detection limits of ED-XRF near the level of WD-XRF. Some secondary targets are applied in the determination of scattering effects, and therefore do not polarise (Compton targets, see Table 1), others determine mirroring effects, *i.e.* direct reflection of the incident beam by the surface of the sample, as in a mirror (Bragg target, see Table 1; (Schramm n.d. a; Schramm n.d. b; Schramm 1998: 7-9)).

A further purpose of secondary targets is to limit the range of wavelengths hitting the sample. The nature of the secondary target determines which range of wavelengths from the primary beam is emitted towards the sample. The energy range of these wavelengths corresponds with a certain range of elements, which are selectively excited by the incident beam. The selection of secondary targets is thus directly related to the elements one wishes to analyse.

ED-XRF can theoretically reach a detection limit of a few ppm, however, depending on sample matrix, trace element concentrations (*i.e.* those present at levels below approximately 1000ppm, or 0.1 percent) are generally difficult to ascertain or judge accurately, since they tend to 'disappear' within the background noise (van Grieken and Markowicz 2002: 104). As described above, using secondary targets to enhance the peak to background ratio can improve detection limits significantly (Fig. 3 shows the principle of background reduction by (P)ED-XRF compared to ED-XRF and WD-XRF).

ED-XRF is well suited for determining alloy compositions of metal objects or analysing non-metallic materials such as ceramics and glass. A limitation of the technique is that only the surface of a sample, to a maximum depth of 1mm, is actually analysed. This may lead to confusing or misleading results if the surface differs from the bulk composition of the sample's body, as when corroded, painted or otherwise covered. Problems also occur when a surface is rough, striated, or heterogeneous. This can often be avoided by scraping or cleaning and polishing the surface prior to analysis or by using different methods of sample preparation (see below).

ED-XRF gives accurate results in a relatively short time. Depending on the set-up of the calibration method, almost all elements (from sodium to uranium) present in a sample can be measured and quantified within a period of 10 to 15 minutes. Another

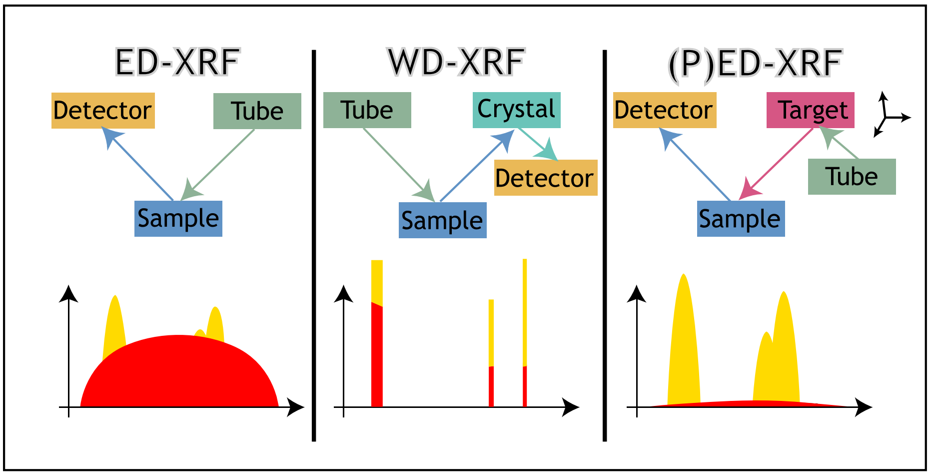


Figure 3. The principle of background noise reduction by (P)ED-XRF, compared to (standard) ED-XRF and WD-XRF (after Schramm n.d. b), fig. 7, p.10).

advantage of the XRF technique, especially for archaeologists, is the possibility of performing non-invasive analysis thereby preserving object interity. In the case of slag and related materials, destruction of artefacts is not an issue. To avoid the aforementioned problems, it is better to prepare a homogeneous sample from the material to be studied.

Slag sample preparation consists of crushing part of a sample into a powder of homogeneous grain size, preferably around 50µm. A pellet is produced by thoroughly mixing the powdered sample with a small amount of industrial wax, which serves as a binder, and then pressing it in a pellet-press for a fixed amount of time at a certain pressure. It is paramount that the utmost care is taken in preparing the pellets, since precision and quality of sample preparation have a considerable influence on the accuracy of the XRF measurements (Buhrke *et al.* 1998; van Grieken and Markowicz 2002: 933-944).

The Spectro X-Lab Pro 2000 (P)ED-XRF Calibration Methods

The Spectro X-Lab Pro 2000 (P)ED-XRF obtains the counts for each element from the detector and submits this data to a calibration process. The combination of measurement, deconvolution, evaluation and data-output is called a *method*.

