Application Note: 40988

The Analysis of Trace Impurities in Titanium Alloys using the Thermo Scientific iCAP 6000 Series ICP

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Key Words

- Metallurgy
- Impurity analysis
- Trace analysis
- Titanium
- Alloy
- Radial iCAP

Key Benefits

- Superior performance: sensitive trace-level impurity analysis
- High resolution allows trace level analysis of spectrally complex samples
- Full wavelength coverage allows interference-free choice of alternate lines
- Simple calibration technique with recovery procedure for method verification

Introduction

The analysis of transition metals and their alloys have always been a challenge to optical spectrometry due to their spectrally rich matrices. Titanium, like iron and tungsten, is very line-rich and will cause excessive spectral interference problems in instruments with inadequate resolution optical systems. On lower resolution ICPs, peaks will more readily interfere and overlap with one another. In severe cases only one peak is seen, and thus a high-resolution optical system is essential. Coverage of a wide wavelength range is also an added advantage since some primary element lines will show spectral interference. Since it is generally best to avoid a spectral interference than to correct for it, the power of having comprehensive wavelength coverage is essential for optimum analysis of alloys.

The analysis of alloys in a production analytical environment has often favored spark optical emission (OE) over ICP-OES. The primary reason for this is speed of analysis since samples do not require dissolution for spark analyses, so the total turnaround time for the production of results is generally quicker.

Although spark OE is a less demanding technique, it is not suitable for all alloy analysis applications. This is due to the dependence of both spark emission and spark ablation on compatible calibration standards of comparable matrices to the sample. Ideally, calibration would be performed with a set of certified reference standards covering concentration ranges of the analytes of interest. In addition, the calibration standards and the samples should have similar spark characteristics for reproducible analysis to be possible and this may require a careful choice of standard reference materials as a prerequisite.

Unfortunately, there are many more alloys than sets of certified reference standards. Also, as the specifications for alloys are modified, the requirements for analyses change and may include elements which, although present in the original alloys as additives, have now become unwanted contaminants similar to the impurities analyzed here. These changing specifications challenge the validity of Certified Reference Materials (CRMs) at an alarming rate. In this case, the flexibility of using synthetic liquid phase standards for use in ICP is a distinct advantage. High purity standard solutions are freely available and with the technique of spiking, perfectly matrix-matched standards can be prepared.

This application note provides an example of these techniques and will examine the procedures and demonstrate their effectiveness for the analysis of Boron, Palladium, Ruthenium and Yttrium impurities in titanium alloy (Titanium 6Al4V).

Background to Titanium 6Al 4V Alloy

Titanium and its alloys, because of their strength-to-weight ratio, have many commercial applications, especially in the aerospace industry. The reactivity of titanium with oxygen creates the thin outer oxide layer which gives it excellent resistance to corrosion. But this reactivity with oxygen and other gases causes brittleness which makes the fabrication processes difficult. Titanium's most common alloy of 6% Aluminum and 4% Vanadium allows for ductile properties during manufacturing and strengthening through heat treating afterwards. This alloy has a good representation of certified reference standards for the major and minor constituents, but as stated previously, new specifications on trace contaminants require the analysis to be carried out by ICP-OES. However, the combination of all three major metals in this alloy (titanium, aluminium and vanadium) produces a large quantity of emission lines and the requirement for an optical system with high resolution and comprehensive wavelength range coverage is essential.

Instrumentation

An iCAP 6500 Radial with a HF resistant sample introduction system (p/n 8423 120 51721) was used for analysis. Table 1 lists the instrument conditions and sample introduction system used.

Parameter	Setting
Pump Tubing	Tygon orange-white sample
	Tygon white-white sample
Pump Rate	40 rpm
Nebulizer	MiraMist
Nebulizer Argon Flow	0.70 L/min or 0.20 MPa
Spray Chamber	Radial HF
Torch Centre Tube	2mm ceramic
RF Forward Power	1150 watts
Coolant Flow	12 L/min
Auxiliary Flow	0.7 L/min
Integration Time	20 seconds
Repeats Per Analysis	3

Table 1: iCAP operating parameters

Preparation of Samples & Standards

Four unknown samples of the Ti alloy (T1, T2, B1 and B2) were dissolved and diluted (1 gram to 50mL) according to ASTM Method E2371-04. This included 15 mL hydrochloric acid followed by 2 mL hydrofluoric acid and 2 mL nitric acid. Clear solutions on completion of the digestion step indicated complete dissolution. Aliquots of these digested samples were then spiked with the four analytes of interest at concentrations equivalent to 0.0025% and 0.0050% in the original solid sample.

