

Trace elemental analysis

Analysis of impurities in non-ferrous metals and nickel-based superalloys using single quadrupole inductively coupled plasma mass spectrometry (ICP-MS)

Authors

Fei Wang¹, Yanping Wang², Run Ye¹,
Alex Li¹, Li Liu², Min Xu¹, Tomoko Vincent³

¹Thermo Fisher Scientific, Beijing, China

²Thermo Fisher Scientific, Shanghai, China

³Thermo Fisher Scientific, Bremen,
Germany

Keywords

Bulk analysis, ferrous, high matrix,
metallurgy, non-ferrous

Goal

The goal of this application note is to demonstrate how ICP-MS can be used for reliable analysis of impurities as well as major components of pure metals and metal alloys.

Introduction

The properties of a material are critical to its successful use in modern applications. Specific mechanical or chemical properties are often dependent on the presence and level of certain elements in the material. As a large proportion of construction materials are based on metallurgical products, it is critical to understand the concentrations of the trace elements in pure metals or alloys. Modern metal-based materials can be classified into non-ferrous and ferrous metals. Ferrous materials are based on iron as the main component, and therefore include different types of steel (i.e., cast iron or stainless steel). This leads to properties such as high temperature resistance as well as the potential for being recycled easily. On the contrary, non-ferrous materials do not contain iron and refer to metals such as aluminium, copper, or zinc, and alloys such as brass.

Both ferrous and non-ferrous materials play crucial roles in various industries, such as modern architecture and construction, automotive, aerospace, electronics, and (clean) energy generation. Understanding the characteristics, properties, and potential impact of processing techniques is essential for metallurgical engineers to design and produce high-quality products for different applications. The exact composition, including

major components, additives, and trace impurities, needs to be thoroughly determined to ensure the final product meets the performance requirements in terms of corrosion and heat resistance, conductivity, or formability.

Inductively coupled plasma mass spectrometry (ICP-MS) is often the technique of choice for the determination of impurities at trace and ultra-trace levels due to its outstanding sensitivity. As a full multi-elemental analysis can be accomplished in only a few minutes, it also allows high sample throughput. However, ICP-MS is also well known for its historically limited ability to analyze samples with elevated matrix load. The sample matrix could significantly affect the sensitivity of the instrument, cause intensity fluctuation of the internal standard (suppression and drift), and lead to increased system maintenance with unwanted downtime due to obstruction of the interface cones, torch and injector, or the nebulizer. To overcome this limitation, samples must be diluted, either using liquid diluents or using argon gas provided directly from the instrument itself.

This application note focuses on the development of a fast, robust, and accurate method for the analysis of bulk and trace elements in ferrous and non-ferrous materials using the Thermo Scientific™ iCAP™ MSX ICP-MS with Argon Gas Dilution (AGD).

Experimental

Experimental optimization of the instrument parameters

An iCAP MSX ICP-MS, operated together with a Thermo Scientific™ iSC-65 Autosampler, was used for all analyses. The sample introduction system consisted of a Peltier cooled (at 2.7 °C), glass cyclonic spray chamber (SavilleX, Eden Prairie, MN, USA), PFA concentric nebulizer (SavilleX), and PLUS torch with a 2.5 mm i.d. removable quartz injector. The built-in argon humidifier was used for humidification of the nebulizer gas to prevent salt deposit on the nebulizer tip, along with integrated Argon Gas Dilution.

To further increase uptime of the instrument, Intelligent Matrix Handling was used, a unique feature of the Thermo Scientific™ iCAP™ MX Series ICP-MS instruments to reduce exposure to sample matrix during sample uptake and wash.

Due to the relatively high sample matrix (0.1%), a high number of complex polyatomic interferences were expected. To remove polyatomic interferences, kinetic energy discrimination (KED) using helium as collision/reaction gas as a comprehensive interference removal approach and was used in this study. However, for some analyte/matrix combinations, the use of

KED may not be sufficient to fully eliminate all interferences so that certain isotopes may not be used for analysis. In general, the use of triple quadrupole ICP-MS systems provides superior interference removal based on the use of reactive gases, such as oxygen or hydrogen. Table 1 summarizes the instrument configuration and analytical parameters.

