The Analysis of Steels and Alloys using Laser Ablation Coupled with the Thermo Scientific iCAP 6500 ICP-OES

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Benefits in Brief

- Unique, enhanced coupling between the Thermo Scientific iCAP 6500 ICP-OES, the Thermo Scientific iTEVA Software and the New Wave Research UP 266 Macro Laser enables unattended analysis of multiple solid samples
- Minimal sample preparation for direct trace element analysis of metals and other solid materials
- Laser ablation enables the pinpoint analysis of sections of material, small samples or large areas of sample using user defined patterns of ablation

Introduction

The analysis of steel and its alloys is a common application in many laboratories around the world. A variety of techniques may be used for elemental analysis of metals and these may include sample dissolution techniques and solid analysis techniques, for example, Spark Optical Emission Spectroscopy (Spark OE) and X-Ray Fluorescence (XRF). For sample dissolution techniques, the samples are dissolved in a combination of acids by either microwave digestion or using a hot plate and then analyzed by Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) or Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or a combination of one or more of these techniques.

The analysis of solid steel or metal alloys typically employs a combination of XRF and Spark OES techniques. In addition, techniques such as Laser/Spark ablation can also be employed in conjunction with ICP to produce metal particles for direct introduction into the instrument.

The technique of Laser Ablation (LA) combined with ICP-OES (LA-ICP-OES or LA-ICP) is becoming increasingly popular because it enables the analyst to analyze metals, refractory elements, insoluble alloys, glass and almost any solid material (including very small samples) without having to dissolve or destroy the sample. Using these combinations of instrumentation also enables the analyst to quickly switch from solid sampling to solution sampling allowing the analysis of both liquids and solids on the same instrument.

When using a Laser Ablation system, the surface of the material is ablated to produce fine particles which are then passed into the torch of the ICP instrument using an argon or helium carrier gas. These particulates are then processed in the plasma similarly to aerosols (as derived from the nebulization of liquid samples). Detection limits are typically in the order of µg/g in the solid when using this approach and the total time for analysis is greatly reduced because the dissolution process is removed from the process.

Instrumentation

The Thermo Scientific iCAP 6500 ICP-OES, with the dedicated radial plasma, is used here for the analysis of a set of certified metal standards with a New Wave UP 266 Macro laser. The iCAP 6500 ICP-OES is a compact, robust instrument which contains all the core technologies of the Thermo Scientific iCAP 6000 Series ICP-OES such as an efficient, robust solid state generator; high resolution echelle spectrometer with excellent detection capability and a CID86 detector with improved dynamic range, non-blooming design and optimum signal-to-noise measurements. Additionally, the iCAP 6500 ICP-OES also has the capability for enhanced accessory interfacing to external accessories including triggering and control. The Thermo Scientific iTEVA Software, combined with the capabilities of the UP 266 Macro Laser, enables the analyst to use the laser as an autosampler which means unattended analysis can be performed for as many samples as will fit into the laser’s ablation chamber.

The iCAP 6500 ICP-OES is connected to the New Wave UP266 Macro Laser Ablation system via a bespoke communications link (see Figure 1) and is also connected to the main instrument PC. The communication link allows the unique triggering and parameter control of the UP266 Laser Ablation system via the iTEVA Software in combination with the New Wave MEO Software. The iCAP 6500 ICP-OES also incorporates enhanced speed of data acquisition which enables the time for the ablation process to be reduced if required, saving valuable time, gas and sample.

Key Words

• Laser ablation
• Steel
• Trace elemental analysis
• ICP

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The ablation gas line may be connected directly into the base of the torch of the iCAP 6500 ICP-OES. In this configuration, the spray chamber and nebulizer of the standard sample introduction system is bypassed and the ablated sample material is passed directly into the plasma using an argon carrier gas. Helium carrier gas, used with much the same flow rate as argon, can also be used and can enhance the laser ablation and sample transport efficiency to the plasma to provide further improved sensitivity as required. Further details on the connections between iCAP 6000 Series ICP-OES, PC and laser units are provided in the User Guide provided with the Laser Ablation unit.

Sample and Standard Preparation
The certified reference standards are chosen from a series manufactured by the National Institute for Science and Technology (NIST) to show typical concentrations of impurities and minor elements in steel. The standards are solid low-alloy steel discs obtained from MBH Analytical Ltd (UK) and are specifically designed to be standards for solid sampling analysis of steels (see Table 1), whether by the two ablation techniques (laser and spark) or spark optical emission spectrometry analysis.

