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WDXRF AND Spark - OES ANALYSIS OF FOUNDRY IRON AND FURNACE SLAGS

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Abstract. A comparative study regarding chemical composition (major elements) of two different types of furnace slag: the blast-furnace and the electric converter ones are presented and discussed. At the same time, by means of an inter-comparison performed on five reference iron samples, we have tried to establish which one of two concurrent methods currently used: optical emission spectroscopy (S-OES) and wave dispersion x-ray fluorescence spectroscopy (WDXRF) gave better results. An ANOVA test showed practically no differences between these methods, while a graphic analysis performed by means of ternary diagrams and principal component analysis evidenced significant differences between the two types of slag analysed.

Key words: WDXRF, Spark-OES, Foundry iron, Slag, Ternary diagram.

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1. INTRODUCTION

The elemental analysis of various products directly related to iron ore processing and iron and steel production could be performed by one or more complementary techniques such as optical emission spectroscopy (S-OES), inductively coupled plasma - optical emission spectroscopy (ICP-OES), wave dispersion x-ray fluorescence spectroscopy (WDXRF), wet chemical analysis, combustion methods, or inert gas fusion. The chosen technique depends on the type of sample to be analysed, on the quantity of available material for analysis, on the accuracy, as well as on the cost constraints. In most cases, the relevant analytical techniques should detect contents up to few mg/kg (part per million).

Among these techniques, WDXRF can be used for direct analysis of solid metal as well as furnace slags samples, petroleum products, cement, coal, and various other materials. It is a fast, non-destructive technique, frequently used in the industrial quality control [1–7].

As oppose to the previous procedure, S-OES, an analytical technique with multiple applications, currently used in metallurgy, can be performed with only minimal surface damage, the amount of material needed for analyses being negligible. For the remaining methods mentioned here, only a small specimen is removed from the sample and is used in the analysis [1].

As both methods have advantages and disadvantages, choosing the most appropriate method could be a challenging task. To accomplish it, we have investigated a set five different foundry iron samples in order to arrive to the most suitable method, and to apply it to investigate the chemical composition of other by-products of iron metallurgy such as different kinds of slag. As C, Mg, Si, Al, S, P and Mn play a significant role in determining the future slag properties, we have confined our investigation to these elements. S-OSL has the advantage of using minute quantities of material but irretrievably lost during the analysis while WDXRF needs significantly more material which remains intact after measurements and thus could be archived.

Slag is a secondary product resulting from the melting of chemical compounds of ore barren, coke, injected coal and flux, in the case of blast-furnace slag, or from the impurities contained in pig iron and scrap iron in the case of the electric converter furnace steel-making [5]. Accordingly, there is a significant difference between these two types of slag regarding the content of residual iron and manganese and unreductible oxides such as MgO, SiO_2, Al_2O_3 and P_2O_5.

This is why, before assessing slag samples, we have performed a comparison between these two methods by measuring a set of five reference samples and analysing the results regarding the contents of above mentioned elements by means of some statistical methods such as one-way ANOVA [8].

Principal Component Analysis (PCA) and Graphic Analysis (GA), the last one performed by means of Ternary Diagrams (TD) are two statistical methods used in exploratory data analysis due to their ability to group data according to their resemblance, and thus making their classification easier [8]. This is why both methods were used to analyse the content of major elements in slag samples.

The results of our study will be further presented and discussed.

2. MATERIALS AND METHODS

2.1. SAMPLES

For the first part of our study, in order to compare and to obtain the best possible results, we have prepared a set of five reference samples, 4213 - 4217 (See Table 1), all of them being certified by the Bureau of Analysed Samples, Ltd., Newham Hall, Middlesbrough, England.