- The ‘measurement’ element of the calibration method refers to all settings for the XRF instrument proper, such as voltage and current, vacuum, sample type (pressed pellet, solid, liquid, *etc.*), number and type of secondary targets and measuring time for each of them.

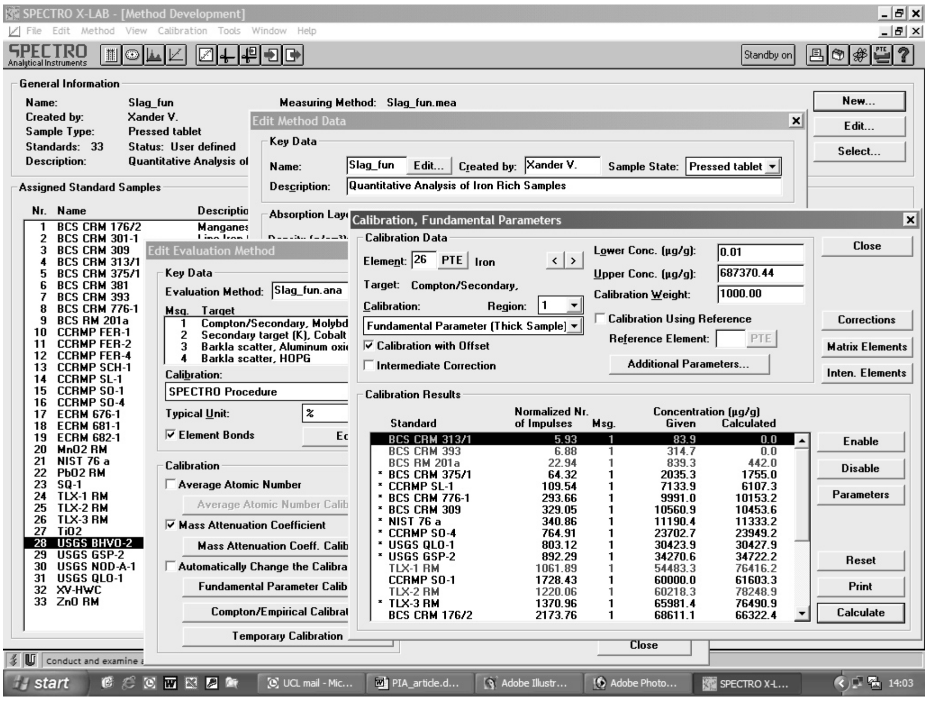
- ‘Deconvolution’ refers to all settings for each target chosen in the ‘measurement’ settings and defines the elements of interest for each. During deconvolution, net count rates for the selected elements are determined from the size and slope of the appropriate peaks, taking into account possible peak overlaps.

- 'Evaluation' refers to all settings pertaining to what is generally termed calibration. This involves the selection of a calibration model such as linear, fundamental parameters *etc*. During evaluation, the correlation between net count rates and actual concentrations are determined. Part of the calibration model uses the differences between known and calculated values of known CRMs which have been measured using the method in question.

- 'Data-output' refers to all settings that define the format in which the data is presented after analysis, such as in oxides or elements, in percentage or ppm.

Optimisation of a method for particular materials and/or elements is achieved by changing the settings of each of the first three parts of the method until the best fit is achieved between given and found concentrations of the CRMs (Fig. 4).

The X-Lab Pro comes with a range of pre-set methods; each is designed for a generic group of sample types, and provides initial screening analyses only (Spectro Analytical Instruments n.d.). None of these methods, therefore, is specifically aimed at, or accurate with, iron-rich materials such as slag. It was therefore necessary to develop a new method to measure the Hammeh material with the necessary precision and accuracy.



General Information

Name: Slag_fun
Created by: Xander V.
Sample Type: Pressed tablet
Standards: 33
Status: User defined
Description: Quantitative Analysis of
Measuring Method: Slag_fun.mea

Assigned Standard Samples

Nr.	Name	Descriptio
1	BCS CRM 176/2	Manganes
2	BCS CRM 301-1	
3	BCS CRM 309	
4	BCS CRM 313/1	
5	BCS CRM 375/1	
6	BCS CRM 381	
7	BCS CRM 393	
8	BCS CRM 776-1	
9	BCS RM 201a	
10	CCRMP FER-1	
11	CCRMP FER-2	
12	CCRMP FER-4	
13	CCRMP SCH-1	
14	CCRMP SL-1	
15	CCRMP SO-1	
16	CCRMP SO-4	
17	ECRM 676-1	
18	ECRM 681-1	
19	ECRM 682-1	
20	MnO2 RM	
21	NIST 76 a	
22	PbO2 RM	
23	SQ-1	
24	TLX-1 RM	
25	TLX-2 RM	
26	TLX-3 RM	
27	TiO2	
28	USGS BHVO-2	
29	USGS GSP-2	
30	USGS NOD-A-1	
31	USGS QLO-1	
32	XV-HWC	
33	ZnO RM	

