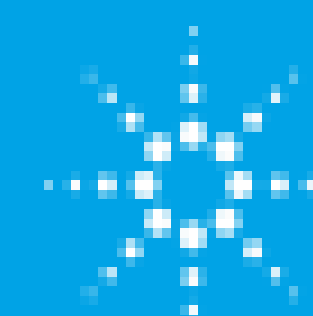


Direct determination of Al, B, Co, Cr, Mo, Ti, V and Zr in HF acid-digested nickel alloy using the Agilent 4210 MP-AES

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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, gas turbine parts and 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. A slight change in composition can adversely affect the properties of the alloy. Therefore, accurate elemental analysis of nickel alloys is extremely important.



In order to analyze the total content in the nickel alloy, 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.

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 (H₃BO₃), prior to analysis. This adds another sample preparation step, reducing laboratory efficiency and introducing a potential source of contamination. This is also not suitable if boron is one of the analytes of interest.

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



The Agilent easy-fit inert torch for 4200/4210 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.

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 instrument utilizes a nitrogen based plasma, eliminating the need for expensive and hazardous gases such as acetylene, increasing safety, and enabling unattended operation even in remote locations. Nitrogen can be supplied by Dewar or the Agilent 4107 Nitrogen Generator. Table 1 lists instrument operating conditions and method parameters used in this method.

Experimental

Table 1. Agilent 4210 MP-AES operating and method parameters

Parameter	Setting
Pump Speed (rpm)	15
Sample & internal standard pump tubing	Orange/ Green Solvaflex
Waste tubing	Blue/Blue Solvaflex
Read time (s)	B: 5, Lu: 3, Zr: 10, Al, Co, Cr, Mo, Ti, V: 1
Replicates	3
Sample uptake delay (s)	30 (Fast pump: ON)
Stabilization time (s)	15
Rinse time (s)	75 (Fast pump: ON)
Nitrogen gas source	Dewar

Standard reference material

Certified reference material (IN 100 alloy-cast; (BCS/SS-CRM No. 345)) from the Bureau of Analysed Samples Ltd

Calibration standards and samples

The sample preparation procedure used a HNO₃-HCl-HF digestion based on a nominal sample weight of approximately 0.15 g. The sample and 3 mL of HNO₃ acid 69% with 9 mL of HCl acid 37% were added into the inert (PTFE) reaction vial and thoroughly mixed. Subsequently, 2 mL of HF acid 48% were added in two portions. The samples were digested using the Milestone UltraWave Single Reaction Chamber (SRC) microwave digestion system.

The digests were made up to a volume of 40 mL using 18 MΩ de-ionized water. Samples were prepared in triplicate. The temperature program used for the microwave digestion process is shown in Table 2.

Table 2. Parameters used for microwave digestion.

Step	Time (min)	Initial temp (°C)	Final temp (°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. All calibration standards were matrix matched, diluted with a solution containing 20% aqua regia/ 5% HF in 18 MΩ de-ionized water. The calibration standards and the concentration ranges, as well as wavelengths, nebulizer flow, background correction for each element are shown in Table 3.

An internal standard solution of 50 mg/L Lu solution in 2% HNO₃ was used. The internal standard was delivered on-line using a Y-connector to combine this solution with the sample prior to nebulization.

Table 3. Standard concentrations, line selection, neb flow

Element & line (nm)	Neb flow (L/min)	Background correction	Interferent (s)	Concentration range (mg/L)
Al 394.401	0.35	Auto		0-288
B 249.772	0.45	FLIC	Ni	0-8
Co 344.917	0.35	Auto		0-576
Cr 435.177	0.45	FLIC	V	0-480
Mo 553.305	0.45	Auto		0-200
Ti 453.324	0.35	Auto		0-240
V 327.612	0.80	Auto		0-72
Zr 383.676	0.40	FLIC	Ti, V, Ni	0-9.6
Lu 261.542	0.45	Auto	Used as internal standard	

Results and Discussion

Calibration

All elements, except B showed excellent linearity with a calibration coefficient of greater than 0.999. B required a rational fit, with a correlation coefficient of 0.997

Method Detection Limits

Method Detection Limits (MDLs) were determined from 10 measurements of the digested acid blank (Table 4). 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).

Results and Discussion

Table 4. The calculated Method detection limits and estimated limit of quantification.

Element & wavelength (nm)	MDL in solution (mg/L)	LOQ in solid sample (mg/kg)
Al 394.401	0.007	6.2
B 249.772	0.003	2.8
Co 344.917	0.10	89
Cr 435.177	0.02	20
Mo 553.305	0.03	24
Ti 453.324	0.03	26
V 327.612	0.03	23
Zr 383.676	0.004	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 mid-range standard was performed every 3 hours. Excellent long term stability was achieved over 8 hours all elements having average recoveries within ±10% of certified values (Figure 1) with precision of less than 5% RSD.