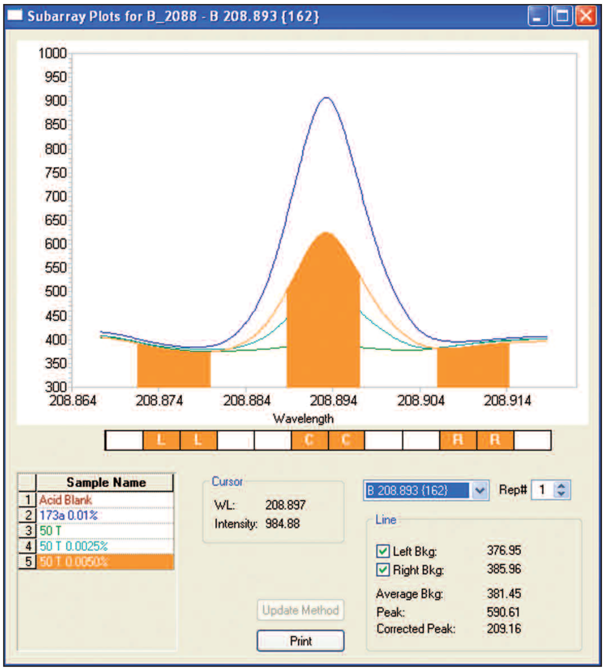
Two aliquots of NIST standard 173a (a Ti base 6% Al/4% V alloy) were used to prepare the calibration standards for the analysis following the same digestion procedures as described above for the unknown samples. One aliquot of the digested NIST 173a standard was used for the blank with no additional elements added. The second aliquot of the digested NIST 173a standard was spiked with single element solutions of B, Y, Pd and Ru (to the equivalent of 0.0100% in solid) to produce the high standard. NIST 173a already contains a small amount of Boron (0.00125%) and thus the concentrations of the standards used for this element were 0.00125% (Blank) and 0.01125% (High Standard).

Element	Standard (% in solid)	
	Blank	High
B	0.00125	0.01125
Pd	0.00000	0.01000
Ru	0.00000	0.01000
Y	0.00000	0.01000

Table 2: Standard concentrations

Method development

Initially, more than one wavelength was selected for each element and the subarrays for each wavelength were examined (see an example in Figure 1) and the most appropriate wavelength was chosen. The spectral interference tables incorporated into the iTEVA software were essential in determining the initial selection of lines, especially with the complex spectrum generated by the matrix. The Fullframe facility in iTEVA maps the entire spectrum and was used in conjunction with the interference tables to identify interference-free lines (see an example of a Fullframe in Figure 2). Subsequently, the subarray plots for each element were examined using iTEVA software, allowing the optimum wavelength and background correction points to be selected. In Figure 1 below, the background points have been relocated to minimize the background signal.



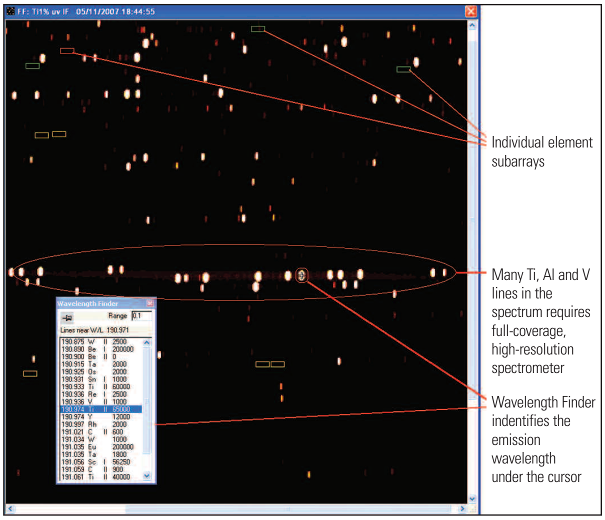
	Sample Name
1	Acid Blank
2	173a 0.01%
3	50 T
4	50 T 0.0025%
5	50 T 0.0050%

Cursor
WL: 208.897
Intensity: 984.88

B 208.893 {162} Rep# 1

Line
☑ Left Bkg: 376.95
☑ Right Bkg: 385.96
Average Bkg: 381.45
Peak: 590.61
Corrected Peak: 209.16

Figure 1: Subarray for Boron sample, spikes and standards in Titanium 6Al 4V Alloy



Range 0.1
Lines near W/L 190.971

```
190.875 W   II  2500
190.890 Be  I   200000
190.900 Be  II  0
190.915 Ta      2000
190.925 Os      2000
190.931 Sn  I   1000
190.933 Ti  II  60000
190.936 Re  I   2500
190.936 V   II  1000
190.974 Ti  II  65000
190.974 Y       12000
190.997 Rh      2000
191.021 C   II  600
191.034 W       1000
191.035 Eu      200000
191.035 Ta      1800
191.056 Sc  I   56250
191.059 C   II  900
191.061 Ti  II  40000
```

Individual element subarrays

Many Ti, Al and V lines in the spectrum requires full-coverage, high-resolution spectrometer

Wavelength Finder indentifies the emission wavelength under the cursor

Figure 2: Fullframe of Ti 6Al 4V alloy spectrum

Sample Analysis & Results

Calibrations were performed using the two standards described above (blank matrix and the 0.0100% analyte spike). The calibration was based on two points, however the validity and linearity of the calibration was verified using two spiked samples at 25% and 50% of the concentration of the high standard. The spiked samples correlated very well and recoveries were well within accepted tolerance levels of ±10%. The unknown samples and spiked samples were analyzed against these calibrations and the standards were also re-analyzed again at the end of the run to check recoveries and the stability of the method.