Conduct and examine

Edit Method Data

Key Data

Name: Slag_fun
Created by: Xander V.
Sample State: Pressed tablet
Description: Quantitative Analysis of Iron Rich Samples

Edit Evaluation Method

Key Data

Evaluation Method: Slag_fun.ana

Msg.	Target
1	Compton/Secondary, Molybd
2	Secondary target (K), Cobalt
3	Barkla scatter, Aluminum oxi
4	Barkla scatter, HOPG

Calibration: SPECTRO Procedure
Typical Unit: %
☑ Element Bonds

Calibration
☐ Average Atomic Number
☑ Mass Attenuation Coefficient
☐ Automatically Change the Calibra

Calibration, Fundamental Parameters

Calibration Data

Element: 26 Iron
Target: Compton/Secondary,
Calibration: Fundamental Parameter (Thick Sample)
Region: 1
☑ Calibration with Offset
☐ Intermediate Correction
Lower Conc. (µg/g): 0.01
Upper Conc. (µg/g): 687370.44
Calibration Weight: 1000.00
☐ Calibration Using Reference
Reference Element:

Calibration Results

	Standard	Normalized Nr. of Impulses	Msg.	Concentration (µg/g) Given	Concentration (µg/g) Calculated
	BCS CRM 313/1	5.93	1	83.9	0.0
	BCS CRM 393	6.88	1	314.7	0.0
	BCS RM 201a	22.94	1	839.3	442.0
*	BCS CRM 375/1	64.32	1	2035.3	1755.0
*	CCRMP SL-1	109.54	1	7133.9	6107.3
*	BCS CRM 776-1	293.66	1	9991.0	10153.2
*	BCS CRM 309	329.05	1	10560.9	10453.6
*	NIST 76 a	340.86	1	11190.4	11333.2
*	CCRMP SO-4	764.91	1	23702.7	23949.2
*	USGS QLO-1	803.12	1	30423.9	30427.9
*	USGS GSP-2	892.29	1	34270.6	34722.2
	TLX-1 RM	1061.89	1	54483.3	76416.2
	CCRMP SO-1	1728.43	1	60000.0	61603.3
	TLX-2 RM	1220.06	1	60218.3	78248.9
*	TLX-3 RM	1370.96	1	65981.4	76490.9
	BCS CRM 176/2	2173.76	1	68611.1	66322.4

Figure 4. X-Lab Pro method development. Showing the 'slag_fun' development screen with the CRMs in the background. The cascading boxes show the method-editing box, the 'evaluation' settings box, and the fundamental parameter calibration box showing the settings for iron (Fe) respectively.

Design and Development of the 'Slag_Fun' Method

Measurement Settings

Development of a new method is initiated most easily by copying an existing one, as similar to the desired method as possible. From the settings of this existing and functioning calibration, a new method is constructed by changing and/or adding settings. In the development of the 'slag' method (a precursor to the 'slag_fun' method) for iron-rich materials, the existing 'oxides' method was used. The 'oxides' method is designed for pelletised samples that consist mainly of element oxides. In samples with medium (5-15%) to high (>20%) percentages of iron oxide(s), however, the matrix effects of the iron tend to swamp and absorb the counts of the lighter elements. Within the Hammeh material, the vast majority of samples consist of at least 40% iron oxide(s), therefore a new calibration method for iron-rich materials was needed.

Before setting the measurement conditions, it had to be determined what parameters were most important. Due to the nature of the research on the Hammeh material, measuring time per sample is far less important than detection limits and accuracy. The nature and origin of the samples (slag from metal production) also defines which elements are to be considered important. With these parameters, an XRF method for iron-rich materials in general, and iron production slag in particular, can be developed.

