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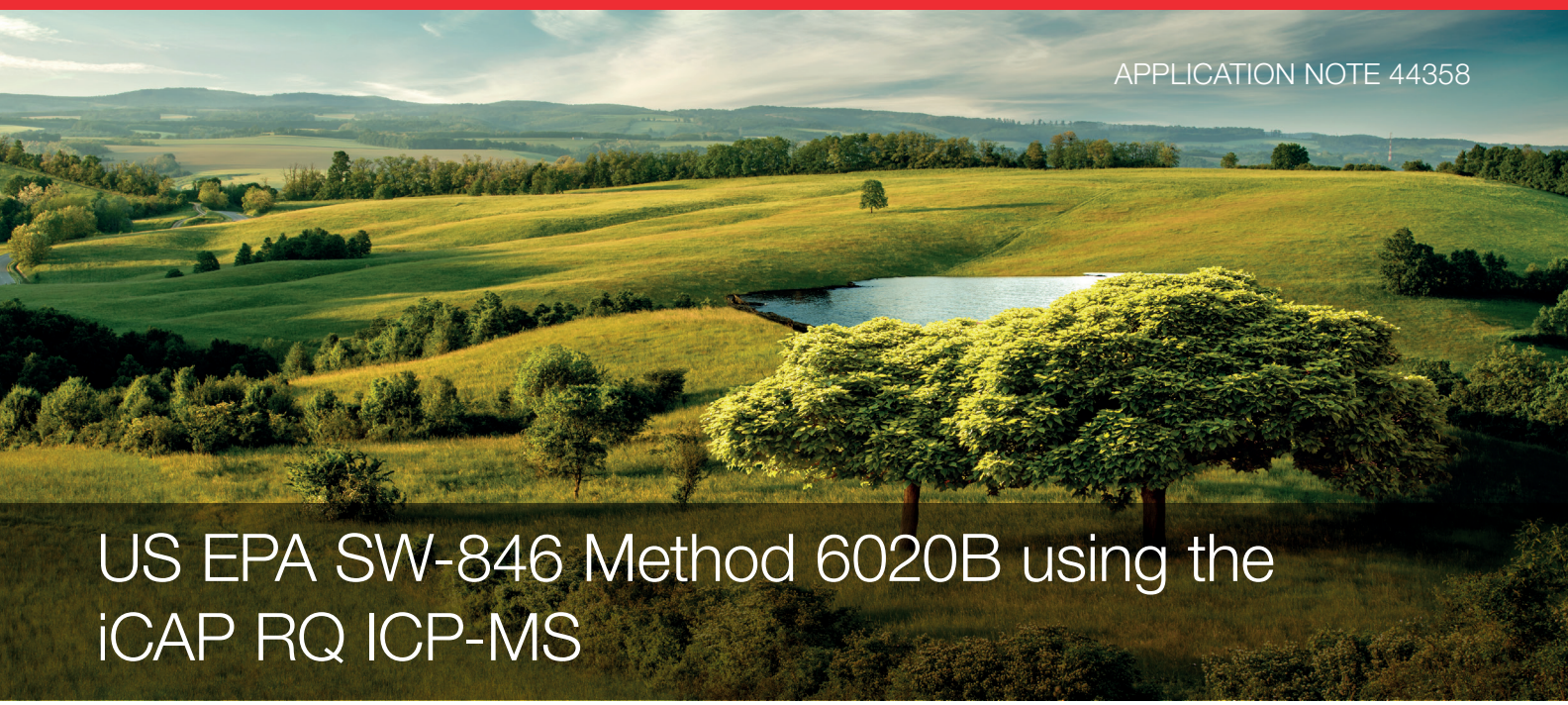

APPLICATION NOTE 44358

US EPA SW-846 Method 6020B using the iCAP RQ ICP-MS

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Keywords

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Goal

This Application Note describes the use of the Thermo Scientific iCAP RQ ICP-MS for SW-846 Method 6020B compliant analysis.

