Determination of Major and Minor Elements in Ferroalloys by Inductively Coupled Plasma Atomic Emission Spectrometry

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Inductively coupled plasma atomic emission spectrometry (ICP-AES) was applied to the determination of major and minor elements in Fe - Mn, Fe - Cr and Fe - Si ferroalloys. The quantitative dissolution of samples and the selection of suitable analytical lines and operating conditions are described. The methods developed were verified using BAM and BAS samples, and were also applied to real metallurgical samples; relative standard deviations of less than 2% were obtained for most elements.

Keywords: *Inductively coupled plasma atomic emission spectrometry; ferroalloys; minor and major element determination; metallurgical samples*

Inductively coupled plasma atomic emission spectrometry (ICP-AES) has some characteristics, such as a wide range of linear response to analyte concentration, high sensitivity and few chemical interferences,[1–6] that make it suitable for the determination of elements in various matrices, *e.g.*, steel, alloys and blood.

The chemical analysis of ferroalloys is important not only to producers but also to the large number of consumers of these materials in the metallurgical industries.[7] Hughes[8] reported the interest in the ICP technique shown by the metallurgical industry.

In this paper we describe the application of ICP-AES to the determination of major and minor elements in various ferroalloys (ferromanganese, ferrochromium and ferrosilicon). The complexity of the samples requires the use of a different dissolution system for each type of ferroalloy. A suitable acid attack was carried out first, followed by an acid or alkaline fusion, any residue recovered is dissolved and added to the original solution. Synthetic solutions were used for calibration.

The reliability of the methods was checked by the analysis of different standard reference materials and of various ferroalloys supplied by the metallurgical industry.

Experimental

Instrumentation

An ARL 3520 ICP sequential emission spectrometer was used. The operating conditions are listed in Table 1. Instrument control and data processing were provided by a Digital DPC-11 computer with associated Digital VT-video and a Digital LA-50 printer.

Preparation of Test Solutions

Representative dried samples were used. The dissolution procedures employed for each type of ferroalloy were as follows.

Ferrochromium

Transfer 1 g of sample into a 400-ml beaker, add 15 ml of hydrochloric acid (ρ 1.18 g ml^{-1}) and 10 ml of nitric acid (ρ 1.42 g ml^{-1}), cover the beaker and heat it gently until reaction has apparently ceased. Add 15 ml of perchloric acid (ρ 1.54 g ml^{-1}) and evaporate the solution to fumes. Allow to cool, add 5 ml of nitric acid (ρ 1.42 g ml^{-1}) and heat again for 10 min. Allow the solution to cool, dilute with approximately 50 ml of water, filter, transfer the filtrate into a zirconium crucible and incinerate it. Fuse the residue with 0.5 g of sodium peroxide. Dissolve the cooled melt, add to the main acid solution and dilute to 1 l with de-ionised water.

Ferromanganese

Transfer 1 g of sample into a 400-ml beaker, add 80 ml of nitric acid (1 + 3) and heat gently until dissolved. Allow the solution to cool, dilute it with aproximately 50 ml of water, filter and proceed as in the ferrochromium procedure. Acidify with 30 ml of hydrochloric acid (ρ 1.18 g ml^{-1}) and dilute the final solution to 1 l with de-ionised water.

Ferrosilicon

Silicon. Transfer 0.25 g of sample into a zirconium crucible and fuse with 8 g of sodium peroxide and 2 g of sodium carbonate at 700 °C. Extract the cooled melt with approximately 50 ml of water and 10 ml of sulphuric acid (ρ 1.84 g ml^{-1}) and dilute to 2 l with de-ionised water.

Minor elements. Transfer 0.5 g of sample into a 250-ml Teflon beaker, add 30 ml of nitric acid (ρ 1.42 g ml^{-1}) and heat

Table 1. Operating conditions for ICP-AES

ARL 3520 sequential spectrometer	Grating: 1080 grooves mm^{-1}
	Spectral range: 170–820 nm in three orders
	Dispersion: 0.926 nm mm^{-1} at 600 nm (1st order)
	0.473 nm mm^{-1} at 300 nm (2nd order)
	0.309 nm mm^{-1} at 200 nm (3rd order)
	Resolution: 0.023 (1st order)
	0.016 (2nd order)
	0.012 (3rd order)
PlasmaTherm r.f. generator	Frequency: 27.12 MHz
	Power: 1.2 kW
Torch	Three concentric quartz tubes, monoblock
Nebuliser	Meinhard concentric
Gas flow-rates	Outer: 12 l min^{-1}
	Carrier: 1 l min^{-1}
	Sheath: 0.8 l min^{-1}

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gently. Add carefully, in small portions, hydrofluoric acid (ρ 1.13 g ml^{-1}) until the sample is dissolved. Add 15 ml of perchloric acid (ρ 1.67 g ml^{-1}) and evaporate the solution to fumes. Allow the solution to cool, add 5 ml of nitric acid (ρ 1.42 g ml^{-1}) and heat again for 10 min. Allow to cool, dilute with 30 ml of hydrochloric acid (1 + 1) and make up to 500 ml with de-ionised water.