At the same time, for spectrometer calibration, we have used a set of five Stan-

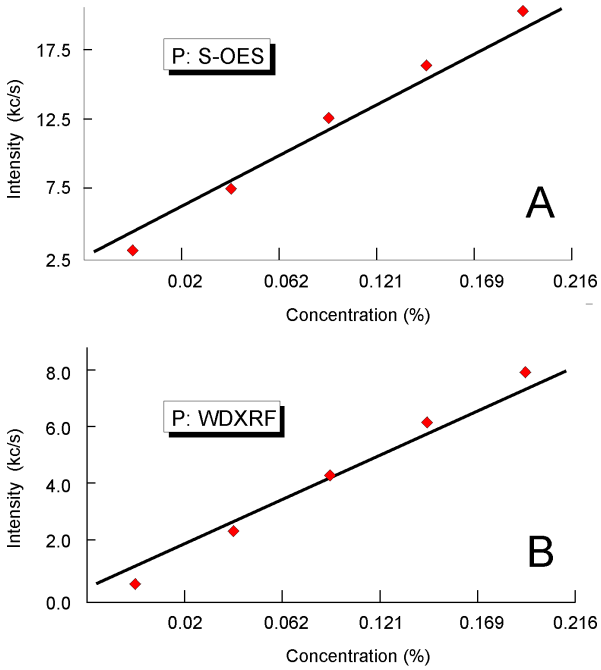

Fig. 1 – The Phosphorus calibration curve by S-OES (A) and WDXRF (B). In both cases, the correlation coefficient between concentrations and line intensities was greater then 0.9992.

dard Certified Reference Materials (SCRM) prepared for British Cast Iron Research Association BCIRA, Alvechurch, Birmingham, UK by using a special method of casting, known to provide material of uniform composition, and suitable to be used as calibration standards in OES analysis.

The high quality of these materials is well illustrated by the corresponding 2D plots (signal amplitude vs. content) which display a perfect monotonous dependency, characterized by correlation factors greater than 0.9992 (Fig. 1). At the same time it is worth mentioning that each measurements was performed five times resulting, in a relative error between 0.5 % and maximum 2 % for each element.

In the case of slag samples, we have analysed seven samples of both blast and electric converter furnaces, randomly chosen, in order to show to which extent the composition of different batches are different. As in previous case, each sample was measured five times, so the final uncertainties were less then 2 %.

2.2. WDXRF MEASUREMENTS

For WDXRF measurements we have used an ARL 9900 Thermo Scientific X-ray fluorescence sequential spectrometer, able to analyse up to 90 elements in nearly any solid or liquid sample. The spectrometer, equipped with a 6th generation

goniometer with a resolution of and fully digitally mastered, allows a fast acquisition of spectra at speeds up to 3270.001^o per minute. Moreover, the presence of a built-in calibration system and of an appropriate soft allow obtaining final data without a need for standard samples.

2.3. SPARK - OES MEASUREMENTS

All S-OSL determinations were performed by an ARL 3460 Thermo Scientific Optical Emission Spectrometer, provided with a Current Controlled Source allowing a faster attack on the sample for short analysis times, and improved precision as well as a Time Resolved Spectroscopy system, which permits clearer differentiation between the useful analytical signals and background, thus achieving better limits of detection.

3. RESULTS AND DISCUSSION

Table 1.

The experimental values of C, Si, S, P and Mn, as obtained by WDXRF (a) and S-OES (b). All contents are expressed in %.

	Element				
Sample	C	Si	S	P	Mn
4213(a)	4.61	0.801	0.015	0.109	0.724
4213(b)	4.70	0.815	0.016	0.107	0.714
4214(a)	4.61	0.709	0.013	0.109	0.716
4214(b)	4.70	0.765	0.014	0.107	0.717
4215(a)	4.61	0.671	0.015	0.102	0.692
4215(b)	4.70	0.654	0.016	0.101	0.689
4216(a)	4.61	0.671	0.015	0.102	0.692
4216(b)	4.70	0.765	0.015	0.104	0.755
4217(a)	4.61	0.796	0.017	0.105	0.757
4217(b)	4.70	0.787	0.016	0.104	0.750
average(a)	4.61	0.760	0.016	0.106	0.730
average(b)	4.70	0.757	0.016	0.104	0.725

The experimental results concerning the content of chosen elements in all 10 samples, as obtained by both methods, are reproduced in Table 1 and illustrated, as a 2D plot in Figure 2. At a detailed analysis of these data we come across similarity, sustained by the numerical value of the correlation coefficient, whose value of 0.9991 shows a perfect match between the average values of the two set of date.At the same time, a one-way ANOVA gives a value smaller then 1 for the t parameter which testifies again that, at $p < 0.01$, both sets of data are not significantly different.

These facts enabled us to consider that both methods have the same accuracy, so that for further analysis of slag samples we could use only one of them, *i.e.* WDXRF for its complete nod-destructive character and the possibility to preserve indefinitely the investigated specimens.

