Determination of trace elements in steel using the Agilent 7900 ICP-MS

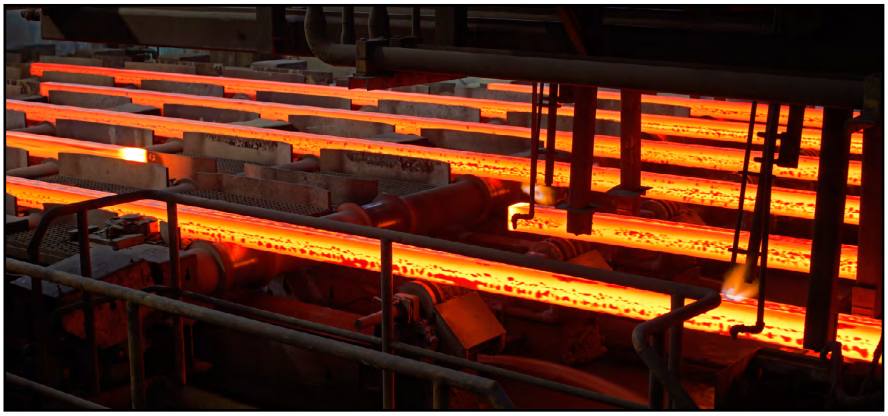
Application note

Metals

Authors

Kazuhiro Sakai

Agilent Technologies, Japan



Introduction

Monitoring and controlling the level of trace element impurities in metals and alloys is important, as impurities can affect the properties of the metal and may degrade the functionality of the finished component. ICP-OES is commonly used for the routine measurement of trace elements in metal samples because of its multi-element capability and tolerance of the high matrix level present in metal sample digests. However, the development of high purity metals and higher-performance alloys requires stricter control of a wider range of trace elements at lower concentrations, so a technique with lower detection limits than ICP-OES is required.

ICP-MS offers low detection limits for the elements of interest, but the technique has not previously been considered suitable for the analysis of high matrix samples such as metal digests. For example, conventional ICP-MS instruments may suffer from signal suppression and/or long-term signal drift due to matrix deposition on the interface cones, which affects the signal stability and the accuracy of the analytical results. To overcome this limitation, Agilent's Ultra High Matrix Introduction (UHMI) aerosol dilution technology has been developed to allow the

Agilent 7900 ICP-MS to measure samples containing higher total dissolved solids (TDS) levels. UHMI includes a modified connecting tube with a gas port to allow the introduction of precisely calibrated argon gas flow between the spray chamber and torch. The additional gas flow dilutes the sample aerosol, reducing the aerosol and matrix loading on the plasma and thereby permitting higher matrix levels to be analyzed without suffering matrix deposition or drift. A further significant benefit of UHMI is that the increased robustness of the plasma reduces signal suppression, ensuring that the analyte and internal standard (ISTD) signals are more consistent across a range of matrix levels. This means that simple, aqueous standards can normally be used, with no requirement to match the matrix of the standards to the major element content of the samples.

UHMI has extended the range of ICP-MS to include applications such as the measurement of high matrix soil samples [1], and salt matrix solutions [2]. In this work we developed a method using an Agilent 7900 ICP-MS with UHMI for the accurate determination of trace elements in steel samples, digested according to a standard method that results in solutions containing 0.5% TDS. The aim of this study was to evaluate the analytical performance and robustness of the new ICP-MS method for the analysis of digested steel samples, with reference to the requirements of ASTM International and Japan Industrial Standards (JIS) methods for steel analysis.

Experimental

Reagents and sample preparation

The three standard and certified reference materials used for this study were SRM 2165 Low Alloy Steel (from National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA), Japanese Steel Standard (JSS) 168-2 Carbon Steel and JSS 152-5 Alloy Steel (both from the Japan Iron and Steel Federation (JISF)).