Target	Type of Targets	Typical Peak Time [µs]	Energy Range [keV]	Tube Voltage [kV]	Elements (K: K-Series) (L: L-Series)	Notes
Mo	Compton/ Secondary	4, 8, 13	25	35 ... 45*	K: 24-39 L: 72-92	
Pd	Compton/ Secondary	4, 8, 13	25	40 ... 50*	K: 26-42 L: 72-92	Alternative Compton target
Al_2O_3	Polarisation (Barkla Scatter)	4, 8	50	50 ... 55*	K: 40-60 L: 90-92	
B_4C	Polarisation (Barkla Scatter)	8,13	25	38 ... 48*	K: 22-42 L: 55-92	For low Z matrix, Alternative Compton target
Co	Secondary	8, 13	12.5	30 ... 35*	K: 19-25 L: 47-62	Useful in Fe/ Co-Matrix
Ti	Secondary	8, 13	12.5	25	K: 11-20 L: 37-51	
Al	Secondary	13	12.5	15	K: 9-12	Na, Mg in fused beads
HOPG	Bragg-Polarisation	8, 13	12.5	10 ... 25*	K: 9-30	The higher the tube voltage, the more Fe intensity

Table 1. X-Lab Pro targets and their tube settings. *Depending on the application (based on Spectro Calibration Manual).

With accuracy considered more important than speed of measurement, it was possible to add a secondary target to the existing 'oxide' method.

Table 1 shows the eight targets available at UCL and their corresponding measurement settings. The column titled 'elements' (Table 1) shows which range of elements is excited by which target, both K lines (primary electron orbit) and L lines (secondary electron orbit). All standard Spectro methods, including 'oxides', use three targets, which Spectro considers sufficient for general screening needs: Compton/Secondary Molybdenum, Barkla Scatter Aluminium Oxide and Barkla Scatter HOPG (*i.e.* Highly Ordered Pyrolytic Graphite).

Since the aim was to develop a method for the analysis of iron-rich samples, it was decided to select a fourth target which counters measurement problems related to medium to very high iron oxide contents. As mentioned above, the matrix effects (*i.e.* absorption of both the primary and emitted radiation by the elements present in addition to those of interest) of iron upon lighter elements are problematic. Within an iron-rich sample, the secondary X-rays of elements lighter than iron are either absorbed or distorted. Therefore, an additional target, cobalt (Co), was selected, since this secondary target specifically excites all elements up to but not including iron (van Grieken and Markowicz 2002: 627-628). The Co target was added on the second position; a choice based on the Spectro Calibration Manual (Spectro Analytical Instruments n.d.), and personal communication with Spectro UK.

Every method should start with a (non-polarising) 'Compton' type target, which provides information about various types of radiation scattering, most importantly Compton and Rayleigh scattering (Fig. 5). Compton scattering, also known as incoherent scattering, occurs when the incident X-ray photon transfers part of its energy onto an electron from an atom within the sample, and an X-ray photon is scattered from the atom in the process. The scattered X-ray photon is of lower energy, and therefore a longer wavelength, than the incident photon. Compton scattering mainly occurs from low atomic number elements. Rayleigh scattering, also known as coherent scattering, occurs when the incident X-ray photon interacts with the whole atom so that the photon is scattered with no change in internal energy to either the scattering atom, or to the X-ray photon. In Rayleigh scattering, X-ray photons of shorter wavelengths have an increased relative chance to be scattered.

The proportion of Compton to Rayleigh scattering therefore provides information on both the X-ray photon energy of the beam and the atomic number of the elements present within the sample (van Grieken and Markowicz 2002: 603-610). With a known beam energy the average atomic number of the sample can be determined (van Grieken and Markowicz 2002: 21-26).

Since the scattering is matrix dependant, the software uses the information from a 'Compton' target on scattering effects and their relations for matrix correction of the results obtained with the targets that follow.

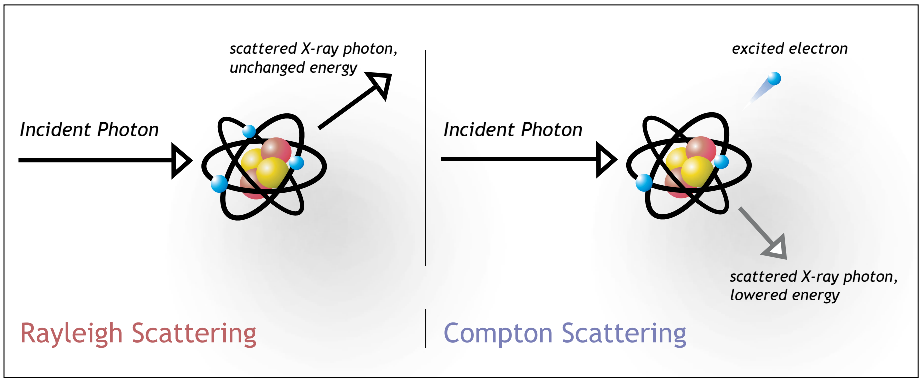


Figure 5. The principle of Rayleigh scattering (on the left) compared to Compton scattering (on the right).