Consequently, in Table 2 we have reproduced the experimental values of the content of main components (as oxides) of both kinds of slag. Even at a first glance it is evident that between blast furnace and electric converter slags there are significant differences, regarding almost all components, excepting calcium oxide whose content seems to be, within experimental uncertainties, very close. At the same time, within the same group of samples, some elements seem to show more variability then the other, variability which in some cases reaches more then 30 % as Manganese in blast furnace or Aluminium in electric converter slag (see Table 2). As significant differences exist not only between the two categories of specimens, but also within each type of slag, to evidence the existing inhomogeneities it is necessary to use both statistic and graphic methods of analysis, such as PCA or TD.

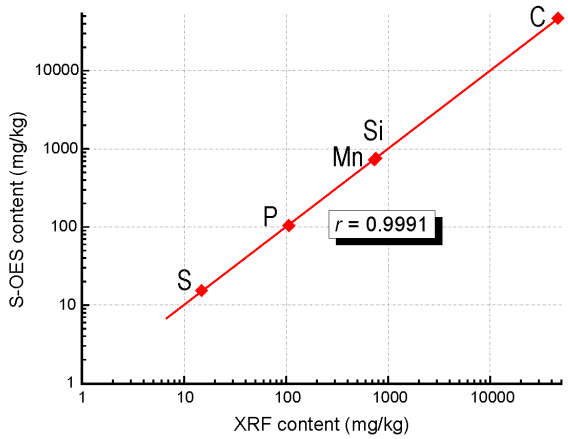

Fig. 2 – A 2D plot illustrating the perfect correlation (r = 0.9991) between XRF and S-OSL results for the same set of samples.

Due to the higher content of silica and calcium oxide, slags, regardless of their origin, could be very well characterized by using TD [9] close to those used in petrology, *i.e.* SiO_2 - (Al_2O_3+MnO+FeO)-(MgO+CaO) diagrams 3. On this diagram, reproduced in Fig. 3, one can see that the two categories of slag form two clusters, the furnace slag showing more homogeneity then the electric converter one, thus confirming the significant differences between them, differences due not only to used raw material but also to a completely different metallurgy.

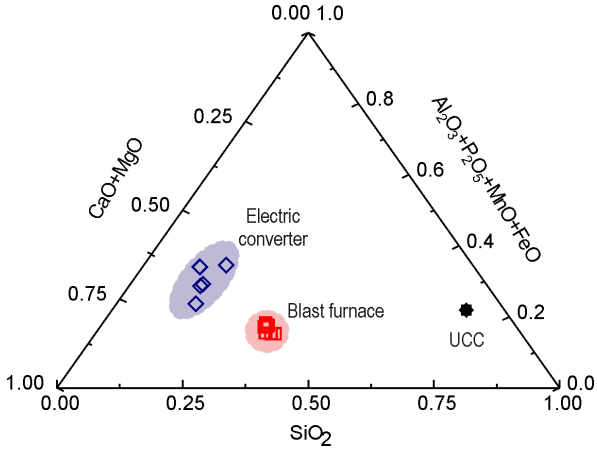

Fig. 3 – A ternary diagram of the two sets of slag as well as the UCC illustrating the differences between all of them.

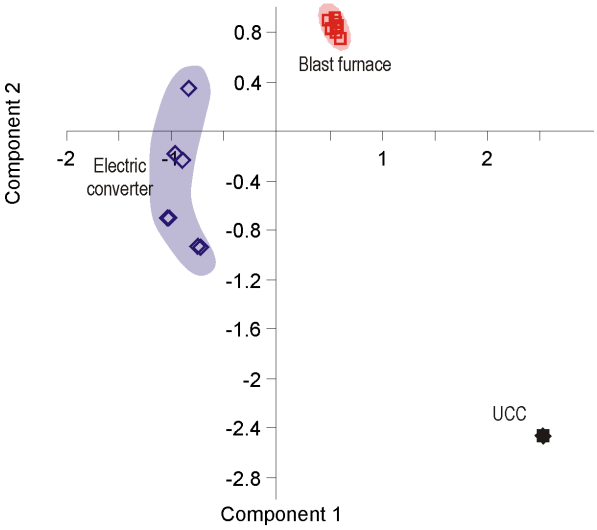

Fig. 4 – A 2D PCA plot (component 1 *vs.* component 2) of the two sets of slag samples illustrating the significant difference between blast and electric converter furnace slag. While the electric converter samples show a relative great dispersion, the blast furnace specimens appeared to be more homogeneous. As in previous Figure, the UCC showed to differ significantly with respect of both of them.