A solution containing nitric acid (61%, EL Grade, Kanto Chemicals, Japan), hydrochloric acid (36%, EL Grade, Kanto Chemicals, Japan), and ultrapure water (UPW) was prepared at a 1:1:1 ratio by volume. Samples were prepared by adding 12 mL of the mixed acid solution to 0.5 g of sample in a beaker. The beaker was covered with a watch glass and, after 10 minutes pre-digestion at room temperature, the solution was gradually heated on a hotplate for approximately 30 minutes to 200 °C. After cooling for about 15 minutes, the sample digest was made up to 100 g with UPW and an aliquot was transferred to a 50 mL autosampler vial for analysis.

This sample preparation method is based on the JIS method G1258, except that the JIS method states an acid mix of 1:1:2 and a sample weight of 0.5 g/25 mL, whereas we used a mix of 1:1:1 and a sample weight of 0.5 g/12 mL in order to digest the samples more quickly and completely. The final sample matrix level measured in this work was 0.5 g of steel in 100 g digest solution, which is consistent with the final sample solutions from the preparation method described in the JIS method. This matrix level is higher than the typical limit for conventional ICP-MS measurement, so it provides a good illustration of the performance of UHMI.

Calibration standards were prepared in the same mixed acid solution (4 mL HNO_3 and 4 mL HCl diluted to 100 g with UPW), but without the addition of any Fe matrix. The use of non-matrix-matched calibration standards further illustrates the benefits of UHMI to reduce signal variation (suppression) due to the high matrix level in the steel sample digests.

A mixed internal standard (ISTD) solution was prepared from single element Sc, Y and Tb stock solutions (Kanto Chemicals, Japan), and added on-line using the standard ISTD mixing tee-connector. Sample tubing of 1.02 mm inner diameter (id) (black/white) and ISTD tubing of 0.25 mm id (blue/orange) was used.

Instrumentation

An Agilent 7900 ICP-MS was used for all measurements. The instrument was equipped with standard nickel sampling and skimmer cones, a standard glass concentric nebulizer, quartz spray chamber and quartz torch with 2.5 mm id injector. The optional UHMI aerosol dilution system was used to allow the high matrix steel sample digests to be measured over an extended period. The 7900 ICP-MS also features a fourth generation collision/reaction cell, the ORS^4. The ORS^4 includes a standard helium (He) mode cell gas line which provides effective removal of most common polyatomic interferences. The optional hydrogen (H_2) cell gas line was used to provide lower detection limits for certain analyte isotopes that suffer intense interference from plasma-derived polyatomic ions, including $^{14}N_2^+$ and $^{12}C^{16}O^+$ on $^{28}Si^+$ and $^{40}Ar^+$ on $^{40}Ca^+$. The 7900 ICP-MS also has the largest operating dynamic range of any quadrupole ICP-MS at up to 11 orders of magnitude, allowing routine measurement of both ultra-trace analytes and major elements in a single analysis. An Agilent ASX-520 autosampler was used to deliver the samples, contained in 50 mL vials, to the ICP-MS. The peristaltic pump speed was set to 0.1 rps throughout the sample analysis and rinse program, to minimize variation due to the physical differences (viscosity, surface tension, etc.) between the simple aqueous calibration standards and the 0.5 % steel digest samples. The plasma and ion lens parameters used are given in Table 1, and the acquisition parameters are listed in Table 2. Cell-related settings were optimized for each ORS[4] mode (He, High Energy (HE) He, H_2), but all plasma and ion lens tuning parameters were consistent for all three cell modes.

