

Robust and accurate analysis of refined nickel using triple quadrupole ICP-MS

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Goal

To demonstrate the applicability of the Thermo Scientific™ iCAP™ TQ ICP-MS with Argon Gas Dilution (AGD) and an integrated *FAST*™ autosampler for robust and accurate analysis of relevant trace elemental impurities in complex matrix samples containing high concentrations of nickel.

Introduction

Nickel (Ni) is a constituent of many alloys and confers resistance and anti-corrosion properties. Nickel alloys are widely used in the manufacturing of mechanical parts in various industries, batteries, and electronics. Considering the importance of such Ni-alloys for some industries (for example, aircraft engine turbine blades), it is imperative to control potential impurities as they can cause weaknesses in the alloy that lead to fracturing and, ultimately, total material failure. Primary Ni needs to achieve a minimum of



99.8% purity following the specifications of the American Society for Testing and Materials (ASTM), which means that the impurities need to be detected at a concentration of 20 mg·L⁻¹ in 1% nickel solution. Inductively coupled plasma – optical emission spectrometry (ICP-OES) is a technique that can be used for trace element analysis in Ni-alloys when impurity determination in primary nickel is required. However, in the process of refining and purification, impurities need to be controlled at much lower concentration levels. For confirmation of the purity of 99.999% (or 5N) nickel, trace metal analysis becomes challenging. For such an analysis, inductively coupled plasma mass spectrometry (ICP-MS) is the best option as it offers significantly lower detection limits for a wider range of trace metals.

A further challenge related to this application is the requirement to analyze high concentrations of the sample matrix, typically resulting in a matrix concentration (expressed as total dissolved solids or TDS) of nickel between 1,000 and 8,000 mg·L⁻¹. Samples containing high TDS can be analyzed using ICP-MS if special configurations of the sample introduction systems are chosen^{1,2} or a more flexible solution, such as inline dilution, is applied to reduce the matrix load.

Besides the requirements for lowest detection limits (typically in the ng·L⁻¹ range), the analysis of some elements is challenging with ICP-MS because of specific interferences caused by the sample matrix. Selenium is considered difficult to analyze in the presence of high concentrations of nickel when using single quadrupole ICP-MS. All major selenium isotopes can be affected by polyatomic interferences, such as ⁶⁰Ni¹⁸O (on ⁷⁸Se) and ⁶⁴Ni¹⁶O (on ⁸⁰Se), rendering low level analysis of this critical contaminant impossible.³ Another element highly interfered in this matrix is cobalt, as its only isotope ⁵⁹Co is surrounded by two major isotopes of nickel, so that a false positive signal caused by peak tailing is possible. To address these challenges, a triple quadrupole ICP-MS, such as the iCAP TQ ICP-MS, is much more suitable as it offers the superior selectivity needed to efficiently eliminate these interferences.

This application note describes an optimized analytical method for the analysis of impurities in a nickel matrix (approx. 12% Ni after dissolution). The analytical platform of choice was an iCAP TQ ICP-MS operated using argon gas dilution (AGD) in combination with a valve system integrated in the autosampler to facilitate robust and accurate routine analysis of metal impurities in samples containing high concentrations of nickel. The combination of inline dilution (addition of the internal standard) and AGD for handling high amounts of TDS allowed the direct analysis of samples containing 6,000 mg·L⁻¹ of nickel.

Experimental

Optimization of instrument parameters

An iCAP TQ ICP-MS was used for all measurements. The sample introduction system consisted of a Peltier cooled (2.7 °C), baffled cyclonic spraychamber, PFA nebulizer, and quartz torch with a 2.5 mm i.d. removable quartz injector. For automation of the sample introduction process, a SC-4DX FAST autosampler (Elemental Scientific, Omaha, NE, USA) was used in combination with the ICP-MS. In order to remove all potentially occurring interferences,

the ICP-MS was operated in SQ-KED and TQ-O₂ mode using the parameters presented in Table 1. In short, the following modes remove spectral interferences in different ways:

SQ-KED – single quadrupole mode with the collision / reaction cell (CRC) pressurized with helium (He) as a collision gas and Kinetic Energy Discrimination (KED) applied. This allows for the removal of common polyatomic interferences typically observed across the mass range of the instrument.

