Application Note

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Accurate Analysis of Factory Effluents using ICP-MS with Aerosol Dilution

Agilent 7850 ICP-MS with UHMI provides the sensitivity, dynamic range, and robustness for analysis of high matrix samples

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Introduction

The composition of industrial wastewater, also referred to as factory or trade effluent, can vary widely depending on the type of industry, manufacturing processes, and the substances or materials that are used or produced in the facility. These types of wastewater tend to contain a complex mixture of chemical and biological components, as well as dissolved salts and minerals. In many countries and regions, industrial sites are required to obtain a permit from the relevant environmental authority that outlines discharge limits, monitoring requirements, and other conditions to ensure compliance with environmental standards. Typically, waste streams are sampled and monitored to ensure that the factory complies with the quality limits (e.g., concentrations for specific chemicals and elements) as defined in the permit.

A fast, robust multi-element technique such as Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) is often used for elemental analysis of factory wastewater, especially of high concentration elements. Regulatory methods for the analysis of wastewater, such as US EPA 200.7, use ICP-OES.[1] Increasingly, however, many laboratories use ICP-Mass Spectrometry (ICP-MS) to determine dissolved metals in effluents and wastewaters, in accordance with regulatory methods such as EPA 200.8 (for wastewaters)[2] or non-regulatory Hazardous Waste Test Methods SW-846 method 6020B (for solids)[3]. ICP-MS is preferred to ICP-OES if better detection limits are required, especially for toxic metals like arsenic, cadmium, lead, and mercury. Given the greater sensitivity of ICP-MS compared to ICP-OES, relatively higher dilution factors are often applied to the samples before analysis by ICP-MS. This extra dilution step takes time and risks the introduction of manual errors during the procedure or contaminants from the diluent.

All Agilent ICP-MS systems have a highly robust plasma, as evidenced by the CeO/Ce ratio of less than 1.5%. They are also equipped with an Ultra High Matrix Introduction (UHMI) system that increases the overall matrix tolerance of the technique using automated aerosol dilution technology.[4] UHMI adds a precisely controlled flow of argon (Ar) gas to dilute the aerosol stream containing the sample, offering a better, simpler, more reliable approach than liquid dilution of samples. When a high matrix sample is introduced to the ICP-MS, the dilution gas reduces the aerosol density and fragments the droplets, leading to higher plasma temperature, better matrix decomposition, fewer interferences, and reduced maintenance. In practice, the UHMI aerosol dilution technique enables samples with high and variable matrix levels to be measured by ICP-MS, without requiring sample-specific dilutions or matrix matching of the calibration standards. Agilent ICP-MS systems also have an exceptionally wide detector dynamic range of 10 to 11 orders of magnitude, so high concentration elements can be measured in the same run as the trace analytes.

In this study, the Agilent 7850 ICP-MS with UHMI was used to analyze 32 elements in factory wastewaters without extra manual dilution of the samples while maintaining the high sensitivity of the technique. The elements included: aluminum, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, phosphorus, potassium, selenium, silver, sodium, strontium, thallium, thorium, tin, tungsten, uranium, vanadium, and zinc.

Experimental

Instrumentation

An Agilent 7850 ICP-MS with UHMI and Octopole Reaction System (ORS^4) collision/reaction cell (CRC) was used for the analysis of wastewater digests. The 7850 ICP-MS was fitted with the standard sample introduction system, consisting of a MicroMist glass concentric nebulizer, temperature-controlled quartz spray chamber, and a quartz torch with 2.5 mm id injector. A nickel-tipped copper sampling cone and a nickel skimmer cone were used. An Agilent SPS 4 autosampler was used to deliver the sample to the ICP-MS.

Agilent ICP-MS MassHunter software includes a series of preset methods to assist the analyst in setting up the method. In this study, a preset method with a suitable UHMI aerosol dilution level (UHMI-8) was selected to accommodate the high-matrix samples. Plasma parameters were applied automatically based on the preset plasma setting, and all lenses were autotuned.

The ORS^4 was used to control polyatomic interferences that impede accurate measurement of some analytes. Samples with high and variable major element content can be difficult to analyze by ICP-MS due to the formation of argon-based interferences (such as $^{40}Ar^{35}Cl$ on ^{75}As and $^{40}Ar^{16}O$ on ^{56}Fe). Plus variable and unpredictable matrix-based polyatomic interferences such as $^{40}Ca^{35}Cl$ on ^{75}As, $^{40}Ca^{16}O^+$ on ^{56}Fe, and $^{39}K^{16}O$ on ^{55}Mn. The ORS^4 cell is the optimum configuration for He mode, effectively reducing all common, matrix-based polyatomic interferences under one set of standard cell conditions by kinetic energy discrimination (KED). Helium KED enables new as well as experienced users to quickly and confidently acquire reliable and accurate data for all elements.

Enhanced (high energy) helium (HEHe) mode is also available to deal with overlaps from high-intensity background species such as Ar_2 on Se at m/z 78, NO/NOH on ^{31}P, and $^{40}Ar^{16}O$ on ^{56}Fe.[5] Also, depending on the objectives of the analysis, analysts can use a reaction gas, such as hydrogen, in the ORS^4 if better detection limits are required for a few selected analytes. Data acquired using H_2 mode for ^{40}Ca (overlapped by ^{40}Ar), iron (^{56}Fe), and selenium (^{78}Se) is reported in this study for comparison purposes with the HEHe mode results for ^{44}Ca, ^{56}Fe, and ^{78}Se.

The 7850 ICP-MS was controlled using ICP-MS MassHunter software version 5.3. Instrument operating conditions are shown in Table 1.

Table 1. Agilent 7850 ICP-MS operating conditions.

ICP-MS Parameter	No Gas	He	HEHe	*H_2
Plasma Mode	UHMI-8			
RF Power (W)	1600			
Sampling Depth (mm)	10			
Nebulizer Gas Flow (L/min)	0.68			
Dilution Gas Flow (L/min)	0.27			
Lenses	Autotune			
Cell Gas Flow Rate (mL/min)	-	5.0	10.0	6.0
Energy Discrimination (V)	5.0	5.0	7.0	3.0
Elements	Be, B	Ag, Al, As, Ba, Bi, Ca, Cd, Co, Cr, Cu, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Sn, Sr, Th, Tl, U, V, W, Zn	Ca, P, Fe, Se	Ca, Fe, Se

*The shaded parameters were set automatically. *H_2 mode was used for comparative purposes with HEHe mode for Ca, Fe, and Se.*

Samples and sample preparation

Five wastewater samples (A to E) were analyzed in this study. The industrial wastewaters were obtained from (A) a university, (B) a printed circuit board plating facility, (C) a chemical manufacturing site, (D) an industrial rubber manufacturer, and (E) a metal processing and coating company.

