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ICP-OES Analysis of FeCr Alloys Prepared by Sodium Peroxide Fusion

Introduction

Ferroalloys, alloys of iron with sufficient amounts of one or more other elements present (V, Mo, Cr, etc.), are important as a source of various metallic elements in the production of all types of steels. They usually have low melting points and can be incorporated readily into molten steel where they provide a certain chemical composition with specified properties.¹

The ferrochrome alloy is produced by electric arc melting of the mineral chromite (FeCr_2O_4). It is largely used for the production of stainless steels. Increasing the amount of chromium content in the steel allows for increased corrosion and oxidation resistance. Other alloying elements, such as nickel (Ni) or molybdenum (Mo), aid in making the steel more passive and increasing its stainless properties.²

The presence of unwanted impurities in the metal and slag may alter reaction temperatures and cause undesirable reactions of their own.¹ The chemical analysis of the chromite ore and its final products are mandatory to assess the quality of the chromite ore and to optimize the grade of stainless steel production. Analysis of waste products is also needed to optimize recovery of chromium and other additives.²

Chromite does not dissolve well in aqua regia or nitric acid, the typical acids used for digestion of samples for atomic spectroscopy.¹ The traditional method for the dissolution of chromite and ferrochrome is time consuming and includes the use of hydrofluoric (HF) and perchloric (HClO₄) acids. Sodium peroxide fusions offer an alternative to working with these high risk acids. Fusions are also less time consuming, providing a safer and more efficient method to obtain full dissolution of ferrochrome samples.³

In this work, we describe the performance of the Optima™ 8300 inductively coupled plasma-optical emission spectrometer (ICP-OES) in analyzing ferrochrome samples prepared by sodium peroxide fusion. The revolutionary radio frequency (RF) generator in the Optima 8300 spectrometer features flat induction plates that replace the traditional helical load coil. The Flat Plate™ plasma induction plate technology delivers a low-flow operating system that does not require coil cooling and is capable of operating at a plasma argon flow as low as 8 L/min.

Several key parameters were evaluated for this particular application: *accuracy* and *precision* by measuring the recovery and the relative standard deviation of three standard reference materials (SRMs), *stability* by plotting the recovery of continuing calibration verification (CCV) samples versus time for more than 12 hours, and *method detection limits* (MDLs) calculated as three times the standard deviation of the measured concentrations of 10 fused matrix blank replicates.

Experimental Conditions

Instrumentation

All samples were analyzed for elemental content using the PerkinElmer® Optima 8300 ICP-OES (Figure 1) with a single-slot one-piece torch (Part No. N0780130). A SeaSpray™ nebulizer (Part No. N0775345) and baffled cyclonic spray chamber (Part No. N0776053) were used for their known ability to handle samples with high levels of dissolved solids. Instrumental parameters used for the analysis are listed in Table 1. The wavelengths and viewing mode are listed in Table 2 (Page 3).

By combining a segmented-array charge coupled device (SCD) detector and an Echelle optical system, the Optima 8300 ICP-OES can measure all the wavelengths simultaneously. Its wavelength flexibility allows the end users to easily add new elements or wavelengths as their program changes.

The Flat Plate technology generates a unique transversely symmetrical plasma that exhibits an extremely flat bottom which caps off the sample and prevents it from escaping around the outside (Figure 2). The symmetry and stability of the Flat Plate plasma, in conjunction with the new torch geometry, allows for a high level of stability and precision.



Figure 1. Optima 8300 spectrometer – the most economical ICP-OES, capable of running at a plasma flow rate as low as 8 L/min.