TQ-O₂ – triple quadrupole mode with the CRC pressurized with oxygen as a reaction gas, Q1 set to analyte mass (M⁺), and Q3 set to product ion mass (MO⁺) in case the analyte is reactive to oxygen, or alternatively to the original mass of the element analyzed (in case an interference is reactive towards oxygen, see Figure 1). This mode allows for complete interference removal and improved detection sensitivity for elements such as phosphorous, sulfur, arsenic, or selenium, among others.

Table 1. Instrument configuration and operating parameters

Parameter	Value	
Nebulizer	Borosilicate glass MicroMist, 400 µL·min ⁻¹ , pumped at 30 rpm	
Spraychamber	Quartz cyclonic, cooled at 2.7 °C	
Injector	2.5 mm i.d., quartz	
Interface	Platinum sampler and platinum skimmer cone with high matrix insert	
Plasma power	1,550 W	
Nebulizer gas	0.22 L·min ⁻¹	
Additional gas flow (Ar)	0.62 L·min ⁻¹	
QCell setting	SQ-KED	TQ-O₂
Gas flow	100% He, 4.5 mL·min ⁻¹	100% O ₂ , 0.34 mL·min ⁻¹
CR bias	-21 V	-6.3 V
Q3 bias	-18 V	-12 V
Scan setting	0.5 s dwell time for P, S, As, and Se, 0.1 s dwell time for others 10 sweeps 3 main runs	
Lens setting	Optimized using autotune	
FAST valve sample loop	2 mL	
Sample up take	45 s	
Wash time	45 s	
Total analysis time	185 s	

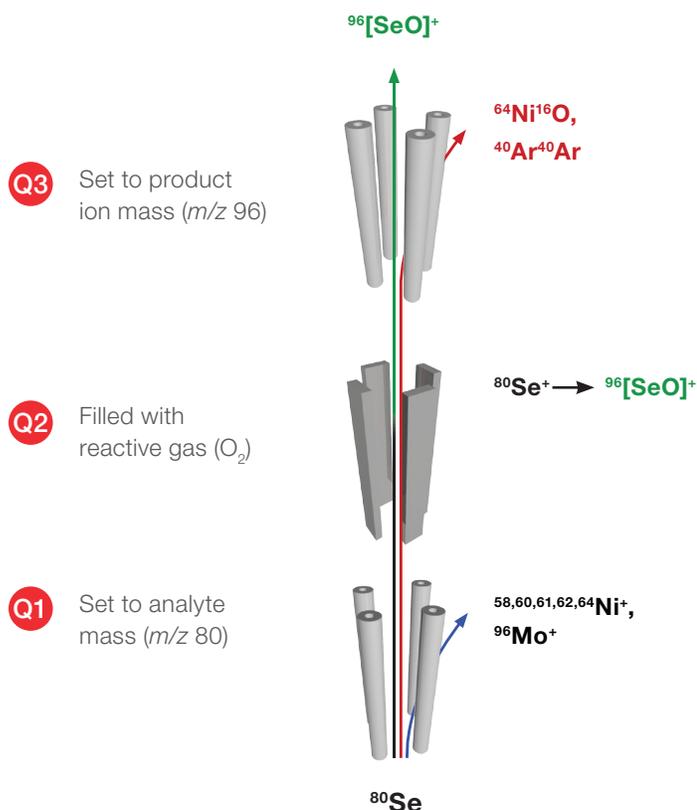


Figure 1. Schematic showing TQ mass shift modes for selenium

The selection of the best analysis conditions for all elements was determined using the Reaction Finder Method Development Assistant, which also optimizes the ions transmitted through the first quadrupole using Intelligent Mass Selection (IMS). This allows for the easiest method setup even for inexperienced users and achievement of the highest detection sensitivity when using measurement modes based on triple quadrupole technology.

Data acquisition and data processing

All parameters in each of the measurement modes were defined automatically using the autotune procedures provided in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software.

The autosampler with the integrated FAST valve system was controlled using the Qtegra ISDS Software as well using a dedicated software plug-in. In total, 21 elements were screened for their presence as impurities in nickel, including non-metals such as phosphorous or sulfur, transition metals, and heavy metals. The consistency of sample preparation and dilution was verified through the analysis of nickel. However, to protect the detection system from the high count rate to be expected when measuring a matrix element, a minor isotope of nickel, ^{61}Ni (with a natural abundance of 1.14%) was selected for analysis.