Preparation of Standard Solutions

Stock standard solutions of 1000 mg l^{-1} of each element were prepared by dissolution of pure metals or analytical-reagent grade salts.

Working standard solutions were prepared by mixing the stock standard solutions of major and minor elements in ratios similar to those of the corresponding test solutions.

Choice of Analytical Lines

The choice of the lines used for the measurements was determined from investigations carried out previously taking into account sensitivity and spectral interferences.[9–11] Tables 2–4 show the selected lines and the measurements made on water and major and minor element solutions at the optimum line for each element in the different ferroalloys studied. The

Table 2. Signals obtained at the optimum lines for each element in ferromanganese

Element/line	λ/nm	Water	Minor elements	1000 μg ml^{-1} Mn	500 μg ml^{-1} Fe	Element*
Cr I	205.552	1.9	2.1	2.0	2.2	5.4 (0.5)
Fe VI	238.200	1.9	1.9	2.0	—	735.2 (100)
Mn II	293.306	2.3	1.9	—	2.0	1520 (500)
P V	213.618	1.9	2.1	2.6	2.3	2.8 (0.5)
Si II	288.158	2.1	2.1	2.4	2.2	5.8 (2.0)

* Concentration of the analysed element (μg ml^{-1}) in parentheses.

Table 3. Signals obtained at the optimum lines for each element in ferrochromium

Element/line	λ/nm	Water	Minor elements	1000 μg ml^{-1} Cr	500 μg ml^{-1} Fe	Element*
Al III	396.152	2.4	2.4	2.4	2.4	2.9 (0.5)
Cr III	267.716	2.4	2.3	—	2.3	3074.9 (500)
Fe I	259.940	2.3	2.6	3.6	—	800.3 (100)
Mn I	257.610	2.1	2.1	3.9	3.0	24.6 (0.5)
Ni III	231.604	2.0	1.9	2.1	2.2	3.4 (0.5)
P V	213.618	1.9	1.8	2.1	1.9	2.1 (0.5)
Si I	251.611	2.2	2.0	2.2	3.0	8.9 (2.0)
Ti III	337.280	2.3	2.1	2.2	2.1	7.0 (0.5)
V II	292.402	2.3	2.4	2.8	2.5	5.5 (0.5)

* Concentration of the analysed element (μg ml^{-1}) in parentheses.

Table 4. Signals obtained at the optimum lines for each element in ferrosilicon

Element/line	λ/nm	Water	Minor elements	1000 μg ml^{-1} Si	1000 μg ml^{-} Fe	Element*
Al III	396.152	2.4	2.2	2.2	2.1	2.7 (0.5)
Ca II	393.366	4.4	8.1	3.7	7.2	79.2 (0.5)
Cu III	327.396	2.0	1.8	1.7	1.9	4.9 (0.5)
Fe I	259.940	2.3	2.3	2.4	—	802.3 (100)
Mg IV	280.269	2.0	3.2	2.6	2.7	124.1 (0.5)
Mn II	293.306	2.3	2.0	2.0	2.0	3.5 (0.5)
P II	177.500	2.1	1.8	1.8	2.2	2.1 (0.5)
Si I	251.611	2.2	2.0	—	2.9	340.4 (100)
Ti V	334.941	2.3	2.1	2.1	2.2	12.3 (0.5)

* Concentration of the analysed element (μg ml^{-1}) in parentheses.

