

## APPLICATION OF SPECTROCHEMICAL ANALYSIS BY SOLID SOLUTION TECHNIQUE TO FERRO-ALLOYS

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**Abstract.** *The paper presents the experimental results obtained on ferro-alloys (ferro-manganese, ferro-chromium, ferro-silicon and ferro-molybdenum) spectrochemical analysis by wavelength- dispersion X-ray fluorescence spectrometry (WDXRF). The samples were prepared by solid solution technique. The precision of the sample preparation method was determined in the case of ferro-manganese. The calibration curves for all chemical elements of interest were established using certified reference materials produced by BAS-England and Brammer Standards-USA. The comparison of the experimental results and the allowed deviations by wet chemical analysis methods confirms the analytical performances of WDXRF spectrochemical method on samples prepared by solid solution technique.*

**Keywords:** *WDXRF, ferro-alloys, analysis.*

### 1. INTRODUCTION

The ferro-alloys are one of the basic raw materials in steel processing. Their chemical composition must be checked to confirm their necessary quality for steel alloying.

The common method used in chemical analysis of ferro-alloys is wet chemical method. Although the wet chemical method presents the advantages of an absolute analysis this method is often laborious and shows high time and reactive consumption. Also the wet chemical method is not fully automated, the operator having a very important role, and this can lead to low precision.

The ferroalloy WDXRF spectrochemical analysis is a modern method that can be fully automated and leads to high precision. The short analysis time (about 30 minutes from the sample taking time) allows to take real time decisions referring to the next utilisation of the ferro-alloy.

The most common sample preparation techniques in ferro-alloys WDXRF spectrochemical analyses are:

a) grinding and pressing technique [1, 2, 4]

In this technique the sample is milled and the powder is formed into a self- supporting pellet or briquette in a hydraulic press at pressure up to 7000 kg/cm<sup>2</sup>. The powder may be briquetted as is, with a binder (such as boric acid, starch or cellulose), with a cellulose or

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other backing, or in a shallow aluminium cup. This sample preparation method shows a low reproducibility due to the following effects:

- particle size effect which leads to inhomogeneities;
- mineralogical effect, notably where the mineralogical composition of the sample is variable.

b) solid solution technique [3, 5]

## 2. EXPERIMENTAL

### 2.1. SOLID SOLUTION SAMPLE PREPARATION TECHNIQUE

This modern preparation technique consists of following processes:

- the ferro-alloy sample is milled up to an established grain size ( $<200\mu\text{m}$ ).
- a measured quantity of ferro-alloy is mixed with the appropriate quantity of oxidizing agents. The mixture is placed on a flux layer in a platinum-gold crucible like in Fig. 1. The platinum-gold crucible is heated in a radio-frequency furnace at very well controlled temperatures.

- in the first stage, the crucible is heated to temperatures about  $800^{\circ}\text{C}$  and the ferro-alloy elements are oxidized. In the second stage, the crucible is heated to temperatures about  $1200^{\circ}\text{C}$ , the flux is fused and the oxides' resulted from the ferro-alloy are dissolved in the melted flux.

- the solution is homogenized by mechanical stirring and is casted in a casting dish where takes place the solidification process. The obtained bead is ready for spectrometer presentation.

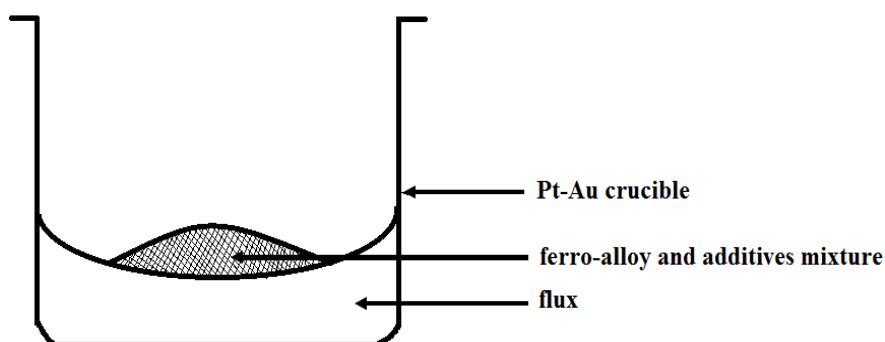


Fig. 1. The position of the sample preparation recipe components in the Pt-Au crucible.

The solid solution technique presents, for ferro-alloy sample's preparation, the following advantages: no mineralogical and particle effects, homogeneous samples, easy to prepare standards, blanks are possible, odd shaped samples can be analyzed, reduction of absorption and enhancement effects, correction possible via standard addition.