All results are given in weight % in the original sample (see Table 3). The comprehensive wavelength coverage and high sensitivity of the optics allowed a large amount of freedom in line choice. Even at these low impurity levels, element lines were chosen for their freedom from interference in the matrix as opposed to maximum sensitivity. Spike recoveries are provided for each sample where applicable. The standard was run twice as an unknown one hour after calibration to demonstrate stability. The recoveries from the individual spikes at 0.0025% and 0.0050% demonstrate the excellent linearity, stability and analytical accuracy that can be achieved from the instrumentation and methodology used.

Element		Sample T1	Sample T1 plus 0.0025% spike	Recovery	% rsd	T1 plus 0.0050% spike	Recovery	% rsd
B_2088	%	0.00054	0.00294	96.0	2.74	0.00545	98.2	0.04
Pd3609	%	0.00017	0.00263	98.4	1.35	0.00500	96.6	2.12
Ru2402	%	0.00004	0.00246	96.8	1.75	0.00503	99.8	0.39
Y_3600	%	ND*	0.00237	94.8	0.49	0.00484	96.8	0.12

Element		Sample B1	B1 plus 0.0025% spike	Recovery	% rsd	B1 plus 0.0050% spike	Recovery	% rsd
B_2088	%	0.00030	0.00280	100.0	1.88	0.00539	101.8	1.03
Pd3609	%	ND*	0.00242	97.2	0.61	0.00501	100.4	4.06
Ru2402	%	ND*	0.00265	106.0	0.05	0.00511	102.2	0.07
Y_3600	%	ND*	0.00245	98.0	0.01	0.00492	98.4	0.50

Element		Sample T2	T2 plus 0.0025% spike	Recovery	% rsd	T2 plus 0.0050% spike	Recovery	% rsd
B_2088	%	0.00051	0.00307	102.4	0.78	0.00564	102.6	0.83
Pd3609	%	0.00016	0.00271	102.0	3.37	0.00539	104.6	1.88
Ru2402	%	0.00007	0.00263	102.4	1.45	0.00522	103.0	0.97
Y_3600	%	ND*	0.00240	96.0	0.32	0.00491	98.2	0.26

Element		Sample B2	B2 plus 0.0025% spike	Recovery	% rsd	B2 plus 0.0050% spike	Recovery	% rsd
B_2088	%	0.00024	0.00277	101.2	1.70	0.00545	104.2	1.92
Pd3609	%	0.00012	0.00282	108.0	0.85	0.00546	106.8	1.29
Ru2402	%	0.00008	0.00267	103.6	2.12	0.00524	103.2	2.08
Y_3600	%	ND*	0.00242	96.8	0.15	0.00491	98.2	0.38

Element		CRM NIST 173a	173a STD	Recovery	% rsd	173a STD 2	Recovery	% rsd
B_2088	%	0.00081	0.01094	101.3	0.19	0.01095	101.4	0.60
Pd3609	%	ND*	0.00994	101.0	0.15	0.01004	102.0	0.27
Ru2402	%	0.00001	0.01004	100.3	0.41	0.01009	100.8	1.31
Y_3600	%	ND*	0.01006	100.6	0.34	0.01014	101.4	0.25

Table 3: Unknown & Spiked Sample Data

* ND - Not Detected, element intensity below the level of the blank.

Difficult matrices such as titanium alloys are made simple to analyze if the instrument has high performance, excellent resolution and versatility.

The high resolution of the iCAP 6000 Series is demonstrated to greatly reduce the possibility of spectral interference and the full wavelength coverage of the spectrometer allows the choice of alternate wavelengths from a library of over 55000 lines when spectral interference is inevitable. In addition, the iCAP 6000 Series is able to differentiate between high intensity and trace-level signals found at nearby wavelengths or orders by virtue of the unique, non-blooming Charge Injection Device (CID) detector and the high resolution optical system. The iCAP 6000 Series and iTEVA software can also use the CID detector to display the full spectrum in a two-dimensional graphic as shown above in Figure 2 which greatly improves the visibility of potential interferences. This Fullframe spectral image can be used to detect interference from the sample matrix and can even be used to generate semi-quantitative analyses.

Conclusion

The iCAP 6000 Series ICP has demonstrated its capability to produce precise and accurate analytical data for trace impurities in spectrally rich metallic matrices such as 2% Titanium solutions. Furthermore, the powerful optical design and CID detector technology of the iCAP 6000 Series allows the analyst to select the most optimal analytical wavelengths for the sample analysis.

The iCAP 6500 has been coupled with a spark ablation accessory (SSEA) for solid metals analysis with great success for selected metallurgy applications. However, for those situations where satisfactory solid standards are not available, solution methods such as this show that the iCAP 6000 Series is the best performing ICP instrument available.

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