Introduction

The Environmental Protection Agency's (EPA) Office of Solid Waste and Emergency Response (OSWER) and Office of Resource Conservation and Recovery (ORCR) regulate all waste under the Resource Conservation and Recovery Act (RCRA). The RCRA's goals are to:

1. Protect the public from the hazards of waste disposal
2. Conserve energy and natural resources by recycling and recovery
3. Reduce or eliminate waste, and
4. Clean up waste that may have spilled, leaked, or was disposed of improperly.

The OSWER/ORCR publication SW-846, entitled "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", is the EPA's official compendium of analytical and sampling methods that have been evaluated and approved for use for analysis relating to the RCRA regulations. SW-846 functions primarily as a guidance document setting forth acceptable, although not required, methods for the regulated and regulatory communities to use in responding to RCRA-related sampling and analysis requirements. SW-846 is a multi-volume document that changes over time as new information and data are developed. It was first issued by the EPA in 1980 and is currently in its fifth edition.

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Instrumentation

All measurements were performed using a Thermo Scientific™ iCAP™ RQ ICP-MS. The instrument was operated using the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. The instrument was tuned daily for optimized sensitivity using Kinetic Energy Discrimination in the Collision Reaction Cell (QCell™) with the Robust 4.5 mm skimmer cone insert (KEDR mode), which was tuned with helium collision gas using the autotune routines included in the software. The system was also fitted with a Teledyne CETAC Technologies ASX-560 Autosampler and a Teledyne CETAC Technologies ASXpress Plus Discrete Sampling System to increase sample throughput.

The instrument parameters that were used during operation are shown in Table 1.

Table 1. Instrument parameters.

Parameter	Value
Pump Tubing	Sample Tygon® orange/yellow Internal Standard Tygon® orange/blue Drain PVC gray/gray
Nebulizer	Burgener Mira Mist®
Spraychamber	Quartz cyclonic spraychamber, cooled to 2.7 °C
Injector	2.5 mm id, Quartz
Interface	Robust Insert (4.5 mm), Ni cones
Pump Speed	30 rpm
RF Power	1550 W
Nebulizer Gas Flow	1.17 L·min^{-1}
QCell settings	KED
Gas Flow	100% helium @ 4.8 mL·min^{-1}
QCell Bias	-18 V
Quadrupole Bias	-21 V
Scan Settings	0.01-0.3 s dwell time per analyte, 10 sweeps

Sample preparation

High purity reagents were used throughout the work described here. Ultrapure water with a resistivity of >18 MΩ·cm (Milli-Q) was used, along with OPTIMA™ Grade nitric acid (Fisher Scientific UK Ltd., UK). All analytical solutions were prepared from ICP-MS grade stock standards from the Thermo Scientific EPA Productivity Pack solutions (Thermo Scientific P/N 4600432 and P/N 4600465).

Calibration standards were prepared using the Low-Level Calibration Stock and the Major Elements Stock solution provided in the EPA Productivity Pack, with standard element concentrations selected to cover the required measurement range of each analyte. These concentrations are summarized in Table 2.

An internal standard mix comprising 100 µg·L^{-1} Sc, 120 µg·L^{-1} Li and 20 µg·L^{-1} Y, In and Bi was introduced online with an internal standard mixing kit. The internal standard elements were appropriately matched to analyte elements.

Quality Control Continuing Calibration Verification (CCV) standards were prepared from the same stock solutions used to prepare the calibration standards. Initial Calibration Verification (ICV) solutions were prepared using a second source Low-Level Calibration Stock and Major Elements Stock solution.

A simulated sludge sample was prepared with concentrations equivalent to those found in NIST SRM 2781 Domestic Sludge, using single element stock standards containing relevant elements at 10 mg·L^{-1}, 1000 mg·L^{-1} and 10000 mg·L^{-1}. The final concentrations are summarized in Table 3, representing a 1:1000 total dilution of a sludge digest.

Samples of tap water taken from the laboratory water supply were also used for long-term studies.

All solutions were acidified with nitric acid to a final concentration of 2% nitric acid v/v.

Table 2. Calibration standard concentrations in µg·L^{-1}.

Standard	Concentration (µg·L^{-1})	Elements
STD 1	2	Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Tl, V, Zn
STD 2	100	
STD 3	1,000	
STD 4	5,000	
STD 5	100,000	Ca, Fe, K, Mg, Na
STD 6	40,000 ; 50	Al , Hg

Table 3. Simulated sample element concentration in µg·L^{-1}.