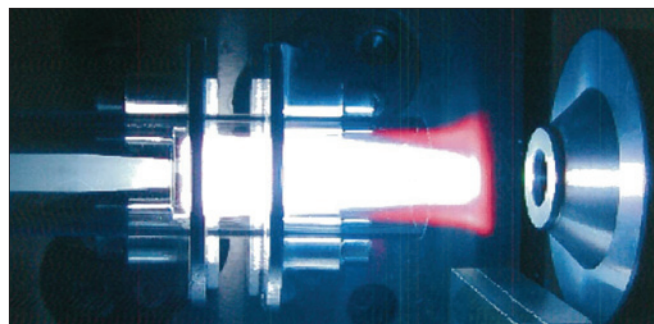


Figure 2. Low-flow operation with Flat Plate plasma induction plate technology.

Another benefit of using the Optima 8300 ICP-OES for fusion samples includes a 40 MHz free-running solid state RF generator. It is capable of handling the high power required to generate a robust plasma which is essential for precise analysis of complex matrices such as fusion samples.

Table 1. Instrumental operating conditions.

Parameter	Value
Instrument	Optima 8300 ICP-OES
Nebulizer	SeaSpray
Spray Chamber	Baffled cyclonic
Torch	Single slot quartz torch
Injector	2.0 mm alumina
Power (W)	1500
Plasma Gas (L/min)	10
Aux Gas (L/min)	0.3
Neb Gas (L/min)	0.65
Sample Uptake Rate (mL/min)	1.5
Sample Tubing	Samples and standards (Black/Black) Internal standard (Green/Orange)
Internal Standard	5 ppm yttrium + 10 ppm cesium (as an ionization buffer)

Table 2. Wavelength and viewing mode for the elemental analysis of dissolved ferrochrome samples.

Analyte	Wavelength	Viewing Mode
Al	394.401	Axial
Ca	317.933	Radial
Co	228.616	Axial
Cr	206.158	Axial
Cu	327.393	Axial
Fe	239.562	Axial
K	766.490	Radial
Mg	279.077	Radial
Mn	257.610	Axial
Mo	202.031	Axial
Ni	231.604	Axial
P	178.221	Axial
S	181.975	Axial
Si	251.611	Axial
Ti	334.940	Axial
V	290.880	Axial
Zn	206.200	Axial

Table 3. FeCr alloy (SRM 64c) recovery – all values are in mg/kg; dashed lines indicate no certified value was provided by the manufacture.

Analyte	Certified	Measured	Recovery (%)
Al	---	658	---
Ca	---	295	---
Co	510	520	102
Cr	680000	655000	96.3
Cu	50	< MDL	---
Fe	249800	260000	104
K	---	4.20	---
Mg	---	23120	---
Mn	1600	1650	103
Mo	---	165	---
Ni	4300	4050	94.2
P	200	191	95.6
S	670	731	109
Si	12200	11450	93.9
Ti	200	205	102
V	1500	1587	106
Zn	---	< MDL	---

Sample Preparation

All samples were prepared by sodium peroxide fusion. In a zirconium crucible, precisely 0.2 g of finely ground sample was fused with 3 g of sodium peroxide (Na₂O₂) and 0.5 g of sodium carbonate (Na₂CO₃). The fused mixture was poured into a beaker containing 250 mL of a 20% acid mixture of 1:1 hydrochloric (HCl) and nitric (HNO₃) acids.

PerkinElmer NIST® Traceable Quality Control Standards for ICP were used as the stock standards for preparing working standards. A four-point calibration curve was used for each measured element.

Results

Accuracy and Precision

The method accuracy was monitored by measuring the recovery of two different SRMs: a high-carbon ferrochromium (FeCr) alloy (SRM 64c) (Table 3) and chromium ore South African Reference Material 8 (SARM 8) (Table 4). The method precision was monitored by measuring the variation of a FeCr slag SRM (SARM 77) analyzed 55 times over a period of 12 hours (Table 5 – Page 4). Both SRMs showed excellent recoveries for all analyzed elements (± 10%).

Table 4. Cr ore (SARM 8) recovery – all values are in mg/kg.