Sample preparation

Precleaned polypropylene bottles were used for the preparation of all blanks, standards, and samples. The bottles were rinsed with ultrapure water ($18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$) and left to dry in a laminar flow clean hood before use.

To test the system performance with relevant sample matrices, a nickel sample (TDS ~12% of nickel sludge sample and nickel standard containing approximately $7,000 \text{ mg}\cdot\text{L}^{-1}$ of nickel), multi-element calibration curves and quality control (QC) checks (see Table 2) were prepared. An internal standard solution containing Ga, In, and Tl, all at $10 \text{ }\mu\text{g}\cdot\text{L}^{-1}$, was added online using the FAST valve internal standard port to correct for potentially occurring matrix effects. All samples were diluted before analysis by a factor of 20 to reduce the amount of total dissolved solids from 12% to about 0.6% using 2% nitric acid. To further reduce the impact of the sample matrix, but without avoiding a larger dilution factor, argon gas dilution was used to enable robust and reliable analysis of this challenging matrix in a routine focused laboratory.

Table 2. Calibration solution concentration. All numbers are in $\text{mg}\cdot\text{L}^{-1}$.

	STD-1	STD-2	STD-3	STD-4	STD-5	QC 1 (CCV)	QC 2 (LCS)
Na	0.5	5	50	500	-	25	-
Mg	0.001	0.01	0.1	1	-	0.05	-
Al	0.001	0.01	0.1	1	-	0.05	-
P	0.001	0.01	0.1	1	-	0.05	-
S	1,000	3,000	-	-	-	-	-
K	0.001	0.01	0.1	1	-	0.05	-
Cr	0.001	0.01	0.1	1	-	0.05	-
Mn	0.0001	0.001	0.01	0.1	-	0.005	-
Fe	0.001	0.01	0.1	1	-	0.05	-
Co	0.001	0.01	0.1	1	-	0.05	-
Ni	500	1,000	2,000	4,000	6,000	-	7,000
Cu	0.001	0.01	0.1	1	-	0.05	-
Zn	0.001	0.01	0.1	1	-	0.05	-
As	0.0001	0.001	0.01	0.1	-	0.005	-
Se	0.001	0.01	0.1	1	-	0.1	-
Cd	0.0001	0.001	0.01	0.1	-	0.005	-
Sn	0.0001	0.001	0.01	0.1	-	0.005	-
Sb	0.0001	0.001	0.01	0.1	-	0.005	-
Pb	0.0001	0.001	0.01	0.1	-	0.005	-
Bi	0.0001	0.001	0.01	0.1	-	0.005	-
U	0.0001	0.001	0.01	0.1	-	0.005	-

Blanks, calibration standards, and quality control (QC) were prepared in 2% nitric acid with single element standards (SPEX CertiPrep, Metuchen, USA). The details of the measurement modes, acquisition parameters, and internal standards for each element (except nickel), are shown in Table 3. Generally, for each element a linear range of at least four orders of magnitude was demonstrated using this method. To verify accuracy of the calibration, two QC samples were analyzed as part of the analytical sequence. QC sample 1 contained all analytes in a concentration corresponding to about 50% of the range covered in the calibration, whereas QC sample 2 contained 7,000 mg·L⁻¹ nickel.

Table 3. Measurement modes and internal standards used for each element with corresponding target isotopes and dwell times

Analyte	Measurement mode	Dwell time (s)	Internal standard
²³ Na	SQ-KED	0.1	⁷¹ Ga
²⁴ Mg	SQ-KED	0.1	⁷¹ Ga
²⁷ Al	SQ-KED	0.1	⁷¹ Ga
³¹ P as ³¹ P ¹⁶ O at 47 m/z	TQ-O ₂	0.5	⁷¹ Ga
³³ S as ³³ S ¹⁶ O at 49 m/z	TQ-O ₂	0.5	⁷¹ Ga
³⁹ K	SQ-KED	0.1	⁷¹ Ga
⁵² Cr	TQ-O ₂	0.1	⁷¹ Ga
⁵⁵ Mn	SQ-KED	0.1	⁷¹ Ga
⁵⁶ Fe	SQ-KED	0.1	⁷¹ Ga
⁵⁹ Co	SQ-KED	0.1	⁷¹ Ga
⁶¹ Ni as ⁶¹ Ni ¹⁶ O at 77 m/z	TQ-O ₂	0.1	⁷¹ Ga
⁶⁵ Cu	SQ-KED	0.1	¹¹⁵ In
⁶⁶ Zn	SQ-KED	0.1	¹¹⁵ In
⁷⁵ As as ⁷⁵ As ¹⁶ O at 91 m/z	TQ-O ₂	0.5	¹¹⁵ In
⁸⁰ Se as ⁸⁰ Se ¹⁶ O at 96 m/z	TQ-O ₂	0.5	¹¹⁵ In
¹¹⁴ Cd	TQ-O ₂	0.1	¹¹⁵ In
¹²⁰ Sn	SQ-KED	0.1	¹¹⁵ In
¹²¹ Sb	SQ-KED	0.1	¹¹⁵ In
²⁰⁸ Pb	SQ-KED	0.1	²⁰⁵ Tl
²⁰⁹ Bi	SQ-KED	0.1	²⁰⁵ Tl
²³⁸ U	SQ-KED	0.1	²⁰⁵ Tl