Twelve aliquots of each effluent/wastewater sample (A to E) were prepared according to the method outlined in JIS K 0102 (Testing methods for industrial wastewater)[6]. 25 mL of the wastewater samples were measured into a 50 mL digestion tube (digiTUBE, SCP Science, Ontario, Canada). 1 mL of concentrated HNO_3 (UltrapurTM-100, KANTO Chemical Co, Japan) was added to the samples and the tubes were then heated to between 120 and 130 ºC on a heat block (Smart Block II, BL TEC, Japan). When the liquid volume had decreased to about 20 mL, the solutions were checked for suspended solids. If any undissolved matter was observed, the sample solutions were reheated to 120 and 130 ºC. If any undigested or solubilized solids remained, the samples were filtered through grade 5A (pore size of 7 µm), 125 mm diameter filter paper (ADVANTEC Toyo, Tokyo, Japan). The sample solutions were then diluted to 25 mL with ultrapure water (UPW, Milli-Q, Merck Millipore). The 12 aliquots of each sample were transferred into a 500 mL PE bottle. A small amount of HCl (Electronic Grade, KANTO Chemical Co) was added (1.5 mL) to ensure the stability of elements such as Sb and Hg. The standard He cell mode of the 7850 ICP-MS removes any Cl-based interferences that would be formed from the added chloride matrix.

The JIS K 0102 sample preparation method was developed for the analysis of some specific elements, so may not be applicable to all elements. Therefore, the focus of this study was on ensuring the accuracy of effluent measurements, rather than evaluating the sample preparation method, which can vary depending on local regulations for wastewater.

Four solution-based certified reference materials (CRMs) were included in the study: NIST 1643f Trace Elements in Water (Gaithersburg MD, USA) and three High Purity Standards Certified Waste Water Trace Metals (CWW-TM) CRMs, A, B, and E (HPS, North Charleston, SC, USA). The NIST 1643f SRM was diluted 10-fold and the CWW-TM-A, B, and E CRMs were diluted 100-fold with the calibration blank solution (4% HNO_3 + 0.5% HCl).

To simulate high matrix wastewater samples, the NIST 1643f and CWW-TM-A, B, and E CRMs were spiked during dilution so that the final concentration of matrix elements was 1000 mg/L (ppm), comprising 250 ppm of each of Na, Mg, K, and Ca. The calibration blank solution (4% HNO_3 + 0.5% HCl) was used as the diluent.

Calibration standards

The calibration standards and samples were prepared in an acid matrix of 4% HNO_3 (Electronic Grade, KANTO Chemical Co) and 0.5% HCl (Electronic Grade, KANTO Chemical Co) using standard solutions from Agilent, SPEX CertiPrep (Metuchen, NJ, USA), and KANTO Chemicals (Japan). Five- or six-point calibrations, including the calibration blank, were prepared at the concentration ranges given in Table 2.

Table 2. Calibration range of analytes. Concentration units: μg/L (ppb).

Elements	Calibration Range	Calibration Points
Al, Na, Mg, K, Ca, P, Fe	5000 to 100000	Five points (including blank)
Hg	0.5 to 10	
Sb, Ag	5 to 100	Six points (including blank)
Be, B, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Sn, Ba, W, Pb, Tl, Bi, Th, U	5 to 500	

The Internal Standard (ISTD) solution containing 10 ppm ^{6}Li, and 1 ppm of Sc, Ge, Y, Rh, In, Te, Tb, Lu, and Ir was added online via a T-connector.

Results and discussion

Calibration

Representative calibration curves are presented in Figure 1. The plots for Na, K, As, and Hg show excellent linearity across the calibrated range, with correlation coefficients of 0.9998 or better.

Detection limits

All analytes were measured using the acquisition parameters listed in Table 1 (UHMI setting of 8). The detection limits (DLs) were calculated from three times the standard deviation (SD) of 10 measurements of the calibration blank and the method detection limits (MDLs) were calculated from three times the SD of the sample preparation blank (Table 3). The comparative MDLs for Ca, Fe, and Se show that lower limits were obtained in H_2 mode than HEHe mode.