The HOPG target should end the measurement, where it determines and resolves mirroring effects as described above. This target was therefore kept at the end and moved to position four. Due to its use in resolving absorption problems related to high iron content, it was decided to place the Co target before the Barkla Scatter Aluminium Oxide target. Generally, the target with the highest excitation energy follows the Compton target, to improve deconvolution of light elements. In this particular case, it was decided to place the Co target first (*i.e.* in the second position), to help this deconvolution by first resolving the iron related matrix effects.

Deconvolution Settings

Moving the original second and third target to the third and fourth positions effectively removed their original deconvolution settings from the software. As well as defining new settings for the Co target, those of the Aluminium Oxide and HOPG had to be reprogrammed. The new Co target was programmed to measure the concentrations of elements 19 to 25, potassium to manganese. The deconvolution sub-settings (settings for intensity and stripping elements, electron line to measure from, deconvolution strategy and background, deconvolution and normalisation regions) were set as they were for these elements in the Aluminium Oxide target. In this last target, elements 19 to 25 are now only measured for intensity, *i.e.* for internal use by the calibration software, but not to determine their actual concentrations. An explanation of the various measurement, line, region and strategy settings, which are related to the particular XRF machine used, is given in the Spectro Calibration Manual (Spectro Analytical Instruments n.d.).

Evaluation Settings

In XRF, the count rate of elements is influenced by the sample matrix. Evaluation procedures are employed in order to determine and correct the relation between the measured net count rates and the given values of standard CRMs. These procedures can be divided into two basic principles. The first is an empirical calculation model where the relation between net count and given values is calculated linearly, and all matrix effects are corrected using real, measured CRMs. The second principle is based on fundamental parameters where inter-element effects are calculated based on physical relations. This implies that fewer actual CRMs are necessary, but the demands on each CRM are much higher. The complete composition of the standard has to be known (the software tolerates a margin of 2.5% either way of 100%), including elements not measurable by XRF, such as oxygen or carbon, to allow theoretical calculations of all inter-element effects.

The 'slag' method was first developed using the "Lucas-Tooth, Price" empirical calibration method, to test settings and effectiveness. This calibration is a mathematical model in which the X-ray fluorescent radiation of the measured element is corrected with the effect coefficients of the compounds present in the sample (Lucas-Tooth and Pyne 1964). The calculated correlation between net count and given values of the CRMs used in the 'slag' method, is represented on or near a line in a graph displaying concentration horizontally and energy vertically, for one element at a time. On measuring an unknown sample, each element count is compared to this line and calibrated accordingly.

When this method was employed, the maximum level of refinement was quickly reached, which still left considerable error margins for certain elements. The same method was therefore rebuilt with the same measurement and deconvolution settings, but now using an adjustable combination of empirical and fundamental parameter models. The new fundamental parameters method is therefore called 'slag_fun' (see Fig. 4).

Certified Reference Materials (CRMs)

In principle, software running an XRF instrument could calibrate raw net counts to actual percentages using theoretically based calculations of inter-element effects. This would imply, however, that the samples analysed have to be of known composition. When measuring unknown samples, this knowledge is not available, so the net count and the calibrations performed on them have to be compared to known samples and their values.

A range of samples with known compositions, as similar as possible to the expected elemental composition (or compositions) and matrix (or matrices) of the unknowns to be analysed, is chosen. Since fundamental parameter analysis also needs the values of elements not measurable under XRF, such as those originating from organic material, one generally uses certified reference materials (CRMs or 'standards') which provide given conentrations for all elements.

Selection and Preparation

For the further development of the 'slag_fun' method, a range of CRMs was selected that was deemed relevant to iron-rich materials. First, related materials, where one could expect a similar matrix and composition, such as iron ore or slag, were chosen. Then CRMs were selected that were similar in matrix, representing major compounds of iron production related samples, such as lime, manganese, silica and alumina. Finally, a few CRMs were selected to ameliorate the calibration of elements that are not well covered by the other standards. A range of standards was created for the same purpose, *e.g.* the 'TLX' standards were prepared to enhance the calibration of lead and zinc. The CRMs currently used in the 'slag_fun' method are shown in Table 2, with the principle reason(s) for their selection.

After selection, the CRMs have to be prepared for measurement in the XRF instrument. This is done in a way that is analogous to the preparation of unknown samples. In fact, the preparation should be as identical as possible, to create comparable sample matrices. The CRMs come as powders, which are first dried for a minimum of 16 hours at 105^{o}C. This is to ensure that the structure and condition of the CRM are the same as when it was tested by the referencing laboratories. Next, the dried powders are mixed with a quantity of industrial wax. The mixture should be as homogeneous as possible to prevent heterogeneous areas or differing matrix effects. In the 'slag_fun' method, a sample composition was chosen with 8g of sample diluted with 0.9g of wax. Different amounts and different ratios are also possible (*e.g.* 4g mixed with 0.9g of wax), but the 8g pellets were considered easier to make and more durable. The mixture is then pressed to a 32mm diameter pellet at 15 tonnes for 2.5 minutes.