Table 1. Instrument configuration and operating parameters

Parameter	Value (general analysis)
Nebulizer	C-Flow 400d (C400d) PFA concentric nebulizer 400 $\mu\text{L}\cdot\text{min}^{-1}$
Peristaltic pump tubing	PVC orange-yellow tubing, 0.51 mm i.d.
Peristaltic pump speed	25 rpm
Humidifier	On
Spray chamber	Glass cyclonic, cooled at 2.7 °C
Torch	PLUS torch
Injector	2.5 mm i.d., Quartz
Interface	Nickel sampler and skimmer cone
Plasma power	1,550 W
AGD setting	AGD Level 5
AGD flow	0.50 $\text{L}\cdot\text{min}^{-1}$
Nebulizer gas	0.45 $\text{L}\cdot\text{min}^{-1}$
QCell setting	He KED
QCell gas flow	100% He 4.2 $\text{mL}\cdot\text{min}^{-1}$
CR bias	-21 V
Q3 bias	-18 V
Scan setting	0.05 s for matrix elements and others are 0.1 s dwell time, 5 sweeps, 3 main runs
Analysis time per sample	Total 2 min 40 s: including uptake (45 s) and wash out (25 s), Step Ahead (17 s), matrix stabilization time (15 s)

Sample preparation

Pre-cleaned (72 hours in 2% HNO₃ (Optima™ grade, Fisher Chemical™)) polypropylene bottles were used for the preparation of all blanks, standards, and samples.

Five certified reference materials (Trace Elements in Nickel-Base Superalloy, NCS Standard Materials Division (Beijing, China) GBW01636, GBW01637, GBW01638, GBW01639, GBW01640) were prepared for this analysis. All samples were digested before analysis.

An aliquot of approximately 0.1 g of each sample was accurately weighed into a Teflon™ beaker and acid digested using a mixture of 1.5 mL HNO₃ (68% Trace Metal™ grade, Fisher Chemical™), 4.5 mL HCl (35% Trace Metal grade, Fisher Chemical) and 1 mL HF (47% Trace Metal grade, Fisher Chemical) using the hot plate digestion at 180 °C for 20 min. After digestion, the samples were made up to 100 mL using ultrapure water, so that the amount of total dissolved solids was around 0.1% in the measured sample solution. No further dilution was applied prior to analysis. One objective of this study was to investigate the instrument's ability not only to determine impurities present at trace levels, but also to measure the major components present in a sample at high levels (high mg·L⁻¹ levels).

To assess the potential for quantitative analysis of impurities, spike recovery tests were performed at a level of 25 µg·L⁻¹ in solutions containing 1,000 mg·L⁻¹ each of Al, Cr, Mn, Fe, Co, Ni, Cu, and Zn, prepared from the 10,000 mg·L⁻¹ single standard solution (SPEX CertiPrep™, Metuchen, NJ, USA).

To demonstrate the capability of the instrument for accurate and precise analysis despite the challenging sample matrix, the internal standards were monitored for matrix suppression.

A sample dilution, calibration blank, a series of standards, and a quality control (QC) were prepared using 2 v/v % HNO₃ (Optima grade, Fisher Scientific). All samples and standards were spiked with an internal standard mix (10 µg·L⁻¹ Rh and Re). The elements and final concentrations are shown in Table 2.

Results and discussion

Sensitivity and linearity

Table 3 summarizes the applied internal standard, instrument detection limits (IDLs), method detection limits (MDLs) obtained, together with the coefficient of determination (R²) for all 21 elements analyzed in this study. Please note that different resolution settings (Normal and High) have been used across the analyte panel. High resolution adjusts the average peak width observed for a given *m/z* ratio to approximately 0.4 amu (instead of approximately 0.7–0.8 amu in normal resolution). This leads to a reduction of the observed signal intensities, which reduces the degradation of the electron multiplier and hence extends the lifetime. The correlation coefficients (R²) obtained for all analytes were found to be greater than 0.9993, which suggests excellent linear response for the established concentration range for each analyte. The IDLs were calculated as three times the standard deviation of ten replicate measurements of the calibration blank. Note that these LODs include the dilution factor applied using AGD. MDLs are based on the instrumental detection limits but consider the dilution factor of 1,000 incurred during the digestion process and describe the minimum of analyte that can be detected in the solid sample material.