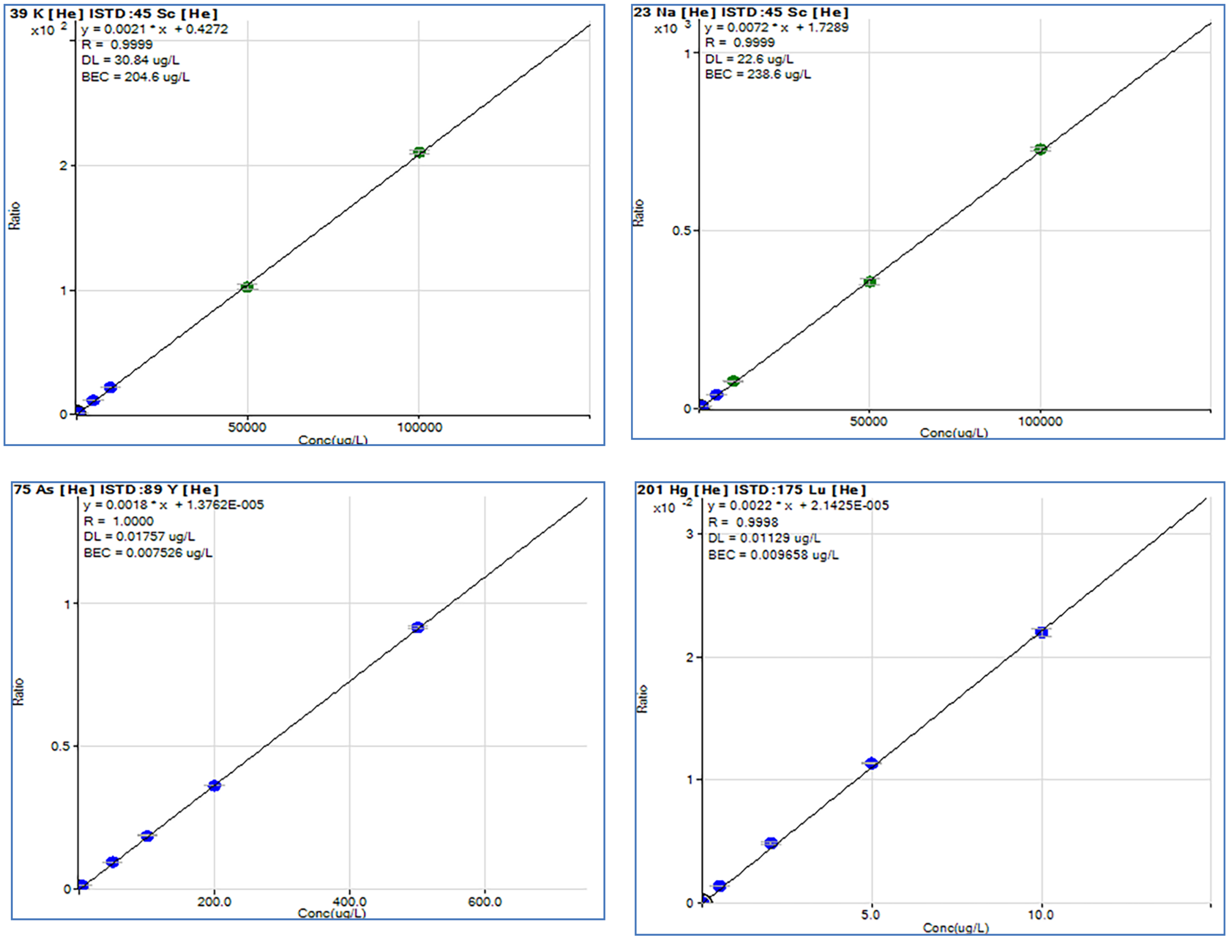


Figure 1. Representative calibration curves for two major (Na and K) and two trace (As and Hg) elements.

Table 3. Detection limits for Agilent 7850 ICP-MS using an aerosol dilution factor of 8 (UHMI-8).

Analyte	ISTD	Gas Mode	DL, ppb	MDL, ppb
9 Be	6 Li	No gas	0.012	0.010
11 B	6 Li	No gas	0.30	0.28
23 Na	45 Sc	He	22.6	29.3
24 Mg	45 Sc	He	0.71	1.69
27 Al	45 Sc	He	0.72	1.27
31 P	45 Sc	HEHe	2.91	4.64
39 K	45 Sc	He	30.8	57.4
40 Ca	45 Sc	H_2	0.31	6.10
44 Ca	45 Sc	HEHe	3.38	21.9
51 V	45 Sc	He	0.024	0.020
52 Cr	45 Sc	He	0.052	0.082
55 Mn	72 Ge	He	0.088	0.091
56 Fe	72 Ge	HEHe	0.12	0.28
56 Fe	72 Ge	H_2	0.041	0.49
59 Co	72 Ge	He	0.004	0.006
60 Ni	72 Ge	He	0.029	0.061
63 Cu	72 Ge	He	0.020	0.036
66 Zn	72 Ge	He	0.043	0.11
75 As	89 Y	He	0.018	0.017
78 Se	89 Y	HEHe	0.16	0.24
78 Se	89 Y	H_2	0.035	0.026
88 Sr	89 Y	He	0.081	0.13
95 Mo	89 Y	He	0.045	0.042
107 Ag	115 In	He	0.002	0.014
111 Cd	115 In	He	0.003	0.005
118 Sn	115 In	He	0.027	0.024
121 Sb	125 Te	He	0.12	0.47
137 Ba	115 In	He	0.029	0.053
182 W	175 Lu	He	0.071	0.22
201 Hg	175 Lu	He	0.011	0.037
205 Tl	193 Ir	He	0.009	0.008
Pb*	193 Ir	He	0.004	0.011
209 Bi	193 Ir	He	0.009	0.014
232 Th	193 Ir	He	0.010	0.008
238 U	193 Ir	He	0.001	0.001

**Pb was measured as the sum of the three most abundant isotopes, 206, 207 and 208. The shaded data obtained in H_2 and HEHe mode is for comparative purposes.*

Analysis of CRMs

The four diluted CRMs containing relatively low concentrations of total dissolved solids (TDS) were each analyzed three times during the sequence, and the mean concentration and recovery were calculated for each analyte (Table 4). All the certified major and trace elements gave recoveries within 90 to 105% of the certified values, confirming the accuracy of the method for the analysis of low matrix waters and wastewaters. Not all the analytes are certified in all the reference materials, so the blank cells in Table 4 indicate the absence of a certified value.

In most real-world environmental samples, as represented by the NIST 1643f SRM, the concentration of calcium (Ca) greatly exceeds that of strontium (Sr). Good recoveries of 97 and 105% respectively were achieved for both ^{40}Ca (determined in H_2 mode) and ^{44}Ca (HEHe mode) in NIST 1643f. However, there was a difference in the ^{40}Ca and ^{44}Ca results in the other CRMs due to a higher concentration of Sr compared to Ca. The three CWW-TM CRMs contain Sr (ranging from 25 to 200 ppb) but no Ca, which leads to the formation of a doubly-charged ion interference by $^{88}Sr^{++}$ on $^{44}Ca^{+}$. The $^{88}Sr^{++}$ interference explains the difference in the measured results for ^{44}Ca and ^{40}Ca in the three CWW-TM CRMs (Table 4). The data highlights an advantage of H_2 mode for removing the ^{40}Ar interference on ^{40}Ca.

To show the effects of the Sr^{++} interference, none of the data presented in Table 4 has been corrected using interference correction equations. However, if interference correction were applied to the ^{44}Ca data obtained in HEHe mode, the results would be equivalent to those generated for ^{40}Ca in H_2 mode.

Table 4. Recovery of certified values for diluted CRMs. Concentration units: ppb.

		NIST 1643f (10x diluted)			CWW-TM-A (100x diluted)		
Element	**Gas Mode**	**Measured**	**Certified**	**Recovery (%)**	**Measured**	**Certified**	**Recovery (%)**
9 Be	No gas	1.35	1.353	99	9.86	10	99
11 B	No gas	13.8	15.08	92	49.0	50	98
23 Na	He	1796	1864	96	<DL	-	-
24 Mg	He	711	738	96	<DL	-	-
27 Al	He	13.7	13.25	104	50.7	50	101
31 P	HEHe	<DL	-	-	<DL	-	-
39 K	He	174	191.33	91	<DL	-	-
40 Ca	H_2	2831	2914	97	<DL	-	-
44 Ca	HEHe	3067	2914	105	373**	-	-
51 V	He	3.46	3.571	97	47.4	50	95
52 Cr	He	1.79	1.832	97	47.7	50	95
55 Mn	He	3.62	3.677	98	48.6	50	97
56 Fe	HEHe	9.53	9.251	103	49.9	50	100
56 Fe	H_2	9.48	9.251	102	48.8	50	98
59 Co	He	2.54	2.505	101	50.3	50	101
60 Ni	He	5.82	5.92	98	49.3	50	99
63 Cu	He	2.12	2.144	99	50.1	50	100
66 Zn	He	7.62	7.37	103	49.9	50	100
75 As	He	5.48	5.685	96	9.55	10	96
78 Se	HEHe	1.19	1.1583	103	9.82	10	98
78 Se	H_2	1.09	1.1583	95	10.2	10	102
88 Sr	He	31.1	31.1	100	48.6	50	97
95 Mo	He	10.9	11.42	96	47.4	50	95
107 Ag	He	0.086	0.09606	90	9.60	10	96
111 Cd	He	0.58	0.583	100	9.84	10	98
118 Sn	He	<DL	-	-	<DL	-	-
121 Sb	He	5.73	5.49	104	10.2	10	102
137 Ba	He	50.5	51.31	98	48.7	50	97
182 W	He	<DL	-	-	<DL	-	-
201 Hg	He	0.022	-	-	0.03	-	-
205 Tl	He	0.66	0.6823	97	9.60	10	96
Pb*	He	1.81	1.8303	99	49.5	50	99
209 Bi	He	1.27	1.25	101	<DL	-	-
232 Th	He	<DL	-	-	0.009	-	-
238 U	He	<DL	-	-	<DL	-	-

