Direct determination of Al, B, Co, Cr, Mo, Ti, V and Zr in HF acid-digested nickel alloy using the Agilent 4210 Microwave Plasma-Atomic Emission Spectrometer

Application note

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Introduction

Nickel alloys are used when good high- and low-temperature strength and corrosion resistance are needed. Typical industrial applications are for fabrication of chemical and petrochemical process vessels and gas turbine parts. The aerospace and military industries are also important users of nickel based alloys, which are frequently used in the manufacture of jet engine parts including turbine blades. The additive elements in the nickel alloy and their concentrations are carefully selected in order to obtain the desired material properties. For example, titanium (Ti) is added to improve corrosion resistance and increase the strength-to-density ratio of the alloy.

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It is also known that low concentrations of boron (B) and zirconium (Zr) improve material hardness [1, 2]. A slight change in composition can adversely affect the properties of the alloy. Therefore, accurate elemental analysis of nickel alloys is extremely important from the metallurgical and engineering point of view.

Elemental analysis of nickel alloys can be performed using non-destructive techniques such as X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM) or arc spark emission spectrometry. However, some of these techniques are limited to analysis of only the exposed surface of the material. In order to analyze the total content in the bulk material, the whole sample must be dissolved (digested) in an acid mix and the resulting digest can then be analyzed using a suitable spectroscopic method such as ICP-OES and more recently MP-AES. In this study, a method to determine the concentrations of Al, B, Co, Cr, Mo, Ti, V and Zr in a nickel alloy using the Agilent 4210 MP-AES, is presented.

Figure 1. Easy-fit inert torch for 4200/4210 MP-AES

Hydrofluoric (HF) acid must be employed during sample preparation to ensure complete dissolution of alloys containing elements such as Ti, Zr, Hf, Nb, Ta, Mo, W, Ge, Sn or Sb. Sample digests prepared in HF cannot be analyzed directly using standard glass and quartz sample introduction systems as the free HF attacks and degrades the glass and quartz components. To prevent degradation, the residual HF needs to be neutralized by adding boric acid (H_3BO_3), prior to analysis. This neutralization process adds another sample preparation step, reducing laboratory efficiency and introducing a potential source of contamination. This preparation process is also not suitable if boron is one of the analytes of interest, as in this particular case.

Therefore, laboratories performing this type of analysis prefer to use an inert sample introduction system, to allow direct analysis of the HF digests without needing a pre-analysis neutralization step [3]. For this application the inert torch for the 4200/4210 series MP-AES was used in conjunction with an inert double-pass spray chamber and the inert OneNeb Series 2 nebulizer, to facilitate the direct analysis of HF digests without prior neutralization.

Experimental

Instrumentation

The 4210 MP-AES is a fast sequential, emission based multi-element analytical technique that uses a microwave-induced plasma for sample excitation. The MP-AES technique utilizes a nitrogen based plasma. This eliminates the need for expensive and hazardous gases such as acetylene, increasing safety, and enabling unattended operation of the instrument, even in remote locations. Nitrogen can be supplied from bottled gas, a Dewar or the Agilent 4107 Nitrogen Generator (with air supplied from an air compressor). For this application, Dewar nitrogen was used to run the MP-AES.

The sample introduction system used featured inert components including an inert double pass spray chamber, the inert MP-AES torch (Figure 1) and the inert OneNeb Series 2 nebulizer. The Agilent nebulizer gas humidifier accessory was fitted to improve long term stability and reduce deposition in the nebulizer from Total Dissolved Solids (TDS) in the digest.

The instrument was controlled by the powerful and easy-to-use MP Expert software. The MP-AES features continuous wavelength coverage that allows the selection of wavelengths that are appropriate for the concentration range required for the analysis and which are relatively free of interferences. Table 1 lists instrument operating conditions used in the method.

Table 1. Agilent 4210 MP-AES operating conditions.

Instrument parameter	Setting
Torch	Easy fit inert torch with alumina injector
Nebulizer	OneNeb Series 2 inert nebulizer
Nebulizer flow	Individually optimized for each element, see Table 5
Nebulizer gas humidifier	Fitted
Spray chamber	Inert double-pass spray chamber
Sample & internal std tubing	Orange/green Solvaflex
Waste tubing	Blue/blue Solvaflex
Pump speed (rpm)	15
Number of replicates	3
Analytes	Al, B, Co, Cr, Mo, Ti, V, Zr (Lu as internal Std)
Read time (s)	B: 5, Lu: 3, Zr: 10, Al, Co, Cr, Mo, Ti & V: 1
Stabilization time (s)	15
Uptake time (s)	30 (fast pump)
Rinse time (s)	75 (fast pump)

Standard Reference Material

A certified reference material (IN 100 alloy–cast; (BCS/SS-CRM No. 345)) from the Bureau of Analysed Samples Ltd was analyzed to validate the method presented in this study. IN 100 alloy is a nickel based alloy that provides high rupture strength at high temperatures. IN 100 alloy has a high concentration of Al and Ti which makes this material particularly attractive on a strength to density basis. The alloy has been successfully utilized in a variety of shapes from turbine blades, vanes and nozzles to integral wheels [4]. Table 2 highlights the certified concentrations of the IN 100 alloy. The IN 100 nickel alloy was sourced from Graham B. Jackson. (Aust) Ltd. and used on an as-received basis.