It should be noted that a higher dilution leads to a decrease of matrix effects, but simultaneously has a negative influence on the peak-background ratio and therefore the accuracy of results. Experiments are currently underway to establish the 'ideal' dilution for iron-rich samples.

Installing the CRMs

The prepared CRMs can now be used in the method. First, they are measured, one by one, using the new method. This results in net counts for the CRM with a theoretical calibration. These results are copied from the measurement data and pasted into the CRM list. Then, the known values of the CRM have to be entered against the calculated values, including the percentages of elements that are either not measurable under XRF or are below the detection limit. Now, the method with its new CRM has to be recalculated by the software, which results in newly calculated values. If any additional CRMs are required, they may be added by following the same procedure.

Although the most important elements to be analysed in iron-rich materials are now well covered by the CRMs in the 'slag_fun' method, development is ongoing. One area of development is the implementation of additional CRMs to cover varying percentages of elements such as potassium, titanium, calcium, manganese and magnesium. Refinement of the current calibration settings per element is also underway.

Application of the 'Slag_Fun' Method

Notwithstanding ongoing development, the method in its present form functions very well, producing more accurate results for iron-rich samples than any other X-Lab Pro method to date. This is demonstrated in Table 3, where analyses of a black-grey tapped smelting slag, HA2002 A7, with 'slag_fun' are set against results of the same sample using a different analytical technique: Wavelength Dispersive Electron Probe Micro Analysis (EPMA), on the JEOL 8600 Microprobe at the Institute of Archaeology, UCL.

Name	Description	Reason(s) for Selection
BCS-CRM 176/2	Manganese Ore	Mn content (Al, Fe)
BCS-CRM 301-1	Lincolnshire Iron Ore	Iron Ore matrix and composition, Ca content
BCS-CRM 309	Sillimanite	Si, Al content
BCS-CRM 313/1	High Purity Silica	Si content
BCS-CRM 375/1	Soda Feldspar	Na content
BCS-CRM 381	Basic Slag	Slag matrix and composition
BCS-CRM 393	Limestone	Ca content
BCS-CRM 776-1	Firebrick	Al, Si, K content: furnace wall elements
BCS-RM 201a	Nepheline Syenite	Na, Al, Si, K content
CCRMP FER-1	Magnetite/Quartz iron formation	Generic Iron standard
CCRMP FER-2	Magnetite/Quartz/Amphibole Iron Ore	Generic Iron standard
CCRMP FER-4	Cherty Magnetite/Chloritic tuff iron formation	Generic Iron standard
CCRMP SCH-1	Schist/Mica Iron Ore	Iron Ore matrix and composition
CCRMP SL-1	Blast Furnace Slag	Industrial Slag composition and matrix
CCRMP SO-1	Champlain Sea Clay	Clay matrix and composition
CCRMP SO-4	Chemozemic Soil	Si, Al, Na, K composition
ECRM 676-1	Iron Ore sinter	Iron Ore matrix, Si, Al
ECRM 681-1	Iron Ore	Iron Ore matrix and composition
ECRM 682-1	Iron Ore	Iron Ore matrix and composition
MnO2 RM	Manganese dioxide laboratory standard	Mn content
NIST 76a	Burnt Refractory	Ceramic matrix and composition (furnace wall)
PbO2 RM	Lead dioxide laboratory standard	Pb content
SQ-1	Spectro Quartz Disc	Company calibration standard
TiO2 RM	Titanium dioxide laboratory standard	Ti content
TLX-1 RM	PbO 15%/ZnO 6% in USGS BHVO-2 matrix	Laboratory mix of CRM with laboratory standards; Pb, Zn, Mg, Ca, Fe content
TLX-2 RM	PbO 10%/ZnO 4% in USGS BHVO-2 matrix	Laboratory mix of CRM with laboratory standards; Pb, Zn, Mg, Ca, Fe content
TLX-3 RM (own standard)	PbO 5%/ZnO 2% in USGS BHVO-2 matrix	Laboratory mix of CRM with laboratory standards; Pb, Zn, Mg, Ca, Fe content
USGS BHVO-2	Basalt Hawaiian Volcanic	Slag-like glassy matrix and composition
USGS GSP-2	Silver Plume Granodiorite	Slag-like glassy matrix and composition
USGS NOD-A1	Manganese Nodule	Mn content
USGS QLO-1	Quartz Latite	Si content, matrix
XV-HWC	Hoechst Wax	Dilution material (C+H)
ZnO RM	Zinc Oxide laboratory standard	Zn content

Table 2. The 33 standards presently used in the 'slag_fun' calibration method on the Spectro X-Lab 2000.