Table 1. Plasma and ion lens parameters

Cell mode	H_2	He	High Energy He
RF power (W)	1600		
Sampling depth (mm)	10		
Carrier gas (L/min)	0.45		
Dilution gas (L/min)	0.54		
Ext 1 (V)	0		
Ext 2 (V)	-190		
Omega Bias (V)	-120		
Omega Lens (V)	12.5		
Cell entrance (V)	-36	-32	-150
Cell exit (V)	-70		-150
Deflect (V)	-1.8	-2.0	-75
Plate B (V)	-60		-150
ORS gas flow (mL/min)	5	4	10
Oct P bias (V)	-20		-100

Table 2. Acquisition parameters

Analyte	Mass	Internal standard	Gas mode	Integration time (sec)
Mg	24	45 Sc	He	1
Al	27	45 Sc	He	3
Si	28	45 Sc	H_2	0.5
P	31	45 Sc	HEHe	5
Ca	40	45 Sc	H_2	0.3
Ti	48	89 Y	HEHe	3
V	51	89 Y	He	0.6
Cr	52	89 Y	HEHe	0.6
Mn	55	89 Y	He	0.6
Co	59	89 Y	He	0.6
Ni	60	89 Y	He	0.6
Cu	63	89 Y	He	0.6
As	75	89 Y	He	3
Se	78	89 Y	HEHe	5
Zr	90	89 Y	He	0.1
Nb	93	89 Y	He	0.1
Mo	95	89 Y	He	0.3
Sn	118	89 Y	He	0.3
Sb	121	89 Y	He	0.3
Te	125	89 Y	He	0.1
La	139	89 Y	He	0.1
Ce	140	89 Y	He	0.1
Ta	181	159 Tb	He	0.1
W	182	159 Tb	He	0.1
Pb	208	159 Tb	He	0.1
Bi	209	159 Tb	He	0.1

Results and discussion

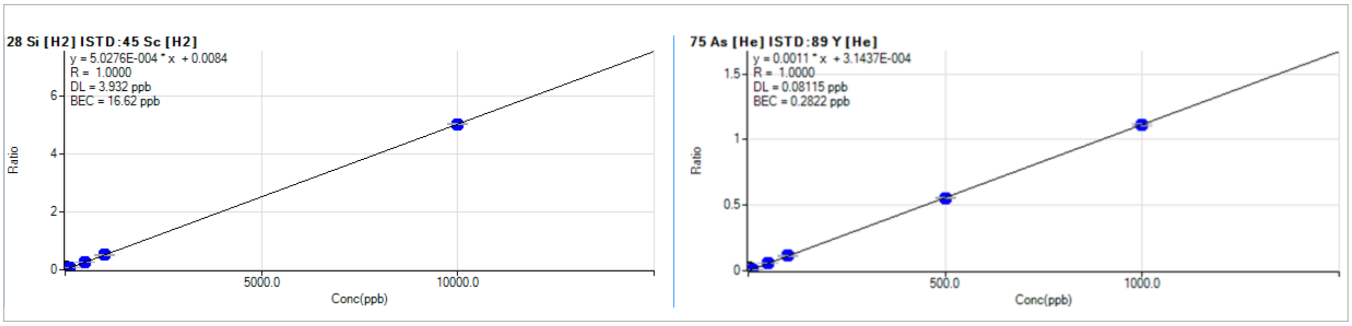


Figure 1. Calibration curves for ^{28}Si in H_2 mode and ^{75}As in He mode, showing reduction of $^{14}N_2$ and $^{12}C^{16}O$ interferences on ^{28}Si, and $^{40}Ar^{35}Cl$ on ^{75}As.