Table 5. Concentrations of elements (%) obtained for BAM reference samples

Element	Fe - Mn BAM 532-1		Fe - Cr BAM 530-1		Fe - Si BAM 529-1	
	Certified	ICP*	Certified	ICP*	Certified	ICP*
Mn	86.48	86.40 ± 0.18	0.16	0.16 ± 2.23	0.04	0.05 ± 1.08
Si	0.83	0.82 ± 0.38	0.49	0.52 ± 2.45	91.11	91.44 ± 1.21
Fe	11.86	12.07 ± 0.12	26.83†	27.45 ± 1.29	6.15	6.42 ± 0.29
P	0.08	0.07 ± 4.75	—	—	0.013	0.009 ± 21.55
Cr	0.27	0.28 ± 0.50	64.91	64.90 ± 0.10	—	—
Al	—	—	0.56	0.61 ± 1.68	0.86	0.91 ± 0.88
Ti	—	—	0.05	0.05 ± 0.68	0.09	0.10 ± 0.36
V	—	—	0.23	0.26 ± 1.16	—	—
Ni	—	—	0.19	0.19 ± 1.76	—	—
Ca	—	—	—	—	0.46	0.51 ± 0.68
Cu	—	—	—	—	0.01	0.01 ± 4.08
Mg	—	—	—	—	0.04	0.04 ± 0.26

* Mean values ± relative standard deviations.
† Value calculated by difference, not included in the standard certificate.

Table 6. Concentrations of elements (%) obtained for BAS reference samples

Element	Fe - Mn BAS 583-1		Fe - Cr BAS 204/4		Fe - Si BAS 305-1	
	Certified	ICP*	Certified	ICP*	Certified	ICP*
Mn	86.42	86.39 ± 0.11	—	0.15 ± 0.74	—	0.15 ± 0.68
Si	0.40	0.41 ± 0.31	0.22	0.21 ± 0.61	75.00	74.93 ± 0.81
Fe	12.30†	12.54 ± 0.28	22.07†	22.13 ± 0.31	23.26†	23.20 ± 0.21
P	0.15	0.12 ± 0.73	0.005	—	0.03	0.03 ± 11.60
Cr	—	0.04 ± 0.98	71.90	71.81 ± 0.46	—	—
Al	—	—	—	0.03 ± 3.80	1.38	1.38 ± 0.31
Ti	—	—	—	0.002 ± 5.63	—	0.10 ± 0.33
V	—	—	0.14	0.15 ± 0.44	—	—
Ni	—	—	—	0.25 ± 0.92	—	—
Ca	—	—	—	—	0.33	0.35 ± 0.31
Cu	—	—	—	—	—	0.08 ± 0.42

* Mean values ± relative standard deviations.
† Values calculated by difference, not included in the standard certificate.

Table 7. Concentrations of elements (%) obtained for ferroalloys supplied by the metallurgical firm Olarra

Element	Ferromanganese		Ferrochromium		Ferrosilicon	
	Certified*	ICP†	Certified*	ICP†	Certified*	ICP†
Mn	75.80	75.56 ± 0.18	—	0.14 ± 0.61	—	0.03 ± 0.90
Si	—	0.34 ± 0.49	—	0.30 ± 0.76	75.05	75.54 ± 0.32
Fe	—	16.59 ± 0.24	—	29.97 ± 0.56	—	22.87 ± 0.34
P	—	0.17 ± 1.17	—	0.01 ± 21.18	—	—
Cr	—	0.19 ± 0.49	71.45	68.31 ± 0.67	—	—
Al	—	—	—	—	—	1.25 ± 0.68
Ti	—	—	—	—	—	0.12 ± 0.52
V	—	—	—	0.07 ± 0.71	—	—
Ni	—	—	—	0.28 ± 0.88	—	—
Ca	—	—	—	—	—	0.23 ± 0.30
Mg	—	—	—	—	—	0.02 ± 0.41

* Values of major elements certified by the supplier.
† Mean values ± relative standard deviations.

concentration of each element used for the study of the optimisation of the analytical lines was close to that present in the relevant ferroalloy reference samples.

It is worth mentioning the difficulty in obtaining a suitable line for phosphorus, which is free from interferences; 213.618 nm for ferromanganese and ferrochromium and 177.500 nm for ferrosilicon were chosen as the most suitable lines for the determination of phosphorus in these ferroalloys.

For the determination of reproducibility in terms of relative standard deviation (RSD), four samples of the different ferroalloys were prepared and six measurements of each element were made on these samples.

Results

Several Bundesanstalt für Materialprüfung (BAM) reference samples were analysed using the procedures described above for the various ferroalloys. The results are given in Table 5. Good agreement was obtained betwen the ICP results and the certified values (relative standard deviations lower than 1% for most elements).

The methods developed were also applied to other reference samples [Bureau of Analysed Samples (BAS)] (Table 6) and five real metallurgical samples of the three different ferroalloys studied (Table 7). Good concordance between the certified values and the results obtained by the ICP technique was obtained.

We conclude, therefore, that ICP-AES is suitable for the determination of minor and major elements in ferroalloys.

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