Table 2. Certified concentrations for the IN 100 nickel based alloy CRM used in this study

IN 100 alloy (BCS/SS-CRM No. 345) Certified concentrations in weight %			
Al	5.58 ± 0.07	Mo	3.01 ± 0.06
B	0.019 ± 0.003	Ti	4.74 ± 0.06
Co	14.71 ± 0.07	V	1.00 ± 0.04
Cr	9.95 ± 0.08	Zr	0.044 ± 0.001

Preparation of calibration standards and samples

The sample preparation procedure used a HNO_3-HCl-HF digestion based on a nominal sample weight of approximately 0.15 g. The sample was accurately weighed and placed directly into the inert (PTFE) reaction vial. 3 mL of nitric acid 69% (Merck) and 9 mL of hydrochloric acid 37% (Merck) were added to the vial and thoroughly mixed. Subsequently, 2 mL of hydrofluoric acid 48% (Merck) were added in two portions. The samples were digested using the Milestone UltraWave Single Reaction Chamber (SRC) microwave digestion system which serves both as a microwave cavity and reaction vessel, that assures high temperature capabilities. Sealing of the vials was not required since the Single Reaction Chamber was pressurized using a nitrogen gas pressure of 45 bar. The digests were made up to a volume of 40 mL using 18 MΩ de-ionized water. Samples were prepared, at least, in triplicate. The temperature program used for the microwave digestion process is shown in Table 3.

Table 3. Parameters used for microwave digestion (where t is the time and T1 and T2 are the programmed initial and final vessel temperatures)

Step	t (min)	T1 (°C)	T2 (°C)	Power (W)
1	25	Ambient	250	1500
2	25	250	250	1500

Calibration standards were prepared from Agilent aqueous single element certified reference materials. In order to match the acid matrix of the digests, all calibration standards were diluted with a solution containing 20% aqua regia / 5% HF in 18 MΩ de-ionized water. The calibration range was determined based on the expected concentration of the elements in the completed digest of the IN 100 nickel alloy used. The calibration standards and the concentrations used are shown in Table 4.

Table 4. Calibration standards used in this study.

Solution	Analyte and Standard Concentrations (mg/L)							
	Al	B	Co	Cr	Mo	Ti	V	Zr
Calibration Blank	0	0	0	0	0	0	0	0
Standard 1	24		48	40		20	6	0.8
Standard 2	72		144	120		60	18	2.4
Standard 3	144		288	240		120	36	4.8
Standard 4	288		576	480		240	72	9.6
Standard 5					50			
Standard 6					100			
Standard 7					200			
Standard 8		1.5						
Standard 9		2.5						
Standard 10		5						
Standard 11		8						

Wavelength selection, background and interference correction

Table 5 lists the emission lines selected for analysis, together with the background and interference correction methods used. The selected wavelengths provide minimal spectral interferences, and wide dynamic range, eliminating time-consuming sample dilutions and re-analysis.

An internal standard (Istd) solution of 50 mg/L lutetium solution in 2% HNO_3 was used. The internal standard was delivered on-line using a Y-connector to combine this solution with the sample prior to nebulization.

When analyzing metal alloys, there can be a wide range of elements present at varying concentrations from hundreds of ppm to % levels, which can result in numerous spectral interferences. The MP Expert software has an extensive wavelength database that helps the analyst to choose the best analytical wavelengths, based on intensity and the potential for spectral interferences. When interferences are present and there are no other lines that either provide the required sensitivity or are free of interferences, Agilent's Fast Linear Interference Correction (FLIC) [5], can be used to apply correction.

FLIC can be used when multiple, partly overlapping spectral components are present in the spectral window, or if there is only a single component present. FLIC also provides the flexibility to correct for structured background. FLIC models are constructed using pure solutions for the blank, element of interest and the expected interfering element(s) within the sample. This modeling provides accurate and automatic correction for interferences identified in your sample spectra.

In this study, FLIC proved effective for resolving interferences encountered in the reference material analyzed. The blank, analyte and interferent solutions used to develop the FLIC models are displayed in Table 6.