Method validation

Reference material analysis

As part of this study, five nickel super alloys certified reference materials were analyzed to validate the proposed method for accuracy and precision. The results obtained show that the determined concentrations of the target analytes matched the certified values, demonstrating the accuracy of method. For all reference materials, at least six individual samples from two independent preparations were measured, so that the method was also demonstrated to deliver excellent precision (Table 4).

Table 2. Summary of the concentration details of the standard calibration, CCV (continuing calibration verification).

All numbers are shown in µg·L⁻¹.

	STD-1	STD-2	STD-3	STD-4	STD-5	STD-6	QC CCV	Spiked recovery
Be, Mg, Ca, Ga, As, Se, Cd, Ag, In, Sb, Pb, Bi	25	50	100	-	-	-	25	25
Al, Cr, Mn, Fe, Co, Ni, Cu, Zn	25	50	100	250,000	500,000	1,000,000	250,000	-

Table 3. Summary of internal standard, R², LODs and for all analytes

	Internal standard	Quadrupole resolution	R ²	LOD (µg·L ⁻¹)	MDL (µg·kg ⁻¹)
⁹ Be	¹⁰³ Rh	Normal	0.9999	<0.001	<0.001
²⁴ Mg		Normal	0.9999	0.69	690
²⁷ Al		High	0.9993	0.05	50
⁴⁴ Ca		Normal	0.9998	0.06	60
⁵³ Cr		High	> 0.9999	0.03	30
⁵⁵ Mn		High	0.9999	0.08	80
⁵⁷ Fe		High	0.9999	0.04	40
⁵⁹ Co		High	> 0.9999	0.006	6
⁶⁰ Ni		High	> 0.9999	0.02	20
⁶³ Cu		High	0.9996	0.02	20
⁶⁶ Zn		High	0.9999	0.051	51
⁷¹ Ga		Normal	0.9999	<0.001	1
⁷⁵ As		Normal	0.9998	0.09	90
⁷⁸ Se		Normal	0.9998	0.79	790
⁸² Se		Normal	0.9998	1.34	1,340
¹⁰⁶ Cd		Normal	> 0.9999	0.041	41
¹⁰⁷ Ag		Normal	> 0.9999	0.001	1
¹¹⁵ In	Normal	> 0.9999	0.001	1	
¹²¹ Sb	Normal	> 0.9999	0.01	10	
²⁰⁸ Pb	¹⁸⁵ Re	Normal	> 0.9999	0.001	1
²⁰⁹ Bi		Normal	> 0.9999	0.001	1

Table 4. Quantitative results obtained for the CRM super alloys. Analyte concentrations are reported as mg·kg⁻¹. The results of the analyte were summarized and shown only for those with reference numbers. Two samples were prepared and analyzed for each Certified Reference Material (CRM), and the standard deviation (stdev) was evaluated using six analysis results.

	GBW 1636				GBW 1637			
	Measured	stdev	Recovery	Reference	Measured	stdev	Recovery	Reference
⁶³ Cu	471.17	8.60	83%	571	293.68	2.29	81%	363
⁶⁶ Zn	10.53	0.42	88%	12	10.50	0.28	81%	13
⁷¹ Ga	29.31	0.64	95%	31	30.49	0.32	90%	34
⁷⁵ As	6.31	0.24	94%	6.7	13.27	0.17	95%	14
⁸² Se	10.91	0.88	111%	9.8	13.76	0.52	115%	12
¹⁰⁶ Cd	0.30	0.06	97%	0.31	0.06	0.04	-	< 0.02
¹⁰⁷ Ag	0.73	0.02	93%	0.78	0.73	0.02	73%	1
¹¹⁵ In	0.73	0.10	83%	0.88	7.25	0.09	101%	7.2
¹²¹ Sb	1.35	0.09	96%	1.4	3.53	0.06	107%	3.3
²⁰⁸ Pb	3.61	0.13	106%	3.4	3.60	0.04	97%	3.7
²⁰⁹ Bi	0.16	0.01	113%	0.14	0.21	0.04	111%	0.19

Table 4. (Continued)