This investigation could be further continued by analysing the degree of homogeneity or inhomogeneity within each kind of slags. For this purpose, we have used the PCA performed in the R mode, so that to classify each set of samples with respect

to the content of main oxides, the results being reproduced in Fig. 4 s a 2D plot of the second principal component with respect to the first one. At the first glance, this graph illustrates not only the significant difference existing between the two kinds of analysed slags, each of them forming a distinct cluster, but also the fact that the samples of the electric converter slag are more dissimilar then the blast furnace ones.

These dissimilarities are better evidenced by PCA than by GA by taking into account that at PCA, all sample characteristics *i.e* variables represented by the content of main oxides are considered separately, while in the case of GA, their number is reduced to three, a number necessary for a ternary diagram. On the other hand, a ternary diagram is more useful as the three parameters could be *a priori* chosen in accordance with some criteria, while in the case of PCA this choice is not available.

Due to its chemical composition and rapid cooling, slag has a partial vitreous structure and shows some similarities with silica rich carbonates rocks, better evidenced on Fig. 3. On this diagram, both kind of slags occupy position specific for carbonates with a variable content of silica. But when compared with typical terrestrial rocks such those which form the Upper Continental Crust (UCC) [10], slags appear to be very different, as proved by Fig. 3 and 4, where the UCC location lies faraway from both kinds of slag.

4. CONCLUDING REMARKS

A comparative study between two high performance analytical methods used in metallurgy: Spark - Optical Emission (S-OES) and Spectroscopy and Wave Dispersive X-Ray Fluorescence (WDXRF) was performed in order to establish which one is more suitable for routine analysis, with a particular reference to furnace (blast or electric) slag. By using two sets of iron calibration samples, a prefect equivalence between these methods was evidenced, further confirmed by statistical descriptors such as Pearson r correlation coefficient and t-test for one-way ANOVA.

Under these circumstances, to analyse a set of 14 slag samples produced by both blast and electric converter, WDXRF was chosen for its totally non-invasive character and the unlimited archive time. The final results showed that by interpreting the raw results produced by WDXRF by means of both graphic and principal component analysis it was possible to show the significant differences existing between the two groups of slag as well as to characterize the degree of inhomogeneity within each of them.

Table 2.

The experimental values of main oxides content as obtained by WDXRF in blast (b) as well as electric converter (bo) furnaces. All contents are expressed in %.

	Component						
Sample	MgO	Al_2O_3	SiO_2	P_2O_5	CaO	MnO	FeO
Blast furnace slag							
1b	5.98	14.10	32.87	1.24	42.76	0.61	0.69
2b	5.76	12.61	33.61	1.24	44.18	0.57	0.49
3b	6.17	14.48	32.29	1.12	42.87	0.40	0.45
4b	5.80	14.80	32.95	1.08	42.41	0.48	0.52
5b	5.39	12.20	35.56	1.05	42.77	0.85	0.58
5b	5.48	12.27	34.71	1.05	43.44	0.76	0.67
7b	5.80	15.63	32.55	1.15	43.07	0.42	0.62
average	5.8	13.7	33.5	1.1	43.1	0.6	0.5
s.d	0.3	1.4	1.2	0.1	0.6	0.2	0.1
Electric converter furnace slag							
1bo	2.19	2.82	15.51	1.02	44.1	5.78	22.77
2bo	2.18	2.80	15.47	1.03	44.03	5.81	22.70
3bo	3.01	1.99	10.80	1.04	48.57	4.45	24.52
4bo	3.02	1.95	10.90	1.05	48.50	4.40	24.49
5bo	2.68	1.80	13.83	1.16	51.01	5.11	19.57
6bo	3.20	1.29	15.11	1.51	54.60	4.78	14.96
7bo	2.18	1.10	13.74	1.28	52.97	4.63	20.57
average	.2.6	2.0	13.6	1.2	49.1	5.0	21.4
s.d	0.5	0.7	2.0	0.2	4.1	0.6	3.4

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