<table>
<thead>
<tr>
<th>Element</th>
<th>NIST 1761</th>
<th>NIST 1763</th>
<th>NIST 1765</th>
<th>NIST 1767</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.055</td>
<td>0.043</td>
<td>-</td>
<td>0.004</td>
</tr>
<tr>
<td>Co</td>
<td>-</td>
<td>0.095</td>
<td>0.0012</td>
<td>0.005</td>
</tr>
<tr>
<td>Cr</td>
<td>0.22</td>
<td>0.5</td>
<td>0.051</td>
<td>0.0015</td>
</tr>
<tr>
<td>Cu</td>
<td>0.3</td>
<td>0.043</td>
<td>0.0013</td>
<td>0.0014</td>
</tr>
<tr>
<td>Mn</td>
<td>0.678</td>
<td>1.58</td>
<td>0.144</td>
<td>0.022</td>
</tr>
<tr>
<td>Mo</td>
<td>0.103</td>
<td>0.5</td>
<td>0.005</td>
<td>0.02</td>
</tr>
<tr>
<td>Ni</td>
<td>1.99</td>
<td>0.51</td>
<td>0.154</td>
<td>0.002</td>
</tr>
<tr>
<td>Si</td>
<td>0.18</td>
<td>0.63</td>
<td>-</td>
<td>0.026</td>
</tr>
<tr>
<td>Ti</td>
<td>0.18</td>
<td>0.31</td>
<td>0.0055</td>
<td>0.006</td>
</tr>
<tr>
<td>V</td>
<td>0.053</td>
<td>0.3</td>
<td>0.004</td>
<td>0.033</td>
</tr>
</tbody>
</table>

Table 1: NIST Calibration Standards used for the Analysis – All Concentrations in %

Samples or standards are prepared (i.e. if the surface has been previously ablated or altered in some way) by skimming the surface using a lathe or by rubbing with abrasive material to smooth and clean the sample surface. The surface should ideally be mounted perpendicular to the laser beam within the ablation chamber to get the maximum benefit of the ablation energies as well as reproducibility.

Method Development
Method development with this hyphenated technique requires the analyst to optimize the laser parameters for the sample type being analyzed in addition to the plasma source for the ICP. In this case, the laser program utilized a pre-ablation step to ensure that any surface contamination was removed before the analytical ablation is performed. The laser parameters are user defined and are required to be optimized for both the sample type and the required sensitivity.

The laser parameters that are user defined were set as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-ablation rate</td>
<td>100µm/sec</td>
</tr>
<tr>
<td>Laser spot size (diameter)</td>
<td>750µm</td>
</tr>
<tr>
<td>Laser output</td>
<td>90%</td>
</tr>
<tr>
<td>Laser firing rate</td>
<td>10Hz</td>
</tr>
<tr>
<td>Laser step rate</td>
<td>30µm/sec</td>
</tr>
<tr>
<td>Carrier gas flow (Ar)</td>
<td>0.5L/min</td>
</tr>
</tbody>
</table>

Table 2: New Wave Macro UP266 Laser Parameters

A “raster” ablation pattern is used here as this is considered to be the most appropriate for bulk analysis applications since it can cover a large area of the material being analyzed. However, multiple pattern types may be used on more than one sample and the sample patterns will be ablated in the order that they are inserted into the work queue. Figure 2 shows an example of a combination of patterns in readiness for analysis. These patterns could also be used on multiple samples with the change of samples controlled by the unique triggering options between the iTeva Software (see Figure 3) and the New Wave MEO Software used to control the New Wave UP266 Macro Laser. These triggering options allow the analysis of multiple samples, each with its own gas flush, pre-ablation and ablation steps controlled by iTeva Software.
The iTEVA Software has an “Optimize Source” feature which can be used to optimize the plasma conditions to maximize the analyte signal intensities. A homogenous solid sample is ablated using a large pattern and the “Optimize Source” feature is then activated during the sample ablation to enable optimization using the analyte signal intensities as required. The plasma parameters established for the application are shown in Table 3 for reference:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump Tubing</td>
<td>NA</td>
</tr>
<tr>
<td>Pump Rate</td>
<td>NA</td>
</tr>
<tr>
<td>Nebulizer</td>
<td>NA</td>
</tr>
<tr>
<td>Nebulizer gas flow</td>
<td>NA</td>
</tr>
<tr>
<td>Spray Chamber</td>
<td>NA</td>
</tr>
<tr>
<td>Auxiliary gas flow</td>
<td>1.0 L/min</td>
</tr>
<tr>
<td>Coolant gas flow</td>
<td>12 L/min</td>
</tr>
<tr>
<td>Center tube</td>
<td>2 mm</td>
</tr>
<tr>
<td>RF Power</td>
<td>1150 W</td>
</tr>
<tr>
<td>Radial Viewing Height</td>
<td>12 mm</td>
</tr>
<tr>
<td>High/Low Integration time</td>
<td>20s UV/20s Vis</td>
</tr>
</tbody>
</table>

Table 3. Sample Introduction and Plasma Parameters
* NA= Not Applicable

After optimization, the Fullframe data acquisition mode was used to identify all elements in the samples and look for possible interferences. A Fullframe is a display of the full spectrum in a two dimensional array showing all the elements present in the sample. It is an excellent method development tool which can be stored indefinitely and can also be used for real time and retrospective semi-quantitative analysis as required.