*Pb was measured as the sum of the three most abundant isotopes, 206, 207 and 208. Blank cells indicate the absence of a reference or certified value. The shaded data obtained in H_2 and HEHe mode is for comparative purposes. **The high measured value for ^{44}Ca in HEHe mode is due to ^{88}Sr^{++} interference on ^{44}Ca^{+} (Ca: 0 ppb, Sr: 50 ppb in CWW-TM-A) – an interference correction equation could be applied to correct for the interference.

Table 4 continued. Recovery of certified values for diluted CRMs. Concentration units: ppb.

		CWW-TM-B (100x diluted)			CWW-TM-E (100x diluted)		
Element	**Gas Mode**	**Measured**	**Certified**	**Recovery (%)**	**Measured**	**Certified**	**Recovery (%)**
9 Be	No gas	50.2	50	100	5.03	5	101
11 B	No gas	201	200	100	26.8	25	107
23 Na	He	<DL	-	-	<DL	-	-
24 Mg	He	<DL	-	-	<DL	-	-
27 Al	He	205	200	103	24.9	25	100
31 P	HEHe	<DL	-	-	<DL	-	-
39 K	He	<DL	-	-	<DL	-	-
40 Ca	H_2	<DL	-	-	<DL	-	-
44 Ca	HEHe	1498**	-	-	180**	-	-
51 V	He	193	200	96	23.9	25	96
52 Cr	He	192	200	96	23.9	25	96
55 Mn	He	197	200	98	24.6	25	99
56 Fe	HEHe	200	200	100	25.6	25	102
56 Fe	H_2	195	200	98	25.0	25	100
59 Co	He	202	200	101	25.5	25	102
60 Ni	He	196	200	98	25.0	25	100
63 Cu	He	197	200	99	25.4	25	102
66 Zn	He	200	200	100	25.3	25	101
75 As	He	48.0	50	96	4.82	5	96
78 Se	HEHe	49.5	50	99	5.08	5	102
78 Se	H_2	49.2	50	99	5.04	5	101
88 Sr	He	197	200	99	24.6	25	98
95 Mo	He	192	200	96	23.9	25	96
107 Ag	He	48.4	50	97	4.93	5	99
111 Cd	He	49.4	50	99	25.1	25	100
118 Sn	He	<DL	-	-	0.06	-	-
121 Sb	He	50.8	50	102	5.02	5	100
137 Ba	He	198	200	99	25.2	25	101
182 W	He	<DL	-	-	<DL	-	-
201 Hg	He	0.16	-	-	0.02	-	-
205 Tl	He	48.6	50	97	4.94	5	99
Pb*	He	198	200	99	25.5	25	102
209 Bi	He	0.01	-	-	<DL	-	-
232 Th	He	<DL	-	-	<DL	-	-
238 U	He	<DL	-	-	<DL	-	-

**Pb was measured as the sum of the three most abundant isotopes, 206, 207 and 208. The shaded data obtained in H_2 and HEHe mode is for comparative purposes. ** The high measured value for Ca is due to $^{88}Sr^{++}$ interference on $^{44}Ca^{+}$ (Ca: 0 ppb and Sr: 200 ppb in CWW-TM-B and Ca: 0 ppb and Sr: 25 ppb in CWW-TM-E) – an interference correction equation could be applied to correct for the interference.*

CRMs spiked with 1000 ppm matrix elements

To simulate a more representative high matrix industrial wastewater sample with a relatively low concentration of analytes, the four CRMs were diluted by a factor of 10 or 100 and then spiked with 1000 ppm matrix elements (250 ppm each of Na, Mg, K, and Ca). The spiked concentrations of matrix elements corresponded to concentrations of 10,000 ppm (NIST 1643f) and 100,000 ppm (other CRMs) in the original CRM samples.

All certified elements recovered within 91 to 110% of the certified values, confirming the accuracy of the method for the analysis of multiple elements in high matrix water (equivalent to 10,000 ppm) and wastewater (equivalent to 100,000 ppm matrix) samples.

Table 5. Recovery of certified values in high-matrix spiked CRMs. Concentration units: ppb.

		NIST 1643f (10x diluted) + 1000 ppm matrix			CWW-TM-A (100x diluted) + 1000 ppm matrix		
Element	**Gas Mode**	**Measured**	**Certified**	**Recovery (%)**	**Measured**	**Certified**	**Recovery (%)**
9 Be	No gas	1.30	1.353	96	9.69	10	97
11 B	No gas	13.83	15.08	92	47.0	50	94
27 Al	He	12.32	13.25	93	49.2	50	98
31 P	HEHe	<DL	-	-	<DL	-	-
51 V	He	3.37	3.571	94	46.4	50	93
52 Cr	He	1.71	1.832	93	47.8	50	96
55 Mn	He	3.44	3.677	94	48.8	50	98
56 Fe	HEHe	9.12	9.251	99	49.1	50	98
56 Fe	H_2	9.34	9.251	101	49.2	50	98
59 Co	He	2.48	2.505	99	45.6	50	91
60 Ni	He	5.87	5.92	99	51.1	50	102
63 Cu	He	2.11	2.144	99	49.7	50	99
66 Zn	He	7.29	7.37	99	46.2	50	92
75 As	He	5.36	5.685	94	9.85	10	99
78 Se	HEHe	1.14	1.1583	98	10.1	10	101
78 Se	H_2	1.08	1.1583	94	9.75	10	97
88 Sr	He	30.9	31.1	99	50.7	50	101
95 Mo	He	11.1	11.42	97	50.9	50	102
107 Ag	He	0.0917	0.09606	95	9.67	10	97
111 Cd	He	0.554	0.583	95	9.38	10	94
118 Sn	He	0.002	-	-	<DL	-	-
121 Sb	He	5.48	5.49	100	10.9	10	109
137 Ba	He	51.9	51.31	101	47.4	50	95
182 W	He	<DL	-	-	1.36	-	-
201 Hg	He	0.030	-	-	0.023	-	-
205 Tl	He	0.637	0.6823	93	9.68	10	97
Pb*	He	1.73	1.8303	94	48.3	50	97
209 Bi	He	1.21	1.25	97	<DL	-	-
232 Th	He	<DL	-	-	0.013	-	-
238 U	He	<DL	-	-	<DL	-	-

**Pb was measured as the sum of the three most abundant isotopes, 206, 207 and 208. The shaded data obtained in H_2 and HEHe mode is for comparative purposes.*

Table 5 continued. Recovery of certified values in high-matrix spiked CRMs. Concentration units: ppb.