The disadvantages of solution techniques are: the volatile elements, like carbon and sulphur can not be analysed because they form volatile compounds; difficult trace element analysis due to dilution; high backgrounds; increased absorption of long wavelengths (light elements).

## 2.2. SAMPLE PREPARATION RECIPE

The ferro-alloy sample's preparation recipes were established for a Philips PEARL'X 3 automatic furnace. For this furnace all the parameters involved in the preparation process can be programmed and controlled leading to a high process reproducibility.

The sample preparation recipes for ferro-manganese, ferro-chromium, ferro-silicon and ferro-molybdenum were optimised.

In the preparation recipe optimisation the following parameters were considered:

## 2.3. THE FLUX TYPE

The most commonly used fluxes in the solid solution techniques are lithium tetraborate ( $\text{Li}_2\text{B}_4\text{O}_7$ ), sodium tetraborate ( $\text{Na}_2\text{B}_4\text{O}_7$ ), lithium metaborate ( $\text{LiBO}_2$ ). Lithium tetraborate was chosen because this flux allows a better light element's analysis (P, Si, Al) due to the weak X-ray absorption. It is less hygroscopic than others fluxes, it has a low viscosity in the molten form and it doesn't crystallise very easily.

## 2.4. SAMPLE/FLUX MASS RATIO

The ratio is optimised for light elements (P, Si, Al) and low concentration analysis. The maximum quantity of sample is limited by the flux capacity to dissolve the sample (saturation point of flux). In addition, higher concentrations of sample reduce the probability of crystallization.

## 2.5. ADDITIVES TO FLUXES

For ferro-alloys some materials must be added to the flux for different purposes. Oxidants are added to oxidise the ferro-alloy particles in order to dissolve them in the flux. The oxidants used are  $\text{NaNO}_3$ ,  $\text{KNO}_3$ , and  $\text{Sr}(\text{NO}_3)_2$ . Heavy absorbers are added to the flux to increase the x-ray absorption and to decrease the matrix effect. As heavy absorber is used  $\text{Sr}(\text{NO}_3)_2$ . Also the Sr is used like internal standard for ferro-manganese analysis. The releasing agents reduce the melt adherence on platinum crucible and dish. The NaI was used like a releasing agent. The fluidization agents decrease the flux acidity and increase the melting fluidity for a better casting. The  $\text{Na}_2\text{CO}_3$  is used as fluidization agent. The additives' quantities are experimentally optimised.

## 2.6. OXIDATION, FUSION, CASTING TEMPERATURES AND TIMES

These parameters are optimised to assure a full oxidation of ferro-alloy material, a good homogeneity of the melt and a complete covering of the casting dish.

## 2.7. BEAD THICKNESS

The bead has low Z components in high concentration and it acts as a light absorber. The primary X-ray radiation has a quite long path (~1mm) for these matrixes. Experimentally a bead thickness of about 3mm is proved to be sufficient to absorb completely the primary X-ray beam.

All chemical substances and the ferro-alloy powders are dried in drying house at  $105^\circ\text{C}$  (the drying time being established by constant weight procedure).

Looses of ignition (LOI) are estimated for additives and ferro-alloys. The sources of LOI in ferro-alloys are C and S because, during the melting process, C and S form volatile compounds.

## 2.8. SAMPLE PREPARATION METHOD PRECISION

The primary source of errors in ferro-alloys WDXRF analysis arises from the sample preparation process. The uncertainty in terms of precision has to be established in order to estimate the overall uncertainty.

The experimental procedure to evaluate sample preparation precision is presented in the case of ferro-manganese.

The procedure consist in the following operations:

- a ferro-manganese sample was drawn from the existent raw material store. The sample was milled up to a grain size <200 $\mu$ m and then homogenised and dried.
- eight beads from this sample were prepared, using the Philips PERL'X3 furnace, in the same conditions (preparation recipe, oxidation-fusion-casting programme parameters and operator).
- these beads were measured, using Philips PW1606 spectrometer, in the following way: each bead measured once; one of the bead measured eight times.
- the precision's for each measurement set,  $\varepsilon_1$  and  $\varepsilon_2$ , are evaluate in terms of relative standard deviations.  $\varepsilon_2$  means the precision of the measurement process and  $\varepsilon_1$  means the overall process precision (sample preparation and measuring). The sample preparation process error is:

$$\varepsilon = \sqrt{\varepsilon_1^2 - \varepsilon_2^2} \quad (1)$$

## 4. RESULTS

The experimental results regarding the sample preparation method precision are presented in Table 1.

