Application Note: 40758

Determination of Trace Elements in Steels and Alloys using the iCAP 6000 Series ICP

Key Words

- ICP
- iCAP Radial
- Alloys
- Microwave digestion
- Steels

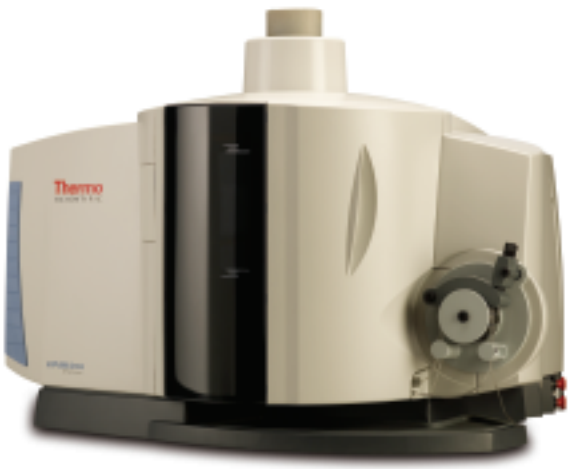
Introduction

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, Ni, Cr and Mn give corrosion resistance while C will improve the hardness of a cutting edge.

In order to maintain consistent quality of the steel it is necessary to determine the trace element composition very accurately. 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 a considerable timesaving.

Samples are traditionally prepared by dissolution using mixed acids in an open beaker[1]. However, this approach can be quite time consuming with resistant samples and result in partial loss of some elements, More recently dissolution in sealed vessels has been used allowing higher temperatures and pressures to be obtained, aiding in the dissolution of the sample. The use of microwave power, rather than a conventional oven, further increases the efficiency of the digestion, and shortens the time required.



Principle

A 0.5 g mass of sample was digested with a mixture of nitric and hydrochloric acids in a high pressure microwave digestion system. The emission signals from the resulting sample solutions were measured directly using ICP-OES. Simultaneous background correction was used to overcome any background shifts.

Instrumentation

A Thermo Scientific iCAP 6500 Radial ICP Emission spectrometer with the standard sample introduction kit was used for this work. An iCAP 6300 Radial ICP is equally suited to this application, and the parameters used apply to both systems. The iCAP 6000 series is the first generation of the new Thermo Scientific breed of ICP emission spectrometer with high-resolution Echelle optics and much improved Charge Injection Device (CID). Advancements in CID technology allow this detector to feature higher sensitivity and lower noise than any of its predecessors. The radial plasma instrument was chosen to reduce matrix interference.

PARAMETER	SETTING
Pump Tubing	Orange/white sample, white/white drain
Pump speed	50 rpm
Nebulizer	Standard concentric
Nebulizer Argon Flow	0.6 L/min
Spray Chamber	Standard cyclonic
Centre tube	1.5 mm
Source Orientation	Radial
RF Forward Power	1150 W
Purge Gas	Argon
Coolant gas flow	12 L/min
Auxiliary gas flow	0.5 L/min
Integration times	15s UV/10s Vis

Table 1. Instrument Parameters

Method

Reagents and equipment

Nitric acid sg 1.42, Analar grade
Hydrochloric acid 35 % v/v, Analar grade
1000 ppm single element stock standards for each element required
Microwave digestion system
Volumetric flasks

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Sample Preparation

The samples were digested in a Multiwave 3000 microwave digestion system by Anton Paar[2]. Masses of 0.5 g of the samples (reference materials) were weighed into digestion vessels and 10 ml of concentrated hydrochloric acid and 2.0 ml of nitric acid 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 rotor and digestion vessels were cooled. The vessels were then cautiously opened and the contents transferred to 100 ml volumetric flasks and diluted to volume with 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.

Standard Preparation

Multi-element working standards were prepared by dilution of the stock standards with mixed acid blank solution. Concentrations used for the analysis are given in Table 2. Reagent blanks were prepared by omitting the samples from two vessels.

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

Table 2. Standard concentrations in parts per million (ppm)

Method Development

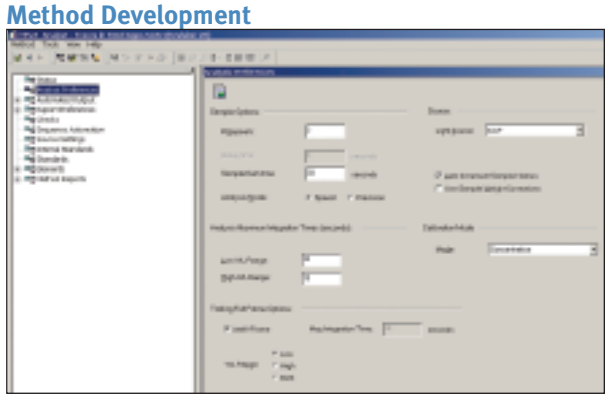

Figure 1. Analysis Preferences method parameters.

Analysis

The subarray plots of a standard, sample and blank were examined to check for any background shifts or spectral overlaps. Element lines were selected for analysis together with simultaneous background correction points.

Calibration was carried out using the working standards. Using iTEVA software, the calibration line was checked to ensure an accurate fit. A dilution (matrix matched for acid content) was used for analysis where the element concentrations exceed the standard's value.

Element concentrations were calculated by direct comparison to the calibration line (Figure 2).

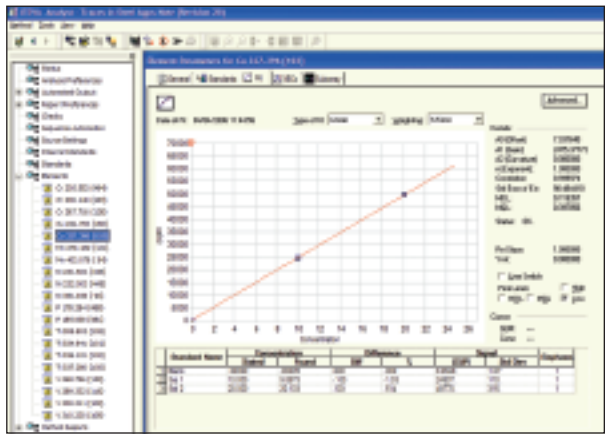

Figure 2. Calibration curve for Cu

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

Table 3. Final results

Results

Sample descriptions:
Sample 1: ECISS Euronorm - ZRM 476-3 (Roheisen)
Sample 2: GBW 01323 (steel, China)

Both were supplied by MBH Analytical Ltd., Holland House, Queens Road, Barnet EN5 4DJ, UK.
Method detection limits (Table 4) 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.

ELEMENT	3σ METHOD DETECTION LIMITS (ppb)
Cr 205.552 nm	1.3
Cu 327.396 nm	4.3
Mn 279.482 nm	11.1
Ni 231.604 nm	1.7
P 178.284 nm	6
Ti 334.941 nm	0.5
V 268.796 nm	4

Table 4. Method Detection Limits

Conclusions

A rapid, precise and accurate method for the determination of minor and trace elements in steel and iron alloys. High-pressure microwave digestion has been used to ensure a complete dissolution of the steel matrix with a minimum digestion time.

Determination using the high-resolution spectrometer of the iCAP 6500, combined with the stability of the mass flow control of all gases, ensures freedom from spectral interferences and gives accurate results in a complex matrix.

References

1) A Handbook of Decomposition Methods in Analytical Chemistry, Bock R, translated by Iain Marr, Blackie Group 1979, ISBN 0 7002 0269 2.

2) Multiwave 3000, Anton Paar GmbH, Anton-Paar-Str. 20, A-8054 Graz, Austria.

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