		CWW-TM-B (100x diluted) + 1000 ppm matrix			CWW-TM-E (100x diluted) + 1000 ppm matrix		
Element	**Gas Mode**	**Measured**	**Certified**	**Recovery (%)**	**Measured**	**Certified**	**Recovery (%)**
9 Be	No gas	54.9	50	110	5.37	5.0	107
11 B	No gas	193	200	96	23.3	25	93
27 Al	He	183	200	91	25.4	25	101
31 P	HEHe	<DL	-	-	<DL	-	-
51 V	He	193	200	97	23.6	25	95
52 Cr	He	188	200	94	22.8	25	91
55 Mn	He	196	200	98	24.2	25	97
56 Fe	HEHe	205	200	103	25.1	25	100
56 Fe	H_2	202	200	101	25.6	25	102
59 Co	He	210	200	105	25.6	25	102
60 Ni	He	211	200	106	26.1	25	104
63 Cu	He	209	200	104	25.6	25	102
66 Zn	He	206	200	103	25.1	25	101
75 As	He	48.4	50	97	4.78	5.0	96
78 Se	HEHe	50.6	50	101	4.96	5.0	99
78 Se	H_2	50.3	50	101	5.16	5.0	103
88 Sr	He	203	200	102	24.7	25	99
95 Mo	He	204	200	102	25.1	25	100
107 Ag	He	53.2	50	106	5.37	5.0	107
111 Cd	He	50.1	50	100	24.4	25	98
118 Sn	He	<DL	-	-	0.073	-	-
121 Sb	He	50.9	50	102	4.88	5.0	98
137 Ba	He	209	200	104	25.4	25	102
182 W	He	<DL	-	-	<DL	-	-
201 Hg	He	0.14	-	-	<DL	-	-
205 Tl	He	48.9	50	98	4.81	5.0	96
Pb*	He	196	200	98	24.3	25	97
209 Bi	He	0.011	-	-	0.014	-	-
232 Th	He	<DL	-	-	<DL	-	-
238 U	He	<DL	-	-	<DL	-	-

**Pb was measured as the sum of the three most abundant isotopes, 206, 207 and 208. The shaded data obtained in H_2 and HEHe mode is for comparative purposes.*

As not all elements are certified in the CRM samples, the matrix spiked CRM samples were spiked at 50 ppb (5 ppb for Hg). The spike recoveries of two of the matrix-enhanced CRMs were mostly within ±10% of the spike level, as shown in Table 6. The results show the accuracy of the method for the determination of 28 analytes in high matrix water and wastewater samples.

Table 6. Spike concentration recoveries of diluted NIST 1643f and CWW-TM-A plus 1000 ppm of matrix elements.

Spike Recovery Test			NIST 1643f (10x diluted) + 1000 ppm Matrix			CWW-TM-A (100x diluted) + 1000 ppm Matrix		
Element	**Gas Mode**	**Spiked Conc (ppb)**	**Measured Unspiked (ppb)**	**Measured Spiked (ppb**	**Recovery (%)**	**Measured Unspiked (ppb)**	**Measured Spiked (ppb)**	**Recovery (%)**
9 Be	No gas	50	1.30	55.7	109	9.69	63.3	107
11 B	No gas	50	13.8	68.2	109	47.0	96.9	100
27 Al	He	50	12.3	57.7	91	49.2	97.4	96
31 P	HEHe	50	<DL	50.2	100	<DL	51.5	103
51 V	He	50	3.37	51.9	97	46.4	95.8	99
52 Cr	He	50	1.71	48.3	93	47.8	98.5	102
55 Mn	He	50	3.44	52.2	98	48.8	97.8	98
56 Fe	HEHe	50	9.12	59.5	101	49.1	100	103
56 Fe	H_2	50	9.34	59.3	100	49.2	99.8	101
59 Co	He	50	2.48	53.8	103	45.6	94.0	97
60 Ni	He	50	5.87	59.1	106	51.1	96.8	91
63 Cu	He	50	2.11	54.2	104	49.7	104	108
66 Zn	He	50	7.29	57.9	101	46.2	94.8	97
75 As	He	50	5.36	54.1	98	9.85	61.8	104
78 Se	HEHe	50	1.14	50.9	100	10.1	64.2	108
78 Se	H_2	50	1.08	51.2	100	9.75	61.9	104
88 Sr	He	50	30.9	82.2	103	50.7	104.5	108
95 Mo	He	50	11.1	64.0	106	50.9	105.7	110
107 Ag	He	50	0.092	53.4	107	9.67	60.0	101
111 Cd	He	50	0.55	51.1	101	9.38	57.9	97
118 Sn	He	50	0.002	49.4	99	<DL	51.5	103
121 Sb	He	50	5.48	55.1	99	10.9	64.2	107
137 Ba	He	50	51.9	105	107	47.4	95.8	97
182 W	He	50	<DL	49.3	99	1.36	48.0	93
201 Hg	He	5	0.030	4.82	96	0.023	4.84	96
205 Tl	He	50	0.64	51.6	102	9.68	62.4	105
Pb*	He	50	1.73	51.4	99	48.3	98.4	100
209 Bi	He	50	1.21	51.5	101	<DL	51.5	103
232 Th	He	50	<DL	47.6	95	0.013	46.4	93
238 U	He	50	<DL	45.6	91	<DL	42.7	85

**Pb was measured as the sum of the three most abundant isotopes, 206, 207 and 208. The shaded data obtained in H_2 and HEHe mode is for comparative purposes.*

Quantitative results and spike recoveries of industrial wastewater samples

Thirty-two elements were quantified in all five industrial wastewater samples (A to E) using the 7850 ICP-MS method, as shown in Table 7. Spike recovery data for all five samples is also given in Table 7. Higher-level spikes were used for the matrix elements, Na, Mg, Al, P, K, Ca, and Fe. Recoveries for all elements were mostly within ±10% of the spike level. The recovery data demonstrates the accuracy of the method for the analysis of industrial wastewater samples using the 7850 ICP-MS with UHMI.

Table 7. Quantitative results and spike recovery data for industrial wastewater samples A, B, and C. Concentration units: ppb.