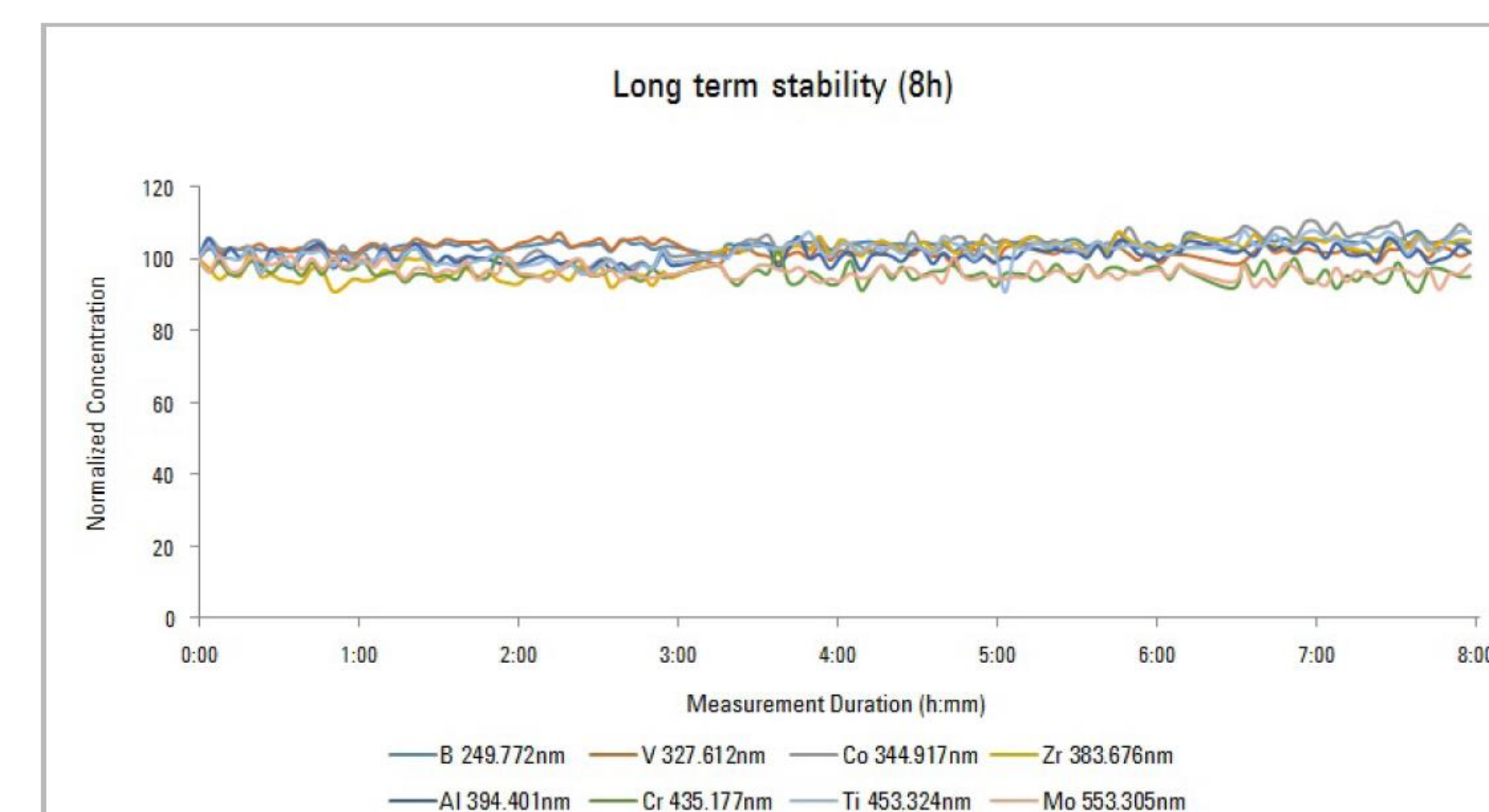


Figure 1. Long term stability for continuous measurement of the IN 100 nickel alloy CRM

Recoveries for IN 100 nickel alloy CRM

The recoveries for all elements determined in the IN100 nickel alloy CRM were within ± 10% of the certified values (Table 5). These results are the average of three separate sets of digestions, 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.

Table 5. Recoveries for elements determined in the IN 100 nickel alloy CRM

Element & wavelength (nm)	Certified concentration (weight %)	Measured concentration (weight %)	Recovery (%)
Al 394.401	5.58	5.53	95
B 249.772	0.019	0.020	105
Co 344.917	14.71	15.52	105
Cr 435.177	9.95	10.68	107
Mo 553.305	3.01	3.01	100
Ti 453.324	4.74	4.55	96
V 327.612	1.00	0.95	95
Zr 383.676	0.044	0.041	93

Conclusions

The results of the IN 100 nickel alloy CRM demonstrate that the Agilent 4210 MP-AES is suitable for the analysis of challenging metallurgical samples due to:

- The wide dynamic range capability demonstrated, 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
- Good long term stability was for the continuous measurement of the IN 100 nickel alloy CRM over a period of 8 hours
- FLIC was useful for the complex interferent signals ensuring good results for all elements with excellent recoveries