Determination of Trace Elements in Steels and Alloys using the Thermo Scientific iCAP 7400 ICP-OES

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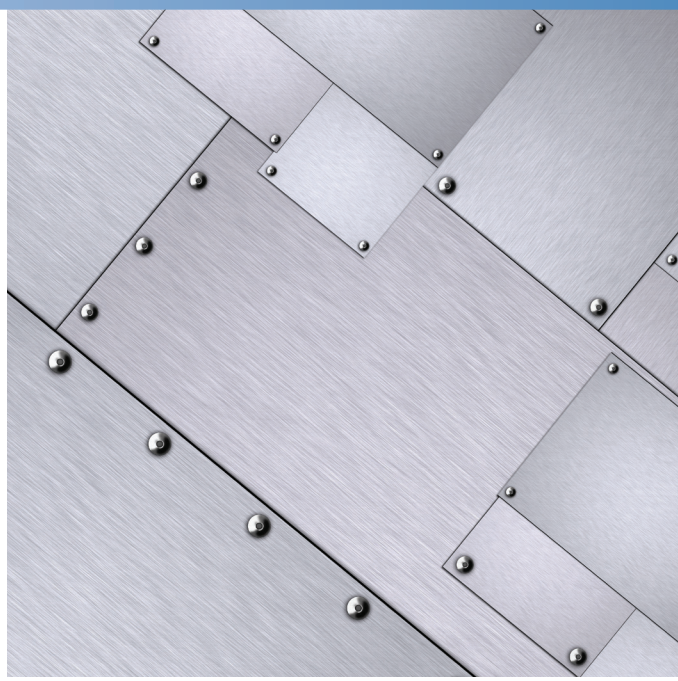
Key Words
Alloys, Microwave digestion, Steels

Goal

The rapid, precise and accurate determination of minor and trace elements in steels and iron alloys is analytically demanding, but of great commercial significance. This note demonstrates that analysis using the Thermo Scientific™ iCAP™ 7400 Series ICP-OES, following closed vessel microwave digestion, provides a cost effective solution.



Introduction

Steels and iron alloys are among the most flexible and widely used metals in industry. They can be formed, drawn, cast or turned to shape with a wide range of finishes such as polishing, plating or simply painting. This flexibility means that they have found a wide range of applications from constructional use to surgical implements. The properties of the steel can be enhanced or changed to suit the application depending on the constituent elements. For example, addition of nickel, chromium and manganese give corrosion resistance whilst the addition of carbon improves the hardness of a cutting edge. In order to maintain a consistent quality of steel, it is necessary to determine the trace elemental composition very accurately. Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) is an ideal technique for this analysis since the wide linear dynamic range allows for the determination of minor and trace elements simultaneously, without the need for additional dilution or pre-concentration techniques, resulting in time and cost efficient sample preparation and analysis.

Traditionally, samples are prepared by dissolution using mixed acids in an open beaker [1]. However, this approach is time consuming and can result in the partial loss of elements, particularly the more volatile elements. In order to aid the digestion of samples, closed vessel dissolution is increasingly used, as it allows for the use of higher temperatures and pressures. The use of microwave power, rather than a conventional oven or hotplate, further increases the efficiency of the digestion and shortens the required time.

Instrumentation

A Thermo Scientific iCAP 7400 ICP-OES radial with standard sample introduction kit was used for this analysis. The radial plasma instrument was seleceted for its robust matrix handling abilities, in order to minimize interferences. The high-resolution Echelle optics and Charge Injection Device (CID) detector are especially well suited to this type of application where trace amounts of an element must be detected in the presence of matrix elements.

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Sample and Standard Preparation

Two samples were obtained: 1) ECISS Euronorm – ZRM 467-3 (Rohesian) and 2) GBW 01323 (steel, China). Both were supplied by MBH Analytical Ltd., Holland House, Queens Road, Barnet EN5 4DJ, UK. The samples were digested in a Milestone ETHOS EZ microwave digester. Masses of 0.5 g of the samples (reference materials) were weighed into digestion vessels and 10 ml of concentrated hydrochloric acid (34 – 37 % Trace Metal Grade, Fisher Scientific, Loughborough, UK) and 2.0 ml of concentrated nitric acid (≥ 68 % Trace Metal Grade, Fisher Scientific, Loughborough, UK) were added. The vessels were closed and fitted into the rotor and digested at 180 °C for 20 minutes. When the microwave program was finished, the digestion vessels were left to cool and the contents made up to 100 g with ultra pure deionised water.