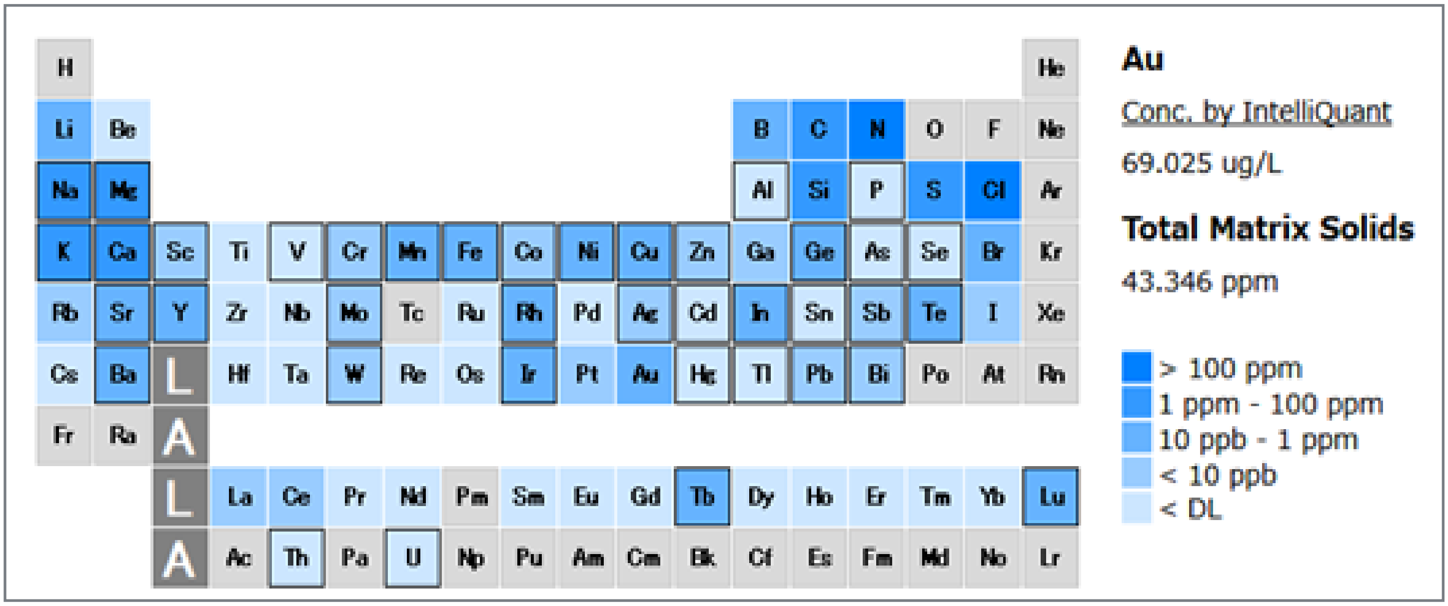
Element	Gas Mode	Spike Conc	Sample A	Spiked Sample A	Recovery (%)	Sample B	Spiked Sample B	Recovery (%)	Sample C	Spiked Sample C	Recovery (%)
9 Be	No gas	100	<DL	104	104	<DL	104	104	<DL	104	104
11 B	No gas	100	43.9	139	95	214	318	104	27.5	133	106
23 Na	He	50000	28678	75685	94	24683	71537	94	61326	NA	-
24 Mg	He	50000	4796	53611	98	5163	53365	96	3541	52241	97
27 Al	He	50000	77.6	48177	96	7.06	47429	95	113	48309	96
31 P	HEHe	50000	2343	52938	101	7.71	49607	99	417	50379	100
39 K	He	50000	11771	59374	95	3290	51537	96	2625	51320	97
40 Ca	H_2	50000	22113	71145	98	157901	NA	-	33667	82738	98
44 Ca	HEHe	50000	22764	72575	100	156026	NA	-	34810	83678	98
51 V	He	100	1.15	103	102	0.09	97.9	98	1.67	101	100
52 Cr	He	100	0.30	102	101	3.68	101	98	7.94	107	99
55 Mn	He	100	22.8	121	98	17.0	113	96	84.2	179	95
56 Fe	HEHe	50000	199	51228	102	400	50458	100	2238	53096	102
56 Fe	H_2	50000	205	51907	103	418	53176	106	2267	53696	103
59 Co	He	100	0.21	101	100	0.44	97.6	97	2.20	101	99
60 Ni	He	100	3.13	102	99	193	285	92	14.6	112	97
63 Cu	He	100	9.64	111	101	43.0	138	95	25.2	124	99
66 Zn	He	100	52.3	151	98	2.04	97.1	95	160	256	96
75 As	He	100	0.78	102	101	0.13	99.6	99	0.81	100	99
78 Se	HEHe	100	0.17	96.9	97	0.15	97.7	98	0.08	97.7	98
78 Se	H_2	100	0.17	93.4	93	0.12	93.4	93	0.06	95.5	95
88 Sr	He	100	83.8	184	100	210	307	96	98.8	196	97
95 Mo	He	100	1.15	105	104	1.26	102	101	1.42	104	103
107 Ag	He	100	0.29	102	102	0.34	98.5	98	0.11	99.6	99
111 Cd	He	100	0.06	103	103	<DL	100	100	0.07	101	101
118 Sn	He	100	0.36	101	101	0.28	104	104	0.23	106	106
121 Sb	He	100	0.53	97.5	97	0.19	93.0	93	0.94	103	102
137 Ba	He	100	22.8	126	103	13.2	115	101	25.3	127	102
182 W	He	100	0.89	91.4	91	<DL	81.6	82	1.02	95.1	94
201 Hg	He	5	<DL	5.48	110	<DL	5.20	104	<DL	4.6	92
205 Tl	He	100	<DL	102	102	<DL	100	100	0.01	101	101
Pb*	He	100	0.66	101	100	0.22	98.0	98	5.00	104	99
209 Bi	He	100	0.03	102	102	0.01	99.3	99	0.07	101	101
232 Th	He	100	<DL	93.0	93	<DL	101	101	0.02	102	102
238 U	He	100	0.01	105	105	0.003	103	103	0.05	104	104

**Pb was measured as the sum of the three most abundant isotopes, 206, 207 and 208. The shaded data obtained in H_2 and HEHe mode is for comparative purposes.*

Table 7 continued. Quantitative results and spike recovery data for industrial wastewater samples D and E. Concentration units: ppb.