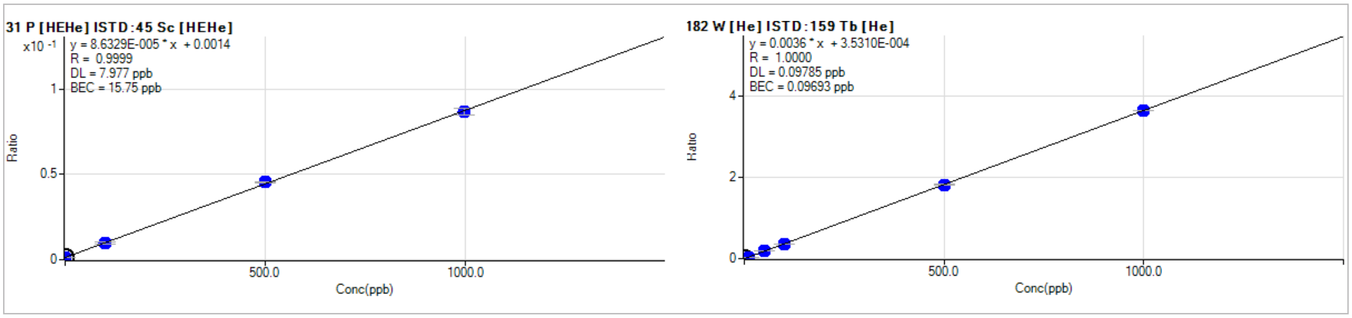


Figure 2. Calibration curves for ^{31}P in HEHe mode and ^{182}W in He mode, showing reduction of $^{12}C^{18}OH$, $^{14}N^{16}OH$, $^{15}N_2H$, $^{15}N^{16}O$ and $^{13}C^{18}O$ polyatomic interferences on ^{31}P.

Calibration linearity

Calibration curves were prepared using calibration standard solutions ranging from 10 ppb to 10,000 ppb. Linear calibrations with a correlation coefficient greater than 0.9999 were obtained for all elements. Figures 1 and 2 show calibration curves for Si, As, P and W, representing elements measured in all three cell gas modes.

Method detection limits

ASTM and JIS methods are commonly used as referee methods to test metals and alloys, such as carbon steel, low-alloy steel, silicon electrical steel, ingot iron, and wrought iron, for compliance with compositional specifications. Table 3 summarizes the analyte lists and required limit of quantification specified in the ASTM and JIS standard methods; for each element, the lowest limit in the five test methods is shown in bold. For example, aluminum can be measured within the range from 0.001% to 1.5% in the solid material (10 mg/kg (ppm) to 15,000 mg/kg), using ASTM E350-12.

Typical 7900 ICP-MS 3 sigma method detection limits (MDLs) for all of the specified elements are also shown in Table 4. MDLs were calculated from the standard deviation of 10 preparation blank samples multiplied by the dilution factor. The results show that the 7900 ICP-MS has sufficient sensitivity to satisfy ASTM and JIS requirements for all elements measured, achieving detection limits much lower than the required values and the typical MDLs possible by ICP-OES [3, 4]. Boron and sulfur are included in the methods, but were outside the scope of this application method. Boron is a highly volatile element, so the sample preparation used in this study was not appropriate to retain B for analysis. Sulfur is difficult to analyze at low enough levels for this application, using conventional quadrupole ICP-MS. Tellurium (Te) is not a required element in any of the standard methods, but it was included in the analyte list because a reference value is provided for Te in the reference material NIST 2165 Low Alloy Steel.

Table 3. Lower limit of quantitation covered by standard test methods for the chemical analysis of metals and alloys, and 3 sigma MDLs for the Agilent 7900 ICP-MS. All data are shown as mg/kg (ppm) relative to the original solid material, for ease of comparison.

Analyte	ASTM E350-12	ASTM A751-14	JIS G1258-1	JIS G1258-2	JIS G1258-3	MDL (mg/kg)
B	5	**2**	10			
Mg		**2**	5	5	10	0.044
Al	**10**		40			0.102
Si	**10**		100			0.861
P	**10**		30			1.675
S	**10**					
Ca	5	**2**	5	10	40	0.298
Ti	20		**10**	10	100	0.045
V	50		**20**	100	100	0.008
Cr	50		100	100	**30**	0.125
Mn	**100**		100	100	1000	0.027
Co	100		**30**	100	100	0.002
Ni	**50**		100	100	100	0.023
Cu	**50**		100	100	300	0.009
As	**5**		10	30	20	0.006
Se	**10**					0.061
Zr	50	**10**	100	100	30	0.018
Nb	20			100	**10**	0.013
Mo	**20**		100	100	200	0.006
Sn	**20**					0.015
Sb	**20**					0.007
Te						0.082
La	**10**	10				0.001
Ce	50	**10**				0.002
Ta		**50**				0.003
W	**50**			1000	1000	0.009
Pb	**10**					0.034
Bi	**50**					0.005