	GBW 1638				GBW 1639			
	Measured	stdev	Recovery	Reference	Measured	stdev	Recovery	Reference
⁶³ Cu	148.2	1.16	86%	172	77.0	2.32	82%	94
⁶⁶ Zn	11.6	0.26	83%	14	14.4	0.40	96%	15
⁷¹ Ga	34.6	0.29	91%	38	50.4	1.36	97%	52
⁷⁵ As	91.7	0.93	96%	96	43.8	1.34	100%	44
⁸² Se	4.2	0.80	103%	4.1	2.6	0.35	103%	2.5
¹⁰⁶ Cd	<MDL	0.06	-	<0.02	0.1	0.03	-	<0.02
¹⁰⁷ Ag	2.7	0.08	106%	2.6	4.7	0.12	106%	4.4
¹¹⁵ In	2.4	0.03	91%	2.6	35.5	1.15	115%	31
¹²¹ Sb	17.5	0.21	109%	16	52.8	1.65	108%	49
²⁰⁸ Pb	4.6	0.10	99%	4.7	8.3	0.08	101%	8.2
²⁰⁹ Bi	1.1	0.16	90%	1.2	2.1	0.01	106%	2

	GBW 1640			
	Measured	stdev	Recovery	Reference
⁶³ Cu	43.0	1.38	81%	53
⁶⁶ Zn	10.4	0.80	80%	13
⁷¹ Ga	46.8	0.82	95%	49
⁷⁵ As	24.8	0.37	99%	25
⁸² Se	2.2	0.18	100%	2.2
¹⁰⁶ Cd	0.06	0.06	-	< 0.02
¹⁰⁷ Ag	5.9	0.07	110%	5.4
¹¹⁵ In	10.6	0.18	106%	10
¹²¹ Sb	34.6	0.34	105%	33
²⁰⁸ Pb	11.0	0.07	100%	11
²⁰⁹ Bi	1.8	0.05	99%	1.8

Spike recovery test

To further validate the accuracy of the analysis, a spike recovery was performed at a concentration of 25 µg·L⁻¹, which added to solutions containing 1,000 mg·L⁻¹ of each Al, Cr, Mn, Fe, Co, Ni, Cu, and Zn. The results obtained from the analysis demonstrated an excellent spike recovery within the range of 85% to 105% for most elements. This indicates the reliability and accuracy of the analysis method used (Figure 1).

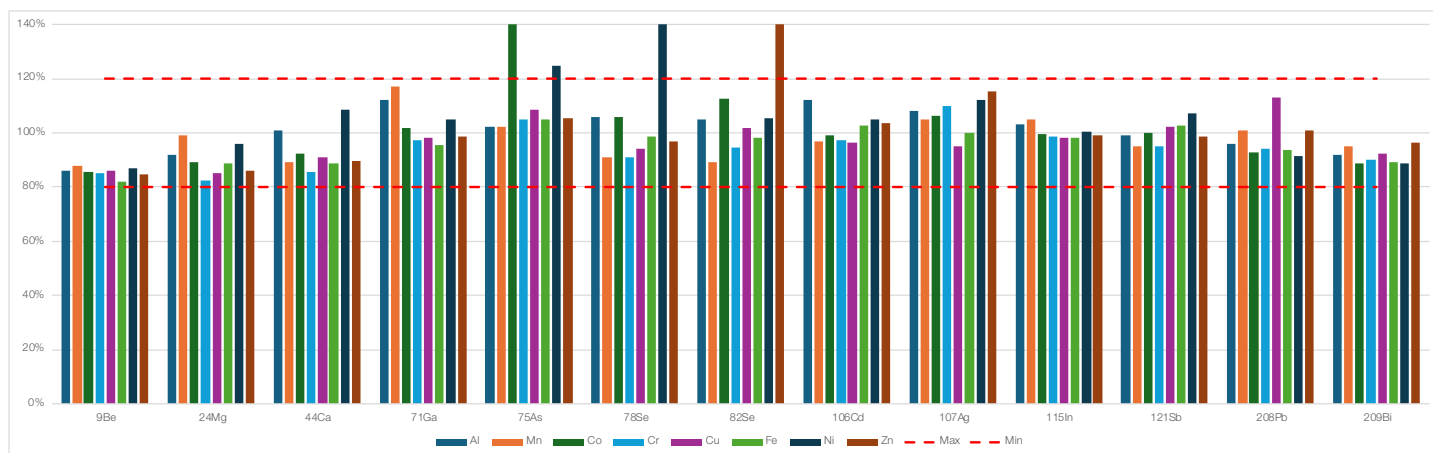


Figure 1. Results of the spike recovery test performed in solutions containing 1,000 mg·L⁻¹ of each Al, Cr, Mn, Fe, Co, Ni, Cu, and Zn