After the selection of several wavelengths for each element, some weak iron lines were selected as internal standard lines. Using the iron as an internal standard in this way compensates for any fluctuation in the transport or ablation efficiencies. Most analyses showed % RSDs to be <5%. The iCAP 6500 ICP-OES was calibrated using the four NIST standards shown in Table 1. Two additional NIST steel standards (NIST 1762 and NIST 1764) were then analyzed as unknowns against these calibrations.

Results
All calibration curves used showed correlation coefficients better than 0.995. The analytical results of the LA-ICP analysis of the NIST standards are shown below in Table 3. The analyzed values are compared against the accepted values as determined by various methods in a variety of laboratories guided by NIST.

<table>
<thead>
<tr>
<th>Element</th>
<th>NIST 1762 % Analysed</th>
<th>NIST 1762 % Accepted</th>
<th>NIST 1764 % Analysed</th>
<th>NIST 1764 % Accepted</th>
<th>Method DL (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al 308.215 nm</td>
<td>0.057</td>
<td>0.069</td>
<td>0.008</td>
<td>0.009</td>
<td>0.003</td>
</tr>
<tr>
<td>Co 228.616 nm</td>
<td>0.063</td>
<td>0.062</td>
<td>0.008</td>
<td>0.009</td>
<td>0.0089</td>
</tr>
<tr>
<td>Cr 267.716 nm</td>
<td>0.83</td>
<td>0.92</td>
<td>1.55</td>
<td>1.48</td>
<td>0.0012</td>
</tr>
<tr>
<td>Cu 327.396 nm</td>
<td>0.11</td>
<td>0.12</td>
<td>0.48</td>
<td>0.51</td>
<td>0.0058</td>
</tr>
<tr>
<td>Mn 279.482 nm</td>
<td>1.89</td>
<td>2.00</td>
<td>1.15</td>
<td>1.21</td>
<td>0.008</td>
</tr>
<tr>
<td>Mo 202.030 nm</td>
<td>0.37</td>
<td>0.35</td>
<td>0.192</td>
<td>0.200</td>
<td>0.008</td>
</tr>
<tr>
<td>Ni 231.604 nm</td>
<td>1.19</td>
<td>1.15</td>
<td>0.223</td>
<td>0.202</td>
<td>0.004</td>
</tr>
<tr>
<td>Si 212.412 nm</td>
<td>0.29</td>
<td>0.35</td>
<td>0.056</td>
<td>0.057</td>
<td>0.002</td>
</tr>
<tr>
<td>Ti 337.280 nm</td>
<td>0.102</td>
<td>0.095</td>
<td>0.022</td>
<td>0.028</td>
<td>0.0007</td>
</tr>
<tr>
<td>V 292.402 nm</td>
<td>0.173</td>
<td>0.200</td>
<td>0.116</td>
<td>0.106</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Table 4: Comparison of analyzed and accepted values in NIST reference materials

The method detection limits shown were estimated using the built-in iTEVA Software facility that utilizes tailored signal to background calculations to estimate method detection limits. The facility is instantly available for all methods which have been calibrated and produces reliable method detection limits that approximate the more traditional 3σ approach.
The majority of the comparison results show good correlation between found and expected values. Almost all of the results fall well within a ±20% range and most values were within a ±10% range of the expected values (see Figure 5). The exception is one of the titanium results which is one of the lower concentration elements analyzed.

Figure 5: % Recovery of NIST standards

Conclusion
The analysis of steels by laser ablation is rapid, powerful and flexible when using the Thermo Scientific iCAP 6500 ICP-OES. The unique triggering options between the Thermo Scientific iTeva Software and the New Wave MEO Laser Software make the combination of the platforms especially powerful with regard to the unattended analysis of multiple samples. The user can analyze as many samples as the laser compartment will accommodate and the autosampler options in the iTeva Software application can be used to control the Laser Ablation accessory effectively.

References
1 New Wave Research Laser documentation: can be requested at: http://www.esi.com/Products/NewWaveResearch/LaserAblation/UPMACRO.aspx