A range of elements from major (sub-percent) to trace (single ppm) levels was determined in SRM NIST 2165 Low Alloy Steel. The results obtained with the 7900 ICP-MS are shown in Table 4, together with the expected values. Excellent agreement was obtained in all cases. In order to further validate the method, a spike recovery test at 100 ppb was carried out for the 11 non-certified elements, and the results are shown in Table 5. Excellent spike recoveries were achieved, with most elements within 95% to 105% recovery.

Table 4. Determination of elements in SRM NIST 2165 Low Alloy Steel. Units: % for certified elements; mg/kg for uncertified elements

Analyte	Cell mode	Certified (%)	Measured (%)	Recovery (%)
31 P	[HEHe]	0.0052 ± 0.0002	0.0052	99
48 Ti	[HEHe]	0.0051 ± 0.0002	0.0050	97
51 V	[He]	0.0040 ± 0.0002	0.0042	106
52 Cr	[HEHe]	0.050 ± 0.002	0.050	99
55 Mn	[He]	0.144 ± 0.003	0.142	99
59 Co	[He]	0.0012 ± 0.0002	0.0013	104
60 Ni	[He]	0.155 ± 0.002	0.155	100
63 Cu	[He]	0.0012 ± 0.0002	0.0012	99
75 As	[He]	0.0010 ± 0.0005	0.0010	104
93 Nb	[He]	0.0004 ± 0.0001	0.0003	85
95 Mo	[He]	0.0055 ± 0.0005	0.0053	96
118 Sn	[He]	0.002 ± 0.001	0.002	95
121 Sb	[He]	0.0010 ± 0.0005	0.0010	102
208 Pb	[He]	0.0003 ± 0.0002	0.00028	93
		Information (mg/kg)	**Measured (mg/kg)**	**Recovery (%)**
24 Mg	[He]	<1	0.4	N/A
27 Al	[He]	60	56	93
28 Si	[H_2]	40	47	116
78 Se	[HEHe]	35	33	95
125 Te	[He]	30	31	105
181 Ta	[He]	40	34	86
209 Bi	[He]	<1	0.6	N/A

Table 5. Recovery test for non-certified elements in SRM NIST 2165 Low Alloy Steel spiked at 100 ppb level. Units: µg/L (ppb)

Mass	Gas mode	Unspiked sample (ppb)	Spiked sample (ppb)	Recovery (%)
24 Mg	[He]	3.3	101	98
27 Al	[He]	271	372	101
40 Ca	[H_2]	18	122	104
78 Se	[HEHe]	161	257	96
90 Zr	[He]	ND	102	102
125 Te	[He]	151	243	92
139 La	[He]	ND	98	98
140 Ce	[He]	ND	98	98
181 Ta	[He]	154	243	89
182 W	[He]	1.0	102	101
209 Bi	[He]	3.1	98	95

ND: Not detected

Results for the two JSS steel CRMs also show excellent agreement with the certified values, although the result for Ca was high in JSS 168-2 (Table 6). Qualifying data was acquired for ^{44}Ca in JSS 168-2 using HE-He and H_2 modes. Both measurements were higher than the expected value but almost the same as the ^{40}Ca value measured in H_2 mode, suggesting the high Ca reading is due to contamination.

Sixty replicates of the spiked Fe sample, containing P at 500 ppb, Si at 2 ppm, and all other elements at 100 ppb, were measured over 6 hours. Long-term stability was excellent (<3.0% RSD) for the elements spiked into the 0.5 % Fe matrix, as shown in Figure 3. The excellent stability and lack of systematic drift demonstrates the superior matrix tolerance of the 7900 ICP-MS with UHMI.