Table 3 also shows results from the linear 'slag' and the original 'oxide' methods to indicate how measurements have improved.

The microprobe analysis was performed by analysing nine (one line of five and one line of four) areas of approximately 300µm x 300µm. Each area was measured at an interval of approximately 300µm, resulting in one line of about 1.8 x 0.3mm and a second line of 1.2 x 0.3mm, continuing in the same direction but 0.8mm to the side of the first. The lines are separated by approximately 1.7mm. From these nine measurements (calibrated against four CRMs), the average value for each element was calculated.

From the similarity that has been demonstrated between the XRF and EPMA results, it could be argued that all samples might be analysed solely using the microprobe. It should be stressed, however, that the strength of the microprobe lies in allowing point analysis (*i.e.* to establish the composition of mineral phases), providing results for 18-20 elements per measurement. The high number of measurements required, combined with the considerable time each measurement takes (>15 minutes each), and the restricted number of elements that can be determined in one measurement, make the microprobe highly unwieldy and inappropriate for bulk analysis.

Table 4 shows stages of the development of the 'slag' and the later 'slag_fun' method, compared to the original 'oxide' method. This is shown through repeated analyses of test sample HAT 1, a black-grey tapped bloomery smelting slag similar to HA2002 A7. Although these stages might be considered arbitrary, it should be noted that these analyses were all performed after major adjustments to the calibration settings. They clearly illustrate significant improvement in the method over time. The detection of lighter elements such as magnesium, aluminium and silicon has improved, as has the sum of the measured elements. The detection and calibration of sodium, the first element measurable under XRF, remains problematic, which may be the combined result of its peak lying at the very edge of the spectrum measured by XRF and absorbing matrix effects of magnesium and iron K-lines.

Table 5 shows how measurements of four CRMs with the 'slag_fun' method compare to the given values of these CRMs. To compensate for organic materials in the CRMs, which are not measurable under XRF, the results have been normalised to 100 percent. This table clearly shows that the results obtained with the 'slag_fun' method are accurate and can be used in quantitative analyses.

Tables 3, 4 and 5 also reveal a few remaining problems that are being addressed. These problems occur mainly at low element concentrations (<2%), of aluminium and magnesium, and low to medium concentrations (<10%) of aluminium. This is very likely due to remaining unresolved matrix and intensity effects between silicon and aluminium, and between aluminium and magnesium.

Conclusion

Tables 3, 4 and 5 show that the 'slag_fun' method improved significantly over time and provides an accurate and valid tool for bulk chemical analysis of iron-rich materials.

Sample	Date analysed	Method / Technique	SiO_2	Al_2O_3	FeO	TiO_2	MnO	CaO	MgO	Na_2O	K_2O	P_2O_5	S	CuO	PbO	ZnO	Sum
HA2002 A7	August 2002	EPMA	23.30	5.17	53.35	0.25	1.37	12.03	2.59	0.30	0.46	1.54	0.34	0.03	0.03	0.02	100.80
HA2002 A7	January 2003	Slag_fun	21.58	4.11	55.84	0.35	1.16	11.52	2.46	n.d.	0.71	1.63	0.18	n.d.	n.d.	n.d.	99.54
HA2002 A7	January 2003	Oxides	30.80	6.49	87.44	0.52	2.05	14.88	3.84	n.d.	1.17	2.24	0.13	n.d.	n.d.	n.d.	149.56
HA2002 A7	August 2002	Slag	17.38	3.26	49.56	0.31	2.08	6.34	1.84	n.d.	0.66	1.09	0.27	n.d.	n.d.	n.d.	82.80

Table 3. Comparison of methods. Results of the 'slag_fun' method, compared with 'true' values obtained through EPMA, and the linear 'slag' and oxide methods. The comparison is performed on sample HA2002 A7, a black-grey iron smelting tap slag. All measurements are expressed as a weight percentage.