The Table 1 shows that the sample preparation and measuring process error is smaller then the precision of wet chemical analysis in conditions of repeatability (allowed deviation in the same laboratory). The conclusion is that the solid solution technique applied to ferro-alloys is enough stable to permit measurements with an accuracy less then wet chemical analysis.

**Table 1. The precision of the sample preparation method.**

Element name	Statistics on first set of measurements (each bead measured once)			Wet chemical precision (abs. dev., %)	Statistics on second set of measurements (one bead measured eight times)			$\varepsilon$
	Mean value (%)	Rel. Std. deviation $\varepsilon_1$ (%)	Abs. std. deviation (%)		Mean value (%)	Rel. std. deviation $\varepsilon_2$ (%)	Abs. std. deviation (%)	
Mn	77.04	0.245	0.189	0.40	76.97	0.064	0.050	0.236
Si	2.40	0.417	0.010	0.07	2.405	0.324	0.008	0.262
P	0.546	0.688	0.004	0.015	0.550	0.440	0.002	0.529
Fe	13.52	0.267	0.036	-	13.51	0.101	0.014	0.247
Cr	0.048	1.352	0.001	-	0.047	1.069	0.0007	0.828

The calibration curves are established using certified reference materials (CRM's) produced by Brammer Standards-USA and BAS-England.

An analytical program is established for each type of ferro-alloy. The samples were measured sixty seconds with a Rhodium X-ray tube using 45kV and 55mA. These parameters were selected to excite all the elements in samples and to obtain a good counting statistic at low concentration levels.

The mathematical model used in regression analysis is [3]:

$$C = D + E * R(1 + \sum_i \alpha_i * C_i) \quad (2)$$

For ferro-manganese and ferro-chromium inter-element coefficients a are theoretical calculated using ALPHAS program [1].

The parameter's witch defines the regression quality are the root mean square standard deviations:

$$RMS = \sqrt{\frac{1}{n-j} \sum_{i=1}^n (C_{chem_i} - C_{calc_i})^2} \quad (3)$$

and K factor:

$$K = \sqrt{\frac{1}{n-j} \sum_{i=1}^n \frac{(C_{chem_i} - C_{calc_i})^2}{C_{chem_i} + C_0}} \quad (4)$$

where:

- $C_{chem}$  is the certificated concentration;
  - $C_{calc}$  is the calculated concentration;
  - n is the number of experimental points (number of reference beads);
  - j is the number of calibration curve coefficients calculated by regression
- $C_0=0.1\%$

The K factor allows to calculate the analytical error at a given concentration level,  $\Delta C$ :

$$\Delta C = K * \sqrt{C_{calc} + C_0} \quad (5)$$

Fig. 2 shows the calibration curve of silicon in ferro-silicon. It can be observed the linearity of this curve on a very wide concentration range. This is a feature arising from the sample dilution in beads (dilution coefficient 1:18).

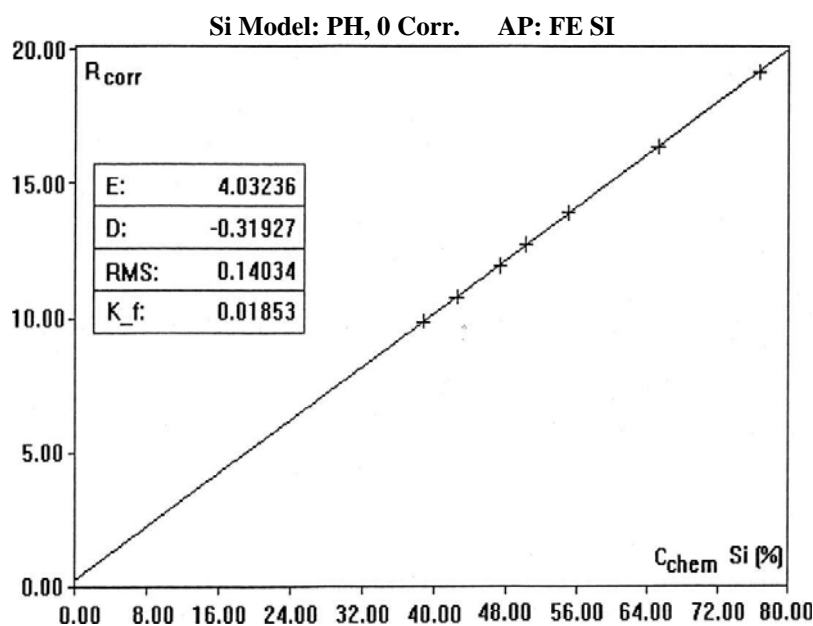


Fig. 2. The calibration curve for silicon in ferro-silicon.