Analyte	Certified	Measured	Recovery (%)
Al	55900	53250	95.3
Ca	1858	1875	101
Co	---	265	---
Cr	335050	345000	103
Cu	---	103	---
Fe	141300	145600	103
K	---	182	---
Mg	88590	94110	106
Mn	1740	1820	105
Mo	---	105	---
Ni	---	1460	---
P	---	17.3	---
S	341	359	105
Si	20100	19510	97.1
Ti	1440	1390	96.5
V	780	821	105
Zn	---	< DL	---

Table 5. Analysis of FeCr slag (SARM 77) over 12 hours (n=55) – all values are in mg/kg.

Analyte	Certified	Average Measured	SD	RSD (%)	Recovery (%)
Al	145540	149800	1283	0.86	103
Ca	26015	24440	319	1.3	93.9
Co	---	79.4	1.9	2.4	---
Cr	85530	93370	442	0.47	109
Cu	---	125	8.6	6.9	---
Fe	53100	52210	2049	3.9	98.3
K	---	1060	14	1.3	---
Mg	138640	143800	1200	0.83	104
Mn	---	1474	24	1.6	---
Mo	---	73.1	6.0	8.2	---
Ni	---	303	16	5.1	---
P	---	< MDL	---	---	---
S	---	2736	95	3.5	---
Si	125410	128000	2008	1.6	102
Ti	---	3201	22	0.69	---
V	---	536	6.5	1.2	---
Zn	---	< MDL	---	---	---

Stability

The instrument stability was assessed by plotting the recovery of SARM 77 as a CCV versus time for more than 12 hours (Figure 3). There was little change in concentration (< 4%) for all elements measured. The excellent instrument stability allows laboratories to confidently run samples without the need for time consuming recalibration or optimization.

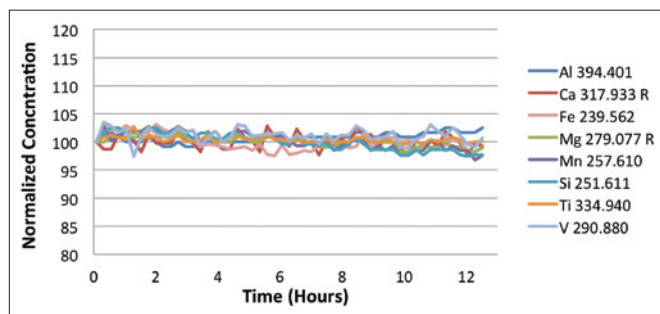


Figure 3. Instrument stability showing the % recovery of CCV (FeCr slag) over time. R = radial viewing.

Method Detection Limits

The method detection limits (MDLs) were calculated based on ten replicate measurements of the matrix blank. The MDL was calculated by multiplying the standard deviation of the ten replicate measurements by three (Table 6). The low-flow plasma was able to achieve MDLs less than or within a reasonable range of the traditional plasma flow rate. This would suggest that the lower Ar flow and hence lower cost of ownership can be achieved without sacrificing performance.

Table 6. Method detection limits for low argon plasma gas flow. All values are in the calibration units of mg/L.

Analyte	MDL
Al	0.0055
Ca (Radial)	0.045
Co	0.0015
Cr	0.0034
Cu	0.0019
Fe	0.018
K (Radial)	0.17
Mg (Radial)	0.037
Mn	0.0010
Mo	0.0019
Ni	0.0022
P	0.017
S	0.0036
Si	0.029
Ti	0.0008
V	0.0015
Zn	0.0012

Conclusions

The Optima 8300 spectrometer demonstrated its ability to run heavy matrix samples using 44% less argon than typical ICP-OES systems while maintaining superior performance. By incorporating Flat Plate™ technology, a robust matrix-tolerant plasma was generated and fusion samples were run successfully with only 10 L/min argon plasma gas flow. The Optima 8300 system maintained remarkable accuracy and precision throughout the 12-hour testing period, demonstrating excellent calibration stability. The method detection limits, when analyzing at a low plasma argon flow, were comparable to higher traditional argon flow ICP-OES systems.

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