Element	Gas Mode	Spike Conc	Sample D	Spiked Sample D	Recovery (%)	Sample E	Spiked Sample E	Recovery (%)
9 Be	No gas	100	<DL	105	105	0.02	103	103
11 B	No gas	100	59.3	157	98	38.2	130	92
23 Na	He	50000	53158	98495	91	539562	NA	-
24 Mg	He	50000	7161	56316	98	6726	56698	100
27 Al	He	50000	132	48851	97	9837	59140	99
31 P	HEHe	50000	7898	55978	96	203	49393	98
39 K	He	50000	25752	73735	96	2984	52989	100
40 Ca	H_2	50000	30635	79093	97	17642	67286	99
44 Ca	HEHe	50000	31928	79151	94	18438	67848	99
51 V	He	100	0.65	101	101	2.49	100	97
52 Cr	He	100	0.38	100	100	127	220	94
55 Mn	He	100	47.5	145	98	34.4	130	95
56 Fe	HEHe	50000	462	49113	97	732	50289	99
56 Fe	H_2	50000	469	49833	99	731	51157	101
59 Co	He	100	0.31	99.2	99	0.65	97.5	97
60 Ni	He	100	4.02	101	97	436	527	91
63 Cu	He	100	18.1	118	100	574	NA	-
66 Zn	He	100	36.5	133	97	49.2	144	95
75 As	He	100	0.99	101	100	0.26	97.6	97
78 Se	HEHe	100	0.16	97.7	97	0.18	94.7	95
78 Se	H_2	100	0.17	93.5	93	0.16	91.8	92
88 Sr	He	100	111	211	101	82.3	180	98
95 Mo	He	100	0.53	103	102	1.00	104	103
107 Ag	He	100	0.06	100	100	0.03	96.4	96
111 Cd	He	100	0.03	102	102	0.04	101	101
118 Sn	He	100	0.21	104	104	3.93	111	107
121 Sb	He	100	0.34	105	104	0.51	111	110
137 Ba	He	100	68.8	172	103	12.1	115	103
182 W	He	100	<DL	101	101	<DL	93.6	94
201 Hg	He	5	<DL	5.32	106	<DL	5.23	105
205 Tl	He	100	<DL	102	102	<DL	101	101
Pb*	He	100	1.02	101	100	8.41	108	99
209 Bi	He	100	0.07	103	103	0.51	101	100
232 Th	He	100	<DL	104	104	<DL	105	105
238 U	He	100	0.01	105	105	0.03	105	105

**Pb was measured as the sum of the three most abundant isotopes, 206, 207 and 208. The shaded data obtained in* H_2 *and HEHe mode is for comparative purposes. NA=not applicable, as the concentration of the spike was too low compared to the quantitative value.*



Au

Conc. by IntelliQuant

69.025 ug/L

Total Matrix Solids

43.346 ppm

- ■ > 100 ppm
- ■ 1 ppm - 100 ppm
- ■ 10 ppb - 1 ppm
- ■ < 10 ppb
- ■ < DL

Figure 2. IntelliQuant periodic table heat-map view of wastewater sample B. The color intensity of each element indicates the concentration of that element in the selected sample, with darker colors indicating higher concentrations. The semiquantitative results can also be reported in a conventional table of concentration values.

Semiquantitative IntelliQuant data

The 32 quantitative elements reported in Table 6 represent a fraction of the information available from an Agilent ICP-MS system operating in He KED mode. When an analyst creates an ICP-MS MassHunter method based on a preset method, the QuickScan function automatically acquires full mass range data for a sample within two seconds. IntelliQuant uses the scan data to calculate the semiquantitative concentrations for up to 78 elements based on a stored mass/response curve. No special setup or separate calibration is needed, simplifying the analysis. QuickScan data is acquired in He mode, so analytes are largely free from errors caused by polyatomic ion overlaps, ensuring the quality of data.

In this study, QuickScan data was collected for each of the five wastewater samples (A to E) and IntelliQuant was used to calculate the concentration of "all elements" measured in each sample. The data can be displayed in a periodic table "heat map", as shown in Figure 2.

IntelliQuant provides users with an excellent overview of the elemental content of a sample, allowing them to identify unexpected elements that were not included in the quantitative analysis. Figure 2 shows a relatively high concentration of gold (Au) in wastewater sample B, sourced from a printed circuit board plating facility, where gold is commonly employed for plating purposes.

Long-term stability

To demonstrate the robustness of the 7850 ICP-MS with UHMI, 160 samples, including QC and calibration solutions, were analyzed continuously over 16 hours. Analyzing varied, high matrix samples can lead to signal changes due to physical effects—the matrix level affects the viscosity of the sample, altering the flow rate and nebulization. To correct for these effects, ICP-MS users typically add ISTDs online. Figure 3 shows that the ISTD recoveries for this sample analysis were within 70–115% throughout the run, with no mass-dependent drift, meeting the JIS K0102 method QC limit requirements of 60–125%.

The recovery data confirms that the high temperature, robust, and matrix tolerant plasma conditions enabled by the UHMI-8 aerosol dilution setting ensured that minimal matrix deposition occurred during the run. The ISTD plots also show that the UHMI provided excellent control of signal suppression, with ISTD signals being consistent for elements covering a range of masses and ionization potentials. The results demonstrate the long-term robustness and high matrix tolerance of the 7850 ICP-MS with UHMI.