Element	Concentration (µg·L^{-1})	Element	Concentration (µg·L^{-1})
Ag	300	Mn	2,000
Al	50,000	Mo	150
As	25	Na	6,500
Ba	2,000	Ni	250
Ca	120,000	P	75,000
Cd	50	Pb	600
Cr	500	Se	50
Cu	2,000	Si	160,000
Fe	85,000	Tl	10,000
Hg	10	V	250
K	15,000	Zn	4,000
Mg	20,000		

Methods and discussion

EPA method 6020B provides guidelines on general laboratory practices such as sample preparation, instrument setup, calibration of analytes, and interference correction equations[1]. It also provides specific rules on various analytical practices that must be followed, including elements covered, required isotopes, quality control practices and instrument validation. The aim of the protocol is to ensure a consistently high quality of analytical data by enforcing compliance with a variety of stringent instrument and analytical performance checks, as outlined in Tables 4 and 5.

A LabBook was setup using Qtegra (ISDS) for the analysis of a selection of elements covered by the US EPA Method 6020B. The sequence used in the sample list is shown in Table 6.

Table 4. Summary of Method 6020B instrument calibration and check requirements.

Check Code	Check Name	Purpose	Frequency	Limits
-	Mass Calibration/ Resolution Setting	Ensures the correct mass is measured at its maximum and that peaks are properly resolved	Verify prior to each analytical run (daily) using a Performance Report	Masses measured must not deviate by more than 0.1 u from their nominal position and peak width must be <0.9 u at 10% peak height
-	Calibration	Calibrates the instrument response for measurement	Daily, or when required	N/A
IDL	Instrument Detection Limit	Estimates the detection limit of the instrument from either: at least 7 analyses of a blank over three non-consecutive days; or, from 3 × SD of the blank measurement used for the calibration	Every 3 months or after major instrument maintenance or hardware replacement	N/A
MDL	Method Detection Limit	Estimates the detection limit of the method from at least 7 analyses of a blank sample processed through all sample preparation steps	Every 3 months or after major instrument maintenance or hardware replacement	N/A

Table 5. Summary of Method 6020B quality control requirements.

QC Code	QC Name	Purpose	Frequency	Limits
ICB	Initial Calibration Blank	Checks the instrument carry over	After initial calibration	<3 × IDL
ICV	Initial Calibration Verification	Checks the calibration against a second source to verify accuracy	After initial calibration	90 – 110%
SIC	Spectral Interference Check	Verifies interference correction performance	After initial calibration	No specific requirements, less than LLOQ recommended
CCB	Continuing Calibration Blank	A continuing periodic check on instrument carry-over	After each calibration and every 10 analyses	< 3 × IDL
CCV	Continuing Calibration Verification	A continuing periodic check on instrument accuracy and drift	After each calibration and every 10 analyses	90 – 110%
PDS	Post-Digestion Spike	Checks the accuracy of analytes spiked into an unknown sample after preparation (digestion)	1 in every 20 samples per matrix	75 – 125%
DUP	Duplicate	Checks for the reproducibility of results by analyzing an unknown sample in duplicate	1 in every 20 samples per matrix	±20% relative percent difference from original sample
SER	Serial Dilution	Checks for matrix effects by assessing the variation of results for an unknown sample before and after dilution	1 in every 20 samples per matrix	±10% of the original dilution result after dilution correction
LCS	Laboratory Control Sample	Checks the accuracy of the entire analytical process	Every 20 samples	80 – 120%
IST	Internal Standard Test	To evaluate performance and make sure that potentially occurring matrix effects can be corrected	Mixed into every sample	70 – 130%

Table 6. Sample list sequence example.