Results and discussion

Several elements pose significant challenges when analyzing them in a matrix containing high levels of nickel. One primary example is selenium (Se), which besides its lower ion yield (based on its elevated 1st ionization potential), is affected by a variety of mostly polyatomic interferences, so that single

quadrupole based ICP-MS instruments do not achieve sufficiently low detection limits.

Using the TQ-O₂ mass shift mode (schematically shown in Figure 1), the first quadrupole (Q1) rejects all ions of lower and higher mass than the analyte, so that an effective ion molecule reaction with O₂ can be induced in the collision/reaction cell (CRC), leading to the formation of a new product ion, SeO. The abundant polyatomic interferences, such as ⁴⁰Ar₂⁺ or all NiO⁺, do not react with O₂. The third quadrupole (Q3) can now isolate the [SeO]⁺ product ions and removes any remaining interferences through a second stage of mass filtration, so that complete interference removal is achieved.

Table 4 shows the detection limits typically achieved using the iCAP TQ ICP-MS using optimized conditions for each element. As can be seen, even for challenging analytes, such as arsenic or selenium, other transition metals or heavy metals, detection limits in the sub ng·L⁻¹ can be achieved.

Table 4. Results for LOD and BEC data for the analysis of 20 elements in 2% industrial grade HNO₃. BEC and LOD values are dependent on the sample type measured. MDLs are obtained by multiplying the applicable dilution factor of 20 (~12% TDS Ni samples dilution factor) into LODs. All values are in µg·L⁻¹.

Analyte	BEC	LOD	MDL
²³ Na	22.8	9.8	195
²⁴ Mg	0.1	0.4	7.6
²⁷ Al	0.3	0.7	14.8
³¹ P as ³¹ P ¹⁶ O at 47 m/z	1.6	0.4	7.8
³³ S as ³³ S ¹⁶ O at 49 m/z	14,482	2,352	47,039
³⁹ K	127	29.4	587
⁵² Cr	0.7	0.1	2.7
⁵⁵ Mn	0.009	0.02	0.3
⁵⁶ Fe	0.9	0.3	6.9
⁵⁹ Co	0.09	0.05	1.0
⁶⁵ Cu	0.2	0.1	1.9
⁶⁶ Zn	0.10	0.02	0.3
⁷⁵ As as ⁷⁵ As ¹⁶ O at 91 m/z	0.007	0.003	0.06
⁸⁰ Se as ⁸⁰ Se ¹⁶ O at 96 m/z	0.05	0.06	1.3
¹¹⁴ Cd	0.003	0.001	0.02
¹²⁰ Sn	0.003	0.005	0.1
¹²¹ Sb	0.002	0.002	0.05
²⁰⁸ Pb	0.007	0.002	0.04
²⁰⁹ Bi	0.008	0.003	0.06
²³⁸ U	0.003	0.0004	0.01

The detection limit (LOD) was determined based on three times the standard deviation of ten replicate measurements of the calibration blank. Method detection limits (MDLs), taking into account the dilution factor required for the samples, are shown together with instrumental detection limits (measured as 3x standard deviation of the calibration blank) in Table 4. Please note that the use of nitric acid of superior purity would lead to a significant improvement of the achievable limits of detection.

