

The analysis of trace impurities in titanium alloys using the Thermo Scientific iCAP 7000 Plus Series ICP-OES

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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, has many emission wavelengths and will cause excessive spectral interference problems in instruments with inadequate resolution optical systems. On lower resolution ICP-OES Spectrometers, 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 wavelengths 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.

Goal

To demonstrate the capability of the Thermo Scientific iCAP 7000 Plus Series ICP-OES for the determination of contaminant elements in titanium alloys as an alternative to spark optical emission spectrometry.

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-OES 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 B, Pd, Ru and Y impurities in a titanium alloy (Ti-6Al-4V).

Background to Ti-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 a 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% Al and 4% V 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 (Ti, Al and V) produces a large quantity of emission wavelengths and the requirement for an optical system with high resolution and comprehensive wavelength range coverage is essential.

Instrumentation

A Thermo Scientific™ iCAP™ 7600 ICP-OES Radial with an HF resistant sample introduction system was used for analysis. Table 1 lists the instrument conditions and sample introduction parts used.

Table 1. Instrument and method parameters.

Parameter	Setting
Pump Tubing (Mini Pump)	Sample Tygon® white/white Drain Tygon® yellow/blue
Pump Speed	40 rpm
Nebulizer	Burgener Teflon™ Mira Mist®
Nebulizer Gas Flow	0.7 L·min ⁻¹
Spray Chamber	HF resistant
Auxiliary Gas Flow	0.7 L·min ⁻¹
Coolant Gas Flow	12 L·min ⁻¹
Center Tube	2 mm ceramic
RF Power	1150 W
Exposure Time	20 s
Repeats	3

Sample and standard preparation

Four unknown samples of the titanium alloy (T1, T2, B1 and B2) were dissolved and diluted (1 gram to 50 mL) according to ASTM Method E2371-13. This included the digestion of sample in 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 SRM 173a (a Ti-6Al-4V alloy) were used to prepare the calibration standards (see Table 2) for the analysis following the same digestion procedures as described above for the unknown samples. One aliquot of the digested NIST SRM 173a was used for the blank with no additional elements added. The second aliquot of the digested NIST SRM 173a 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 SRM 173a already contains a small amount of B (0.00125%) and thus the concentrations of the standards used for this element were 0.00125% (blank) and 0.01125% (high standard).

Table 2. Standard concentrations.

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

Method development and analysis

A LabBook was created in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. Initially, more than one wavelength was selected for each element and the subarrays for each wavelength were examined and the most appropriate wavelength was chosen. The spectral interference tables incorporated into the Qtegra ISDS Software were essential in determining the initial selection of wavelengths, especially with the complex spectrum generated by the matrix.

The Fullframe capability of Qtegra ISDS Software allows to map the entire spectrum and was used in conjunction with the interference tables to identify interference-free wavelengths (see an example of a Fullframe in Figure 1). Subsequently, the subarray plots for each element were examined using Qtegra ISDS Software, allowing the optimum wavelength and background correction points to be selected.



Figure 1. Fullframe of Ti-6Al-4V alloy spectrum.

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 $\pm 10\%$. 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.

Results

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 wavelength choice. Even at these low impurity levels, element wavelengths were chosen for their freedom from interference in the matrix as opposed

to maximum sensitivity. Spike recoveries are provided for each sample where 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.

Table 3. Analysis results for unknown titanium alloy samples and spiked NIST SRM 173a. All concentrations in %.

Element and wavelength (nm)	Sample T1	Sample T1 plus 0.0025% spike	Recovery (%)	RSD (%)	T1 plus 0.0050% spike	Recovery (%)	RSD (%)
B 208.893	0.00054	0.00294	96.0	2.74	0.00545	98.2	0.04
Pd 360.955	0.00017	0.00263	98.4	1.35	0.00500	96.6	2.12
Ru 240.272	0.00004	0.00246	96.8	1.75	0.00503	99.8	0.39
Y 360.073	0.00000	0.00237	94.8	0.49	0.00484	96.8	0.12

Element and wavelength (nm)	Sample B1	B1 plus 0.0025% spike	Recovery (%)	RSD (%)	B1 plus 0.0050% spike	Recovery (%)	RSD (%)
B 208.893	0.00030	0.00280	100.0	1.88	0.00539	101.8	1.03
Pd 360.955	-0.00001	0.00242	97.2	0.61	0.00501	100.4	4.06
Ru 240.272	0.00000	0.00265	106.0	0.05	0.00511	102.2	0.07
Y 360.073	0.00000	0.00245	98.0	0.01	0.00492	98.4	0.50

Element and wavelength (nm)	Sample T2	T2 plus 0.0025% spike	Recovery (%)	RSD (%)	T2 plus 0.0050% spike	Recovery (%)	RSD (%)
B 208.893	0.00051	0.00307	102.4	0.78	0.00564	102.6	0.83
Pd 360.955	0.00016	0.00271	102.0	3.37	0.00539	104.6	1.88
Ru 240.272	0.00007	0.00263	102.4	1.45	0.00522	103.0	0.97
Y 360.073	0.00000	0.00240	96.0	0.32	0.00491	98.2	0.26

Element and wavelength (nm)	Sample B2	B2 plus 0.0025% spike	Recovery (%)	RSD (%)	B2 plus 0.0050% spike	Recovery (%)	RSD (%)
B 208.893	0.00024	0.00277	101.2	1.70	0.00545	104.2	1.92
Pd 360.955	0.00012	0.00282	108.0	0.85	0.00546	106.8	1.29
Ru 240.272	0.00008	0.00267	103.6	2.12	0.00524	103.2	2.08
Y 360.073	0.00000	0.00242	96.8	0.15	0.00491	98.2	0.38

Element and wavelength (nm)	CRM NIST 173a	173a STD	Recovery (%)	RSD (%)	173a STD 2	Recovery (%)	RSD (%)
B 208.893	0.00081	0.01094	101.3	0.19	0.01095	101.4	0.60
Pd 360.955	-0.00016	0.00994	101.0	0.15	0.01004	102.0	0.27
Ru 240.272	0.00001	0.01004	100.3	0.41	0.01009	100.8	1.31
Y 360.073	0.00000	0.01006	100.6	0.34	0.01014	101.4	0.25

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 Thermo Scientific iCAP 7000 Plus Series ICP-OES 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 wavelengths when spectral interference is inevitable. In addition, the iCAP 7000 Plus Series ICP-OES 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 7000 Plus Series ICP-OES and Qtegra ISDS Software can also use the CID detector to display the full spectrum in a two-dimensional graphic as shown above in Figure 1 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 7000 Plus Series ICP-OES 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 7000 Plus Series ICP-OES allows the analyst to select the most optimal analytical wavelengths for the sample analysis. The iCAP 7600 ICP-OES Radial 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 7000 Plus Series ICP-OES is the best performing ICP-OES instrument available.

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