Sample	Date analysed	Method	SiO_2	Al_2O_3	FeO	TiO_2	MnO	CaO	MgO	Na_2O	K_2O	P_2O_5	S	CuO	PbO	ZnO	Sum
HAT 1	03/01/2003	Slag_fun	25.85	4.26	51.63	0.40	1.04	17.63	1.99	n.d.	0.90	0.96	0.26	n.d.	n.d.	n.d.	104.92
HAT 1	11/09/2002	Slag_fun	24.94	4.79	46.57	0.37	0.95	14.40	2.52	0.37	0.89	0.97	0.28	n.d.	n.d.	n.d.	97.05
HAT 1	09/09/2002	Slag_fun	23.28	3.45	39.25	0.23	1.74	9.66	0.74	n.d.	0.93	0.81	0.26	n.d.	n.d.	n.d.	80.35
HAT 1	09/09/2002	Slag	9.49	1.83	28.10	2.37	0.61	53.62	1.77	n.d.	2.52	0.24	0.07	n.d.	n.d.	n.d.	100.62
HAT 1	07/06/2002	Slag	14.07	3.48	40.37	0.11	0.72	10.37	1.49	n.d.	0.70	0.54	0.21	0.01	n.d.	n.d.	72.06
HAT 1	05/03/2002	Slag	9.53	1.84	27.23	2.30	0.59	51.72	0.80	n.d.	2.33	0.29	0.07	n.d.	n.d.	n.d.	96.70
HAT 1	02/05/2002	Oxides	21.58	3.52	46.92	0.37	1.13	14.87	1.07	n.d.	0.82	1.10	0.10	n.d.	n.d.	n.d.	91.48

Table 4. Development of the 'slag' and 'slag_fun' methods over time. Results are shown with the most recent on top, and are off-set against the results obtained with the 'oxides' method at the bottom. All measurements were performed on test sample HAT 1, a black-grey iron smelting tap slag. All measurements are expressed as weight percentage.

Sample	Sample Type	Method / Given	SiO_2	Al_2O_3	FeO	TiO_2	MnO	CaO	MgO	Na_2O	K_2O	P_2O_5	S	Sum
BCS-CRM 381	Basic Slag	Slag_fun	9.88	0.11	17.53	0.33	3.31	49.86	0.06	0.76	0.03	17.91	0.23	100.00
		Given	9.15	0.70	17.82	0.36	3.29	51.05	1.07	n.d.	n.d.	16.36	0.20	100.00
BCS-CRM 301-1	Lincolnshire Iron Ore	Slag_fun	10.93	5.65	44.92	0.23	1.75	31.87	2.66	0.06	0.46	1.20	0.27	100.00
		Given	10.62	6.12	44.04	0.23	1.79	32.44	2.48	0.10	0.46	1.15	0.57	100.00
CCRMP SL-1	Blast Furnace Slag	Slag_fun	36.00	8.72	0.92	0.39	0.87	36.77	14.42	0.09	0.59	0.01	1.22	100.00
		Given	35.93	9.68	0.93	0.38	0.87	37.69	12.34	0.39	0.51	0.02	1.27	100.01
BHVO-2	Basalt CRM	Slag_fun	50.16	14.91	11.09	2.59	0.14	10.96	7.02	2.29	0.50	0.30	0.03	99.99
		Given	50.42	13.64	11.19	2.76	0.13	11.52	7.31	2.24	0.53	0.27	n.d.	100.01

Table 5. Comparison of given values of four CRMs, with the values of the same standards obtained with the 'slag_fun' method. All results have been normalised to remove differences caused by elements not measurable under XRF and loss on ignition (LOI). All measurements are expressed as a weight percentage.

Calibration settings for the measurement of certain elements will be adjusted further, and more CRMs will be added, but already the method as it stands is far more reliable and accurate for iron-rich samples than the original Spectro methods.

Preliminary analyses of several examples of Hammeh tapped smelting slag similar to HA2002 A7 and HAT 1, using the 'slag_fun' calibration method, show the same consistently low FeO, high CaO nature, *i.e.* leanness. This low FeO content of the slag indicates a higher yield of metallic iron during the smelting process, with CaO replacing part of the FeO in the slag. Comparison to the composition of the local ore at Mugharet al-Warda, seems to indicate that to a large extent the Ca may stem from there (Serneels and Crew 1997). The formation of the Hammeh slag, and therefore it's composition, may have been influenced further by technical ceramic material (furnace wall and tuyère nozzles) and charcoal ash contributions (Crew 2000).

Primarily, 'slag_fun' provides a necessary tool for the archaeometric study of the Hammeh material, as shown by the identification of the high lime content discussed above. Since development, it has also benefited several other research projects involving iron-rich slag at the Institute of Archaeology, UCL, including iron production slag from Nigeria (Ige and Rehren 2003), Wales (Stanway 2003) and Zimbabwe (Chirikure 2002), as well as lead slag from Greece (Anguilano 2002). The creation of 'slag_fun' has furthermore resulted in a 'manual' for method building, and prompted (and supplied the basis for) the current development of a calibration method for ceramics.

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All figures are by the author.

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