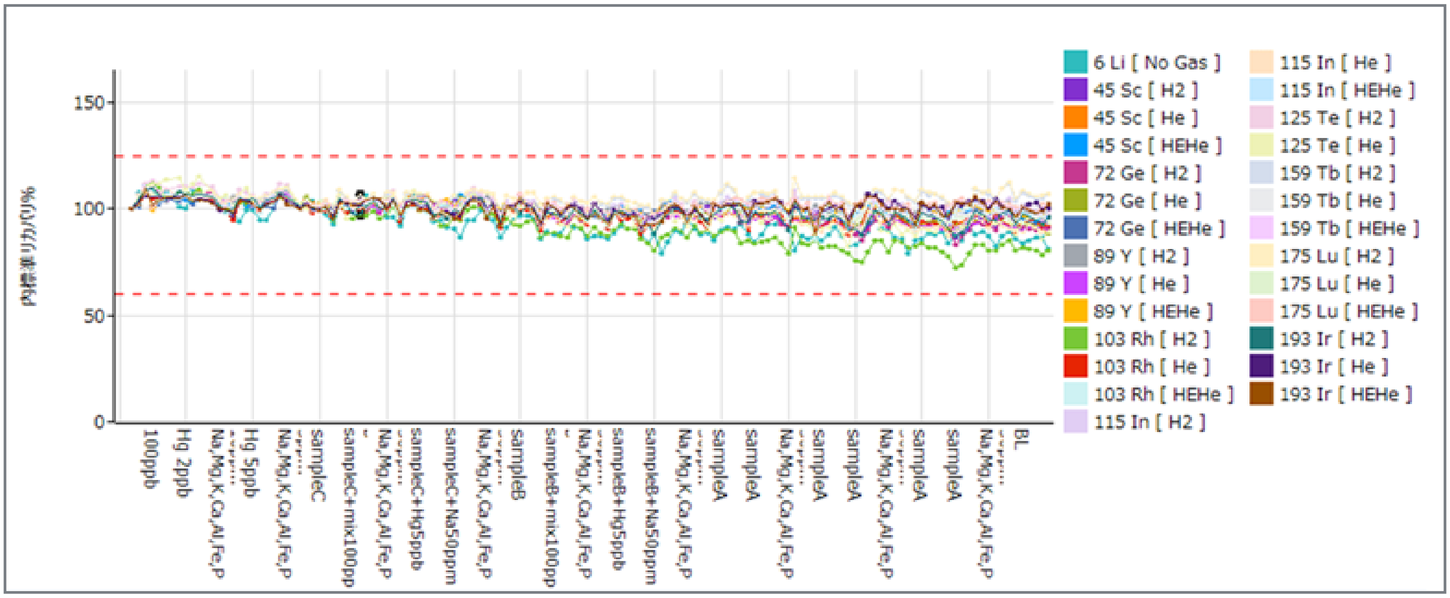


Figure 3. ISTD stability during the measurement of 160 solutions over 16 hours using the Agilent 7850 ICP-MS with UHMI. ISTD recoveries normalized to the calibration blank for all samples. The red dotted lines indicate the range of 60–125%, as specified in JIS K0102. Due to limited space, not all sample names are shown.

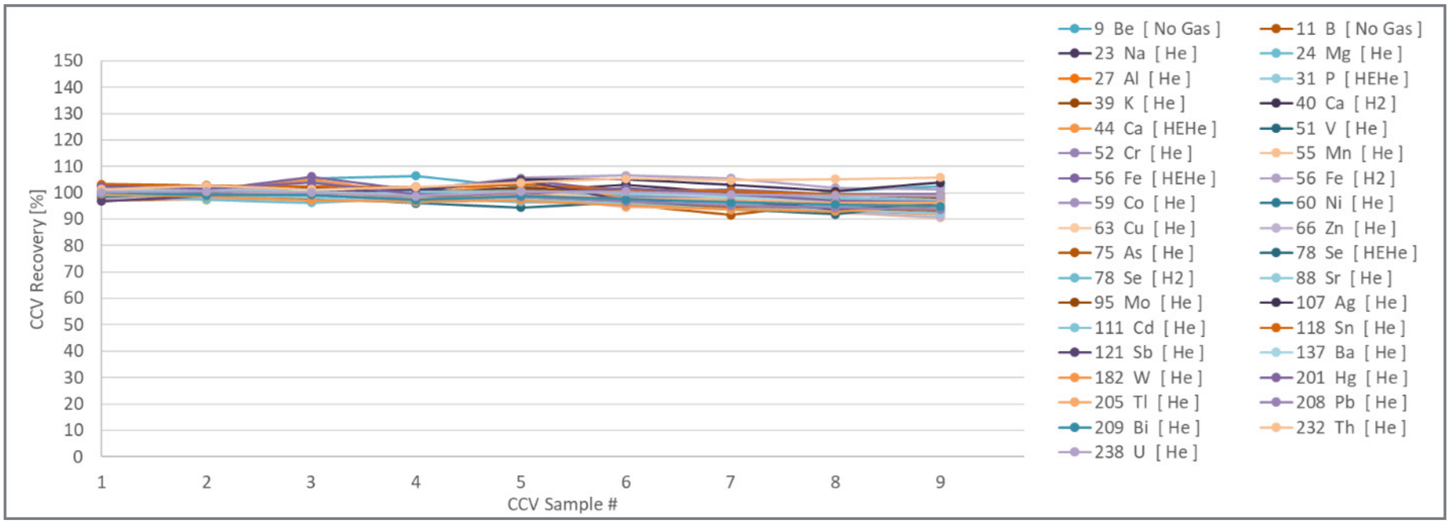


Figure 4. CCV recoveries over the 16-hour analytical sequence.

The diluent (4% HNO_3 and 0.5% HCl) was used as the continuing calibration blank (CCB) and a midpoint calibration standard was used as the continuing calibration verification (CCV) solution. The CCB and CCV checks were measured after every 10 samples throughout the analytical sequence. All the elements measured in the CCV were within ±10%, with no QC failures, as shown in Figure 4, further confirming the excellent stability of the 7850 ICP-MS.

Conclusion

The Agilent 7850 ICP-MS with UHMI aerosol dilution technology was used to determine 32 major and trace elements simultaneously in five industrial wastewater samples following minimal conventional dilution of the samples. The high sensitivity and 10 orders of dynamic range of the 7850 ICP-MS enabled all elements to be analyzed with a single, efficient method. Many of the method and instrument settings were loaded from Agilent ICP-MS MassHunter software using a preset UHMI-8 method and autotune, saving the analyst time and effort during method development.

High matrix samples can be challenging for ICP-MS to handle over long runs due to signal drift, suppression, and polyatomic interferences. This study confirmed the tolerance of the plasma and effectiveness of the ORS^4 collision/reaction cell during the measurement of four matrix-spiked CRMs and spiked real-world wastewater samples. The spiked concentrations of matrix elements corresponded to concentrations of 10,000 ppm (NIST 1643f) and 100,000 ppm (other CRMs) in the original CRM samples.

- Almost all elements measured in the CRMs and spiked wastewaters recovered within ±10%, demonstrating the effective control of polyatomic interferences of the ORS^4 in helium (He) and enhanced helium (HEHe) mode.
- Excellent results were obtained using a single cell gas methodology, which is useful for routine monitoring of environmental samples.
- If greater flexibility is needed, hydrogen gas can be added to the ORS^4 to provide even lower detection limits for Ca, Fe, Se under UHMI-8 conditions.
- Although rare for environmental samples, this study has shown that samples that contain a higher concentration of Sr than Ca are affected by a $^{88}Sr^{++}$ doubly-charged ion interference on $^{44}Ca^+$. To achieve an equivalent concentration for ^{44}Ca as acquired for ^{40}Ca in H_2 mode, analysts could apply an interference correction equation to correct the HEHe result for ^{44}Ca.
- Extra “all-element” semiquantitative data obtained by IntelliQuant in He KED mode provided users with a valuable overview of each sample's elemental profile.
- The 7850 with UHMI-8 plasma conditions provided optimum matrix tolerance when analyzing high matrix samples over 16 hours, as shown by the excellent ISTD and CCV stability results.

The 7850 ICP-MS method's high sensitivity, accuracy, precision, and stability confirmed its suitability for the routine analysis of factory wastewaters and its ability to meet typical discharge or regulatory limits.

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DE48129942

Printed in the USA, April 16, 2024
5994-7290EN

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