Table 5. Line selection, nebulizer flow, background and interference correction methods for each element

Element	Wavelength (nm)	Nebulizer Flow (L/min)	Background/Interference Correction	Interferent(s)	Calibration fit	Calibration Correlation coefficient
Al	394.401	0.35	Auto		Linear	0.999
B	249.772	0.45	FLIC + IStd	Ni	Rational	0.997
Co	344.917	0.35	Auto		Linear	0.999
Cr	435.177	0.45	FLIC+ IStd	V	Linear	0.999
Mo	553.305	0.45	Auto		Linear	0.999
Ti	453.324	0.35	Auto		Linear	0.999
V	327.612	0.80	Auto+ IStd		Linear	0.999
Zr	383.676	0.40	FLIC + IStd	Ti, V, Ni	Linear	0.999
Lu	261.542	0.45	Auto	Used as Internal Standard		

Table 6. FLIC sequence matrix listing the solutions used to develop the FLIC models (interferent solution concentration in mg/L shown in parentheses)

Element & wavelength (nm)	Blank solution	Analyte solution	Interferent solution 1	Interferent solution 2
B 249.772	Calibration Blank	B (10)	Ni (10000)	
Cr 435.177	Calibration Blank	Cr (1000)	V (1000)	
Zr 383.676	Calibration Blank	Zr (100)	Ti (1000)	V (1000)

The determination of chromium in the IN 100 alloy CRM provides a good example of how FLIC modelling enables the user to remove interferences when determining challenging samples where interferences are present. The chromium concentration in the IN 100 alloy is high. For that reason, the Cr 435.177 nm wavelength was selected for analysis as it is a fairly insensitive line and almost free of interferences, except for the nearby V(I) signal at 435.287 nm. Figure 2 shows the signal for Cr 435.177 nm (red trace) with the interfering element (V) modeled using FLIC (green trace) enabling the user to determine Cr in the sample directly.

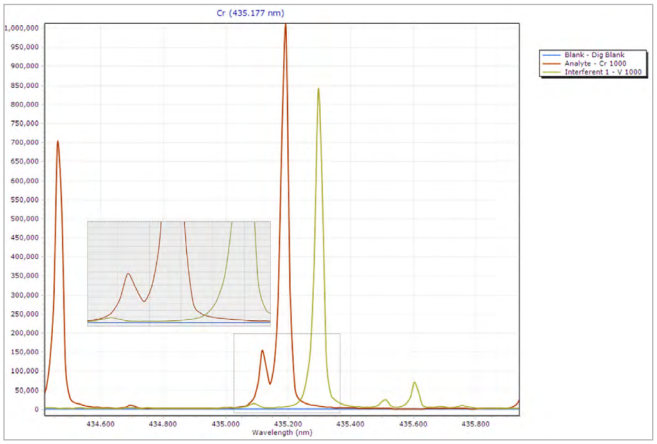

Figure 2. Spectral interferences for Cr at the 435.177 nm wavelength, resolved using FLIC

Results and discussion

Method Detection Limits

Method Detection Limits (MDLs) were determined by running the digested acid blank 10 times under the method conditions after calibration. The MDL is defined as 3 times the standard deviation (S) of the concentration readings for each element. The Limit of Quantification (LOQ) for this analysis was estimated as 10 times the standard deviation of the concentration readings, multiplied by the average dilution factor used during sample preparation (267x).

Table 7. Method detection limits and estimated limit of quantification

	Element and Wavelength (nm)							
	Al 394.401	B 249.772	Co 344.917	Cr 435.177	Mo 553.305	T 453.324	V 327.612	Zr 383.676
MDL in solution (mg/L)	0.007	0.003	0.10	0.02	0.03	0.03	0.03	0.004
LOQ in the solid sample (mg/kg)	6.2	2.8	89	20	24	26	23	3.5

Long term stability

To check instrument stability during a long term measurement, the digested IN 100 nickel alloy sample was analyzed every 4 minutes over 8 hours of continuous measurement. A periodic calibration reslope, which included the blank and one standard (Standard 3), was performed every 3 hours. Excellent long term stability was achieved over 8 hours of operation with all elements in the method having average recoveries within ±10% of certified values (Figure 3) with a long term measurement precision of less than 5% RSD (Table 8).