Linearity assessment

For all analytes, the linearity of the method was demonstrated over at least four orders of magnitude (see Table 2 for applicable calibration ranges). As part of the quantitative assessment of the samples, not only should impurities present in the raw nickel be addressed, but also the approximate content of nickel should be determined to reflect potential issues occurring during sample preparation. To measure highly intense signals caused by high concentrations, the iCAP TQ ICP-MS can use variable resolution settings for both quadrupoles (Q1 and Q3). In particular, changing the average resolution of the third quadrupole (Q3) from normal resolution (about 0.75 amu peak width) to high resolution (about 0.35 amu peak width) can allow intense signals to be attenuated and enable

their direct measurement without negative impact on the lifetime of the detection system.

Figure 2 shows a calibration curve for ^{61}Ni (determined as $^{61}\text{Ni}^{16}\text{O}$) using TQ- O_2 mode (nickel shows only a limited reactivity towards O_2 and hence reduces the expectable count rate even further) and high resolution for Q3 and over for concentrations of 0, 500, 1,000, 2,000, 4,000 and 6,000 $\text{mg}\cdot\text{L}^{-1}$ with a correlation coefficient of better than $R^2 = 0.9999$. This allows the verification of the concentration of nickel present in a sample in the same run and hence confirms the complete and successful digestion and sample preparation.

Similarly, the calibration curves for challenging analytes, such as Se and As, (Figures 3 and 4) show that all interferences have been fully removed using TQ- O_2 mode. At the same time, the use of TQ- O_2 mode, inducing a mass shift reaction for both analytes, also increases the detection sensitivity and leads to improved limits of detection. As both elements are critical impurities, the calibrated range was between 0.0001 and 0.1 $\text{mg}\cdot\text{L}^{-1}$ for arsenic and between 0.001 and 1 $\text{mg}\cdot\text{L}^{-1}$ for selenium. Again, correlation coefficients of better than 0.999 were achieved.

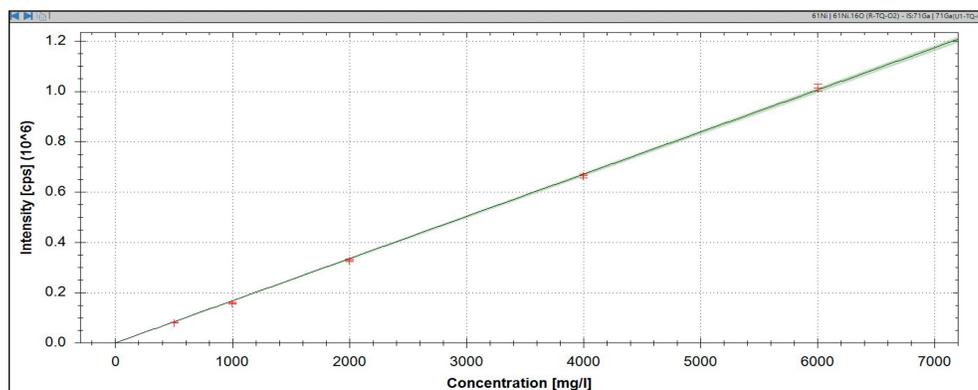


Figure 2. Calibration curve for ^{61}Ni as $^{61}\text{Ni}^{16}\text{O}$ at 77 m/z in TQ- O_2 mass shift mode

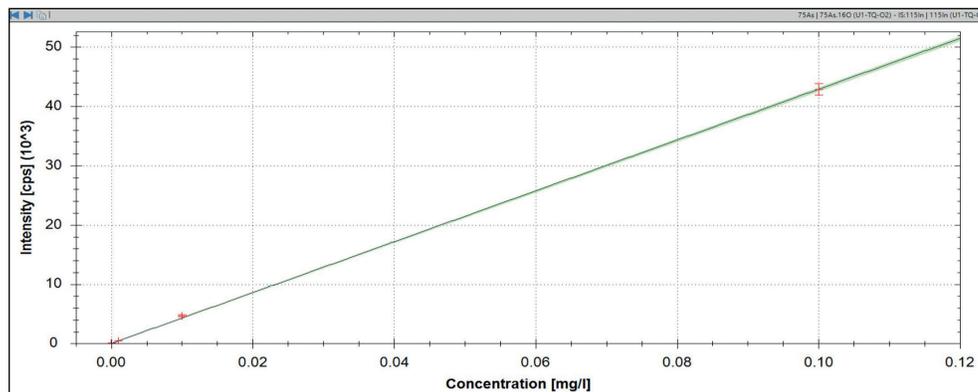


Figure 3. Calibration curve for ^{75}As as $^{75}\text{As}^{16}\text{O}$ at 91 m/z analyzed in TQ- O_2 mass shift mode