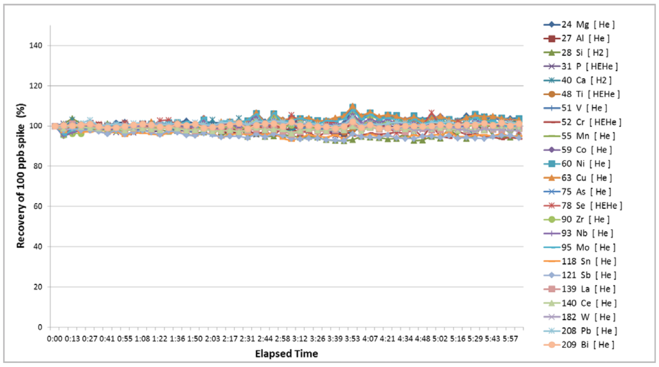


Figure 3. Six hour stability of trace elements spiked into 0.5% Fe solution.

Table 6. Determination of elements in CRMs JSS 152-5 Alloy Steel and JSS 168-2 Carbon Steel

		JSS 152-5 Alloy Steel			JSS 168-2 Carbon Steel		
Analyte	**Gas mode**	**Measured (%)**	**Reference (%)**	**Recovery (%)**	**Measured (%)**	**Reference (%)**	**Recovery (%)**
27 Al	[He]				0.051	0.047	108
28 Si	[H_2]	0.23	0.25	91	0.23	0.23	100
31 P	[HEHe]	0.013	0.016	82	0.005	0.006	83
40 Ca	[H_2]				0.0009	0.0006	145
48 Ti	[HEHe]				0.066	0.066	100
51 V	[He]	0.10	0.11	94			
52 Cr	[HEHe]	0.50	0.52	95	0.011	0.011	96
55 Mn	[He]	0.40	0.42	96	0.41	0.40	103
60 Ni	[He]	1.84	1.96	94	0.011	0.013	88
63 Cu	[He]	0.44	0.45	99			
75 As	[He]				0.010	0.009	114
95 Mo	[He]	1.03	1.03	100	0.103	0.094	109
118 Sn	[He]				0.005	0.005	106

Conclusions

The Agilent 7900 ICP-MS with ORS^4 and optional UHMI enables the analysis of high matrix steel sample digests, which simplifies sample preparation and opens up applications previously beyond the capabilities of ICP-MS. In this study, a method has been developed for the analysis of elements of interest in steel samples prepared using acid digestion. The method shows good accuracy and stability for major (% levels in the solid metal) and trace level (ppm in the solid) elements in three steel reference materials, measured as 0.5% Fe sample digests. This demonstrates that the Agilent 7900 ICP-MS with UHMI offers the required matrix tolerance and dynamic range to measure these high matrix samples, while also offering significantly lower detection limits than the established techniques used for this application.

Steel analysis standards specified by ASTM and JIS recommend a variety of analytical techniques for the elemental analysis of steel samples. However, this study has shown that ICP-MS is suitable for the analysis of almost all of the required elements, following a relatively simple sample preparation procedure and without the need to matrix match the calibration standards for Fe concentration.

References

1. Kazuo Yamanaka and Steve Wilbur, Maximizing productivity for high matrix sample analysis using the Agilent 7900 ICP-MS with ISIS 3 discrete sampling system, Agilent publication 5991-5208EN (2014)

2. Wim Proper, Ed McCurdy and Junichi Takahashi, Performance of the Agilent 7900 ICP-MS with UHMI for high salt matrix analysis, Agilent publication 5991-4257EN (2014)

3. Cheng Yonga, *Procedia Engineering*, 24, 447 – 453 (2011)

4. Tran T. Nham, Analysis of Metals in High Alloy Steel by ICP-OES, Agilent publication ICPES-6 (2010)

www.agilent.com/chem

Published August 20 2015
Publication number: 5991-6116EN

Agilent Technologies