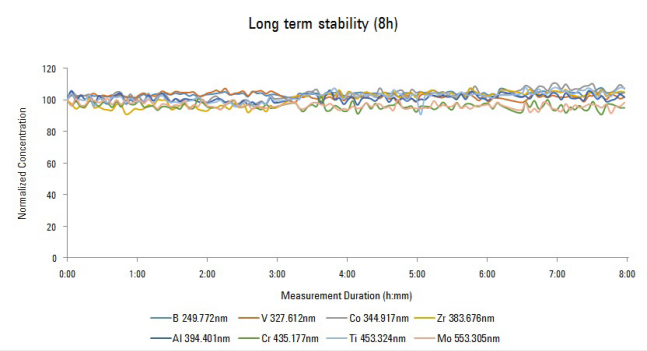

Figure 3. Long term stability for continuous measurement of the IN 100 nickel alloy CRM over 8 hours

Recoveries for the IN 100 nickel alloy CRM

The recoveries for all elements determined in the IN 100 nickel alloy CRM were within ± 10% of the certified values, highlighting the suitability of this method for determining nickel based alloys (Table 9). These results are the average of three separate sets of digestions, made at least in triplicate, analyzed twice. The results also demonstrate the wide dynamic range capability of the Agilent 4210 MP-AES, as elements were determined over a wide concentration range from ppm to % level in a single reading, without dilution.

Recoveries for the IN 100 nickel alloy CRM without HF

HF acid is needed in the digestion process to ensure complete dissolution and good recovery for Ti, Mo and Zr in the IN 100 nickel alloy CRM. To demonstrate the effectiveness of HF in achieving complete digestion, two IN 100 nickel alloy CRM samples were digested using only HCl-HNO_3 and analyzed. The recoveries for the elements analyzed were compared against those obtained with HF present in the acid mix. As expected, the recoveries were quite poor for Mo, Ti and Zr when using only an aqua-regia digest (Figure 4).

Table 8. Long-term precision for 8 hours continuous measurement of the IN 100 nickel alloy CRM.

Element & wavelength (nm)	Al 394.401 nm	B 249.772 nm	Co 344.917 nm	Cr 435.117 nm	Mo 553.305 nm	Ti 453.324 nm	V 327.612 nm	Zr 383.676 nm
Precision (%RSD)	2.1	1.3	3.1	2.2	2.1	3.0	1.7	4.5

Table 9. Recoveries and calculated uncertainties for elements determined in the IN 100 nickel alloy CRM

Element and wavelength (nm)	**Certified Concentration (weight %)**	**Certified Uncertainty * (weight %)**	**Measured Concentration (weight %)**	**Calculated Uncertainty* n=22 (weight %)**	**Recovery (%)**
Al 394.401 nm	5.58	0.07	5.33	0.12	95.4
B 249.772 nm	0.019	0.003	0.020	0.0003	105.4
Co 344.917 nm	14.71	0.07	15.52	0.20	105.5
Cr 435.177 nm	9.95	0.08	10.68	0.14	107.4
Mo 553.305 nm	3.01	0.06	3.01	0.05	100.0
Ti 453.324 nm	4.74	0.06	4.55	0.08	96.0
V 327.612 nm	1.00	0.04	0.95	0.01	95.0
Zr 383.676 nm	0.044	0.001	0.041	0.001	93.1

* This value represents the half width confidence interval C(95%), which is calculated as t x S_m / √(n), where "t" is the appropriate two sided Student's t value at the 95% confidence level, and S_m is the standard deviation (of the intralaboratory means for the CRM, or the replicate readings for the IN 100 alloy sample determinations).

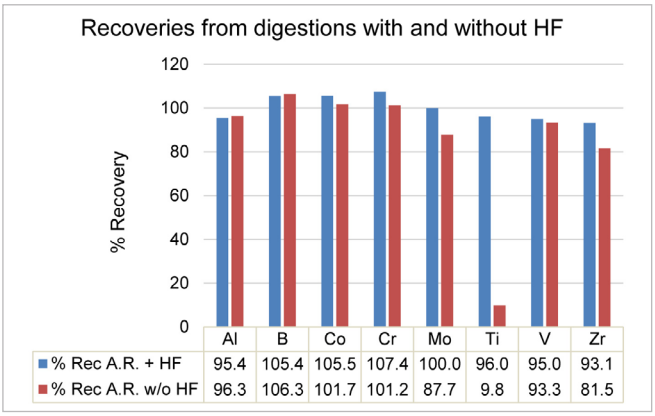

Figure 4. Recoveries for selected elements in the IN 100 nickel alloy CRM, comparing digests prepared with aqua-regia only (red) and using HF + aqua-regia (blue).

Conclusions

The results from analysis of the IN 100 nickel alloy CRM demonstrate that the Agilent 4210 MP-AES is an excellent technique for the analysis of challenging metallurgical samples. The wide dynamic range capability was demonstrated as elements were determined over a wide concentration range from hundreds of ppm to % level in the same sample, without any pre-analysis dilution, in a single reading with excellent recoveries. Good long term stability was also demonstrated for continuous measurement of the IN 100 nickel alloy CRM over a period of 8 hours. FLIC was able to successfully model the complex interferent signals and apply correction, ensuring good results for all elements with excellent recoveries across a concentration range of three orders of magnitude.

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