Sample Name	Sample Type	Purpose	
Blank	Blank	Instrument Calibration	
STD-1	Calibration Standard		
STD-2	Calibration Standard		
STD-3	Calibration Standard		
STD-4	Calibration Standard		
STD-5	Calibration Standard		
STD-6	Calibration Standard		
ICV Low	QC Sample	Initial Calibration Verification for low level trace elements	Initial Verification
ICV High	QC Sample	Initial Calibration Verification for high level trace elements	
ICB	QC Sample	Initial Calibration Blank Check to verify carryover is minimized	
SIC	QC Sample	Check blank levels in the presence of interferences	
Sample 1	Unknown	Unknown Sample 1	
Sample 1 DUP	QC Sample	Unknown Sample 1 Repeated for method repeatability verification	
Sample 1 SER	QC Sample	Unknown Sample 1 diluted with 2% nitric acid (1+4) for matrix tolerance verification	
Sample 1 SPK	QC Sample	Unknown Sample 1 Spiked for method accuracy verification	
10 Unknown Samples	Unknown	10 Analyses of unknown samples	Continuing Analysis Block
CCV low	QC Sample	Continuing Calibration Verification to verify accuracy of low level elements	
CCV high	QC Sample	Continuing Calibration Verification to verify accuracy of high level elements	
CCB	QC Sample	Continuing Calibration Blank to verify carryover is minimized	
10 Unknown Samples	Unknown	10 Analyses of unknown samples	
Sample SPK	QC Sample	20th Unknown Sample in Block Spiked for method accuracy verification	
CCV low	QC Sample	Continuing Calibration Verification to verify accuracy of low level elements	
CCV high	QC Sample	Continuing Calibration Verification to verify accuracy of high level elements	
CCB	QC Sample	Continuing Calibration Blank to verify carryover is minimized	

Results

Instrument detection limits (IDLs) were established using Qtegra, which calculated the IDL as the concentration equal to three times the standard deviation of the blank solution analysis.

Method detection limits (MDLs) were established by measuring a blank solution (2% HNO_3 v/v). This solution was analyzed ten times with each analysis having three replicates. In accordance to EPA methodology for determining the MDL[2], the MDL was calculated as the concentration equal to three times the standard deviation of the blank solution analysis added to its background equivalent concentration (BEC). The ten repeat analyses were averaged to give the final MDL.

The IDLs and MDLs are summarized in Table 7, and show limits below 1 µg·L^{-1} for trace elements. Those elements with higher IDLs and MDLs are matrix elements that typically exist in very high levels in environmental samples. These MDLs are well below required limits of detection for regulatory bodies.

Method performance was verified by analyzing the simulated sample and the sample spiked with the equivalent of 50 µg·L^{-1} for each target element. The results of the unspiked and spiked samples, as well as calculated spike recoveries, are shown in Table 8.

The Spectral Interference Check (SIC) solution is used to demonstrate that the instrument is free of interferences on the analyte masses. The solution comprises a heavy matrix that produces polyatomic species that, once analyzed with the method, should give results less that the Lower Limit of Quantitation (LLOQ). The EPA defines the LLOQ as the lowest point of quantitation, which is taken as the lowest point in the calibration curve: 2 µg·L^{-1} in this work. Results for the SIC solution show that all interferences are effectively removed for the trace analytes, and are summarized in Table 8.

Table 7. Method and Instrument Detection Limits in µg·L^{-1}.

Element	IDL	MDL
^{9}Be	0.126	0.176
^{23}Na	2.63	4.34
^{24}Mg	0.769	1.30
^{27}Al	0.435	1.46
^{39}K	3.53	5.39
^{44}Ca	8.27	7.38
^{51}V	0.016	0.024
^{52}Cr	0.029	0.043
^{55}Mn	0.046	0.072
^{57}Fe	0.362	1.63
^{59}Co	0.003	0.014
^{60}Ni	0.013	0.041
^{63}Cu	0.072	0.123
^{66}Zn	0.116	0.232
^{75}As	0.014	0.044
^{77}Se	0.014	0.448
^{107}Ag	0.016	0.304
^{111}Cd	0.005	0.020
^{121}Sb	0.001	0.074
^{137}Ba	0.033	0.062
^{202}Hg	0.002	0.010
^{205}Tl	0.002	0.039
^{208}Pb	0.002	0.024

The results for the simulated sludge sample show sample concentration recoveries within ±20% of the true values. The spike recoveries are within the EPA limits of ±25%, which highlights the accuracy of the method. For Al, Na, Mg, K, Ca and Fe, the analyte signal is very high and obscures the signal from the 50 ppb spike; therefore, the results are not included in