However, as indicated previously, for some elements individual matrices generated specific interferences in amounts that could no longer be fully removed using KED alone, hence leading to false positive results. As was significantly biased in the presence of cobalt (Co) due to the formation of isobaric $^{59}\text{Co}^{16}\text{O}^+$, whereas Fe revealed significant false positive results in presence of Ni and Zn, respectively. In this latter case however, the interferences can be avoided by appropriate selection of the isotopes to be monitored. While ^{78}Se returns a false positive in presence of $1,000\text{ mg}\cdot\text{L}^{-1}$ Ni matrix, it can be monitored with good accuracy using ^{82}Se . Likewise, ^{82}Se is interfered with in the presence of $1,000\text{ mg}\cdot\text{L}^{-1}$ Zn but can be measured using ^{78}Se . Here, the high amounts of interferences such as $^{62}\text{Ni}^{16}\text{O}$ on ^{78}Se and $^{66}\text{Zn}^{16}\text{O}$ on ^{82}Se lead to the incorrect results. Whereas for these cases, a triple quadrupole ICP-MS would be able to avoid all interferences,^{1,2} the results in general provided excellent recoveries for the remaining analytes in all matrices.

Evaluation of long-term robustness

To simulate high-throughput analysis, a larger batch containing the sample solutions already previously analyzed was scheduled for analysis.

Following calibration of the instrument, several blocks with samples containing the certified reference materials (diluted to 0.1% matrix content in the digestion process) or single element standard solutions containing $1,000\text{ mg}\cdot\text{L}^{-1}$ were scheduled for analysis, together with the required QC checks. The total number of analyses was 258 (including 160 metallurgy matrix samples and 21 calibrants and 56 QC checks), requiring a total analysis time of approximately 9 hours (Figure 2).

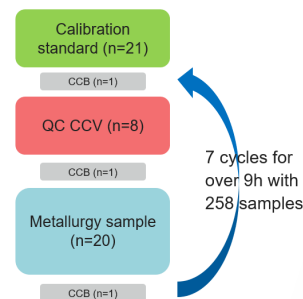


Figure 2. Schematic overview of the batch analyzed for testing the long-term performance of the proposed method. Seven blocks, containing 20 metallurgy matrix samples each, were analyzed.

Figure 3 shows the recovery for all analytes analyzed as part of the continuing calibration verification check (CCV, $n=7$) for all 21 isotopes. As described in Table 2, the QC checks covered both typical impurities, which were tested at a concentration of $25\text{ }\mu\text{g}\cdot\text{L}^{-1}$, but also matrix elements found in high concentrations in ferrous and non-ferrous materials. Here, the QC check was performed at a concentration of $250\text{ mg}\cdot\text{L}^{-1}$. The data indicates excellent recovery (within 90% to 105%). The iCAP MSX ICP-MS therefore allows for robust and reliable long-term analysis even for challenging matrices, as found for the analysis of metallurgical samples.

The response of the internal standards was again observed to be consistent regardless of the matrix composition and well within the commonly accepted range of 80–120% of the response in the initial blank measurement for the calibration curve. Both internal standards (Rh and Re) showed predictable recovery (within approximately 83% to 112%) over the entire runtime of the batch, demonstrating robust analytical performance over 9 hours.

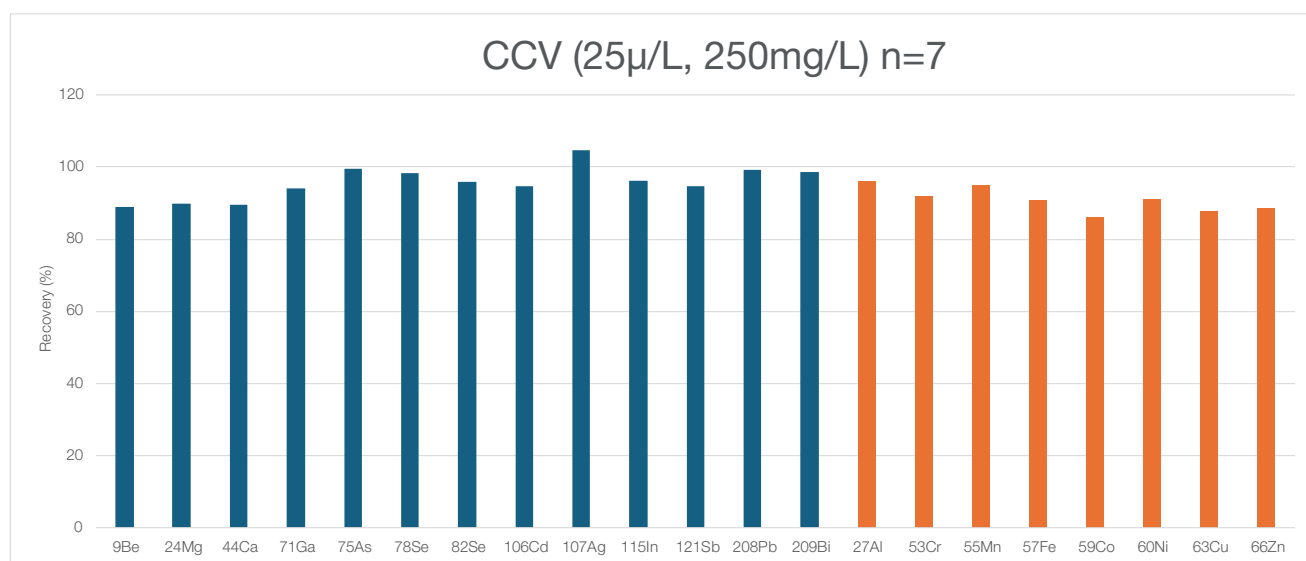


Figure 3. QC calibration verification results with the 21 isotopes measured. The blue bar is $25\text{ }\mu\text{g}\cdot\text{L}^{-1}$ and the orange bar is $250\text{ mg}\cdot\text{L}^{-1}$ (refer to Table 2).

Conclusions

The iCAP MSX ICP-MS was used to analyze 20 elements in digested nickel superalloys certified reference materials, as well as selected single element standard solutions containing 1,000 mg·L⁻¹ of elements typically used for the preparation of non-ferrous materials and alloys. Among the analytes, several critical interferences can cause unexpected bias, however He KED mode allowed consistent removal in most cases. This analytical method was rigorously tested, and the results obtained clearly demonstrated the following analytical advantages:

- The use of a single measurement mode in combination with other features to increase productivity of the instrument allowed the total analysis time to be reduced to <3 min/sample (including uptake and wash time).
- The analysis results for the 20 elements under investigation (comprising both major components as well as trace and ultra-trace level impurities) showed excellent agreement with certified values.
- The developed method provides the required detection limits and a linear response for all analytes and allows coverage of a dynamic range between 25 to 1,000,000 µg·L⁻¹.

The use of Argon Gas Dilution (AGD Level 5) was proven to be an effective way to overcome the challenges associated with high and moreover variable matrix content. Dilution is accomplished automatically inside the instrument with no additional sample handling required. AGD is fully integrated and supported in the Qtegra ISDS Software, so that it is easy to set up and operate.

Acknowledgments

We thank NCS Testing Technology Co., Ltd. (Beijing, China) for sample preparation.

References

1. Manecki, M.; Kutscher, D.; McSheehy Ducos, S. Thermo Fisher Scientific, Application Note 43404 - Accurate measurement of elemental impurities in metals and metal alloys using triple quadrupole ICP-MS, 2020. <https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/AN-43404-ICP-MS-Impurities-Metals-Alloys-AN43404-EN.pdf>
2. Vincent, T.; Rantanen, M.; Kalliovaara, E.; Köymäri, H. Thermo Fisher Scientific, Application Note 44463 - Robust and accurate analysis of refined nickel using triple quadrupole ICP-MS, 2020. https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-44463-icp-ms-refined-nickel-an44463-en.pdf?icid=CAD_blog_mining_2023Aug

 Learn more at thermofisher.com/icpms