All of the samples produced clear solutions after digestion although a small quantity of white material, assumed to be silica, was observed in several of the solutions. This was filtered off before analysis.

Multi-element working standards were prepared from 1000 mg/L single element solutions (Fisher Scientific, Loughborough, UK) by dilution with mixed acid blank solution. Concentrations used for the analysis are given in Table 1. Reagent blanks were prepared by omitting the samples from two vessels.

Table 1. Concentration of standards in units of parts per million (ppm)

Element	Blank	Standard 1	Standard 2
Cr	0	2	20
Cu	0	10	20
Mn	0	20	100
Ni	0	1	10
P	0	1	10
Ti	0	0.5	5
V	0	2	20

Method Development

The subarray plots of a standard, sample and blank were examined to check for any background shifts or spectral overlaps. Element wavelengths were selected for analysis together with simultaneous background correction points. Sample introduction and plasma conditions were optimized to give maximal signal-to-background ratios (SBRs) and these optimized parameters are shown in Table 2.

Working standards were used to produce element calibration fits in the Thermo Scientific Qtegra™ Intelligent Scientific Data Solution, these calibration lines were checked to ensure an accurate fit and correlation coefficients (R2) of better than 0.998 were obtained for all elements examined. For analysis where the element concentrations exceeded the standard's value, a dilution (matrix matched for acid content) was used.

Table 2. Optimal sample introduction and plasma parameters.

Parameter	Setting
Plasma view	Radial
Pump tubing	Sample I.D. = 1.016 mm Drain I.D. = 1.524 mm
Pump speed	50 rpm
Spray-chamber	Standard cyclonic
Center Tube	1.5 mm
Nebulizer	Standard concentric
Nebulizer gas flow	0.6 L/min
Auxiliary gas flow	0.5 L/min
Coolant gas flow	12 L/min
RF Power	1150 W
Integration time	15 s UV / 10 s Vis

Results

Method detection limits (Table 3) were calculated by calibrating the instrument with the standards stipulated in the method and reanalyzing the sample blank. The standard deviation of ten replicates of the blank was multiplied by 3000 to give a 3σ detection limit in parts per billion in solution, which are shown in Table 3.

Table 3. Method Detection Limits in units of ppb.

Element / Wavelength (nm)	3σ Method Detection Limit (ppb)
Cr 205.552	1.3
Cu 327.396	4.3
Mn 279.482	11.1
Ni 231.604	1.7
P 178.284	6
Ti 334.941	0.5
V 268.796	4

The digested samples, detailed above, were then analyzed and the results compared to their certified values, the data from this analysis is shown in Table 4.

Table 4. Elemental composition of measured samples compared with the certified value in units of %

Element / Wavelength (nm)	ZRM 476-3 Measured %	ZRM 476-3 Expected %	GBW 01323 Measured %	GBW 01323 Expected %
Cr 205.552	0.0649	0.0648 ± 0.0012	0.368	0.389 ± 0.006
Cu 327.396	0.2349	0.2445 ± 0.0025	0.276	0.277 ± 0.009
Mn 279.482	1.009	0.987 ± 0.008	1.46	1.44 ± 0.02
Ni 231.604	0.0576	0.0549 ± 0.0014	0.161	0.166 ± 0.004
P 178.284	0.0901	0.0908 ± 0.0023	0.011	0.013 ± 0.001
Ti 334.941	0.0202	0.0222 ± 0.0005	0.268	0.285 ± 0.006
V 268.796	0.0101	0.0115 ± 0.0002	0.148	0.158 ± 0.005

Conclusion

The results presented in Table 4 show excellent agreement between the measured and specified elemental concentrations for both samples. ICP-OES is a rapid, precise and accurate means for determining minor and trace elements in steel and iron alloys. The use of closed-vessel microwave digestion ensures excellent elemental recoveries and the complete dissolution of the steel matrix, whilst minimising digestion time. Furthermore, the enhanced matrix handling abilities of the iCAP 7400 ICP-OES radial and CID based detector technology, were found to be especially well suited to this type of application.

References

1.'A Handbook of Decomposition Methods in Analytical Chemistry,' Bock, R., translated by Iain Marr, Blackie Group, Glasgow, 1979.

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