Tables 2 - 5 summarise the regression results for ferro-manganese, ferro-chromium, ferro-silicon and ferro-molybdenum respectively.

**Table 2. The regression results for ferro-manganese.**

Element name	CRM's name	Concentration's (%)		RMS (%)	K factor	Analytical errors $\Delta C$ (%)	Wet chemical uncertainties (%)
		Certified	Calculated				
SI	Femnl	0.40	0.415	0.00872	0.0096	0.007	0.04
	BS120d *	0.57	0.565			0.008	0.04
	BS120c *	0.64	0.630			0.008	0.04
	BS120b*	0.72	0.713			0.009	0.04
	BS120	0.80	0.802			0.009	0.04
	BS208/2d *	0.98	0.970			0.010	0.04
	BS208/2b *	1.25	1.248			0.011	0.06
	BS208/2	1.41	1.406			0.012	0.06
	Femn2	1.88	1.894			0.014	0.06
	Femn2a *	2.05	2.051			0.014	0.08
MN	BS208/2d *	54.93	55.23	0.3215	0.0394	0.29	0.80
	BS120d *	57.44	57.43			0.30	0.80
	Femn2c *	62.42	61.89			0.31	0.80
	BS 120c*	63.43	63.57			0.31	0.80
	BS208/2b *	70.75	70.73			0.33	0.80
	BS 120b *	70.92	71.05			0.33	0.80
	Femn2	76.05	76.09			0.34	0.80
	BS208/2	77.	77.21			0.34	0.80
	BS120	78.3	78.35			0.35	0.80
	Femnl	79.08	78.86			0.35	0.80
	Femn2a *	84.21	83.92 »			0.36	0.80
BS 120a *	85.59	85.92	0.36	0.80			

Note:\* means that these standards were obtained using standard addition technique.

**Table 3. The regression results for ferro-chromium.**

Element name	CRM's name	Concentration's (%)		RMS (%)	K factor	Analytical errors $\Delta C$ (%)	Wet chemical uncertainties (%)
		Certified	Calculated				
CR	BS130/1a *	41.55	41.56	0.3251	0.0413	0.27	0.35
	BS130/2a *	42.36	42.58			0.27	0.35
	BS130/3	47.85	47.73			0.29	0.35
	BS130/1	51.60	51.45			0.30	0.35
	Fecr/1a *	52.33	52.45			0.30	0.35
	BS130/2	52.60	52.47			0.30	0.35
	BS130/2b *	62.70	62.37			0.33	0.45
	BS130/1b *	62.77	62.88			0.33	0.45
	Fecr/1	63.57	63.17			0.33	0.45
	BS204/4	73.88	74.10			0.35	0.50
	BS204/4b *	85.71	86.06			0.38	0.50

Note:\* means that these standards were obtained using standard addition technique.

**Table 4. Regression results for ferro-silicon.**

Element name	CRM's name	Concentration's (%)		RMS (%)	K factor	Analytical errors $\Delta C$ (%)	Wet chemical uncertainties (%)
		Certified	Calculated				
SI	BS140/1a *	36.16	36.17	0.1403	0.0185	0.11	0.50
	BS140/4a *	39.84	39.83			0.12	0.50
	BS140/1	45.20	45.24			0.12	0.50
	37E	46.5	46.44			0.13	0.50
	BS140/4	49.80	49.93			0.13	0.50
	BCS305-1a*	60.00	59.73			0.14	0.50
	BCS305-1	75.00	75.13			0.16	0.50

Note:\* means that these standards were obtained using standard addition technique.

**Table 5. Regression results for ferro-molybdenum.**

Element name	CRM's name	Concentration's (%)		RMS (%)	K factor	Analytical errors $\Delta C$ (%)	Wet chemical uncertainties (%)
		Certified	Calculated				
MO	BCS231/4b*	42.00	41.88	0.3383	0.0424	0.28	0.40
	BCS231/4a*	56.00	56.04			0.32	0.40
	508-1	59.65	59.91			0.33	0.40
	BCS231/4c*	64.40	64.73			0.34	0.50
	Femo-68	68.00	67.62			0.35	0.50
	BCS231/4	70.00	69.74			0.35	0.50

Note:\* means that these standards were obtained using standard addition technique.

## 5. CONCLUSION

Comparing the analytical errors with the uncertainties of wet chemical methods (allowed deviations between two laboratories) shown in Tables 2-5 in can be concluded that the WDXRF analysis of ferro-alloys using solid solution technique leads to higher accuracy's. Also, the method is faster and can be easily automated.

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