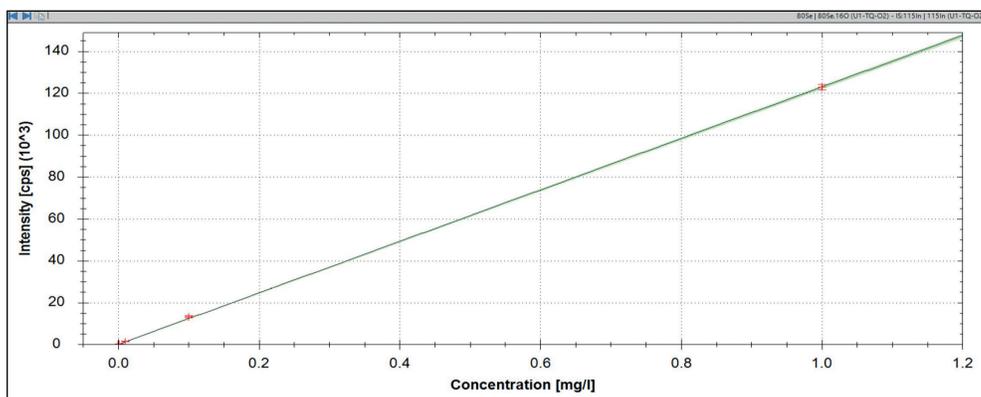


Figure 4. Calibration curve for ^{80}Se as $^{80}\text{Se}^{16}\text{O}$ at 96 m/z in TQ- O_2 mass shift mode

Robustness and productivity

Analysis of a high matrix sample requires robust analytical instrumentation; assessing method robustness in routine use is critical. To demonstrate the applicability of the proposed method in a routine laboratory, the same batch sequence (a series of >50 nickel sludge samples with ~12% TDS after digestion) was repeated twice a day for five consecutive days (plasma was ignited every testing day) without any system maintenance (such as cone cleaning etc.). All results demonstrate that the proposed setup is meeting the demands of analyzing solutions containing elevated amounts of nickel as the principal component of the matrix.

Table 5 shows a comparison of results obtained for a single sample out of the batch as an example. For simplicity, the table only displays the results obtained on days 1, 3, and 5. Very comparable results are obtained on all days, so that robust analysis of this challenging sample matrix is proven. In some cases, especially for elements typically found in higher concentrations, carry-over between different samples may be an issue, leading to slight variations in the results.

To simulate a typical data analysis experiment in routine, >50 samples were analyzed in ~6 h. For routine sample analysis, assessing the accuracy and precision of the acquired data is critical and, therefore, quality control samples were regularly analyzed as part of the batch sequence. Continuing calibration verifications (CCVs) and laboratory control standards (LCSs) can be performed periodically throughout the analytical run and automatically evaluated using the built-in feature set for quality control in the Qtegra ISDS Software.

Table 5. Assessment of trace elements impurities in a ~12% TDS Ni sludge sample (3 out of 5 working days). All concentrations reported in $\text{mg}\cdot\text{L}^{-1}$.

Analyte	Working day 1	Working day 3	Working day 5
^{23}Na	2,835	3,381	3,342
^{24}Mg	29.5	32.3	30.1
^{31}P as $^{31}\text{P}^{16}\text{O}$	0.3	0.6	0.3
^{33}S as $^{33}\text{S}^{16}\text{O}$	65,348	68,382	71,597
^{39}K	11.1	12.2	10.3
^{52}Cr	0.007	0.006	0.007
^{55}Mn	0.03	0.03	0.03
^{56}Fe	0.02	0.01	0.02
^{59}Co	15.6	15.7	15.5
^{61}Ni as $^{61}\text{Ni}^{16}\text{O}$	108,146	116,937	115,046
^{65}Cu	0.02	0.02	0.02
^{66}Zn	0.009	0.009	0.008
^{75}As as $^{75}\text{As}^{16}\text{O}$	0.01	0.01	0.01
^{80}Se as $^{80}\text{Se}^{16}\text{O}$	0.2	0.2	0.2
^{114}Cd	0.01	0.01	0.01
^{120}Sn	0.001	0.001	0.001
^{121}Sb	0.2	0.2	0.1
^{208}Pb	0.005	0.005	0.005
^{209}Bi	0.0001	0.0001	0.0001
^{238}U	0.0003	0.0003	0.0005

Both CCVs (5 samples in total per batch) and LCSs (10 samples in total per batch) were intermittently analyzed throughout the analytical run, indicating excellent agreement to the expected levels and hence suggesting the suitability of the method for routine use (Figures 5 and 6). Whereas the CCV samples contained all analytes of interest in the concentration indicated in Table 2, the LCS contained 7,000 mg·L⁻¹ of nickel to verify the correct determination of the matrix concentration.

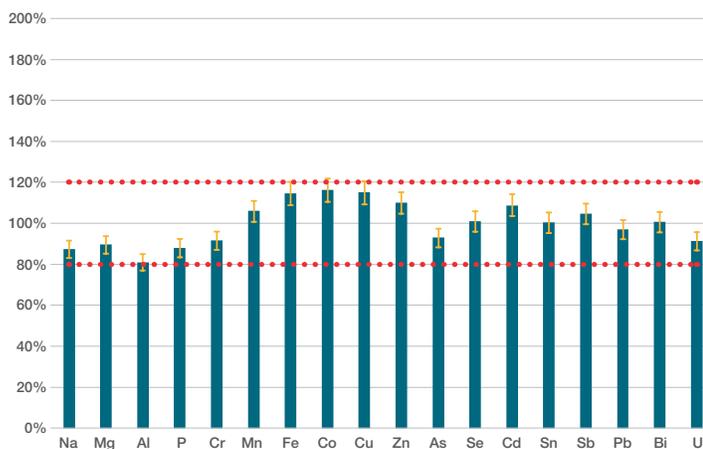


Figure 5. Recovery of elements in a QC standard (continuing calibration verification standards, concentration details shown in Table 2). Minimum and maximum dotted lines indicated acceptable interval ($\pm 20\%$) for recoveries and standard deviation values were derived from $n=10$ assessments.

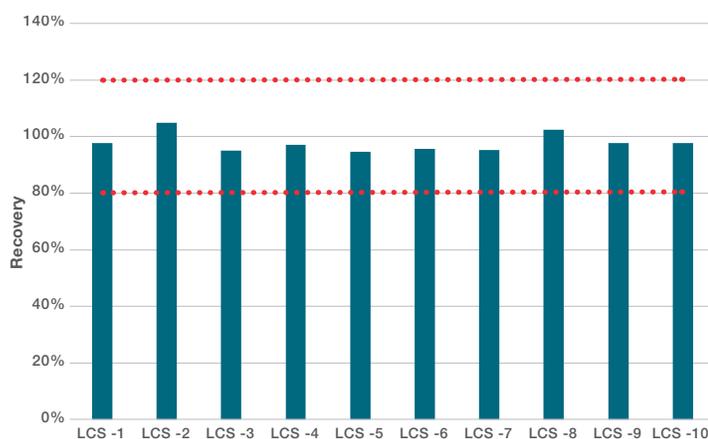


Figure 6. Results for QC 2 analysis (LCS with a Ni 7,000 mg·L⁻¹ standard solution) assessed continuously over five working days. Minimum and maximum dotted lines indicated acceptable interval ($\pm 20\%$) for recoveries.

Conclusions

The developed method allows reliable determination of a wide variety of impurities observed in nickel of different purity grades. The combination of automated inline dilution and argon gas dilution allows the analysis of samples containing up to 12% nickel after only 20-fold dilution. At the same time, quantitative assessment of a wide variety of contaminants is possible with high linearity and sensitivity, allowing assessment not only of impurities in crude products but also in refined and highly purified materials for use in demanding technical applications. The study also demonstrates that the proposed setup does allow the robust daily use in a routine laboratory, as excellent day-to-day reproducibility has been demonstrated without the need for maintenance or cleaning of the instrument.

Leveraging the possibility of triple quadrupole ICP-MS to use a combination of conventional modes for interference removal, such as He KED in combination with TQ acquisition modes for comprehensive interference removal for challenged analytes, ultra-trace multi-element analysis is achieved without sacrificing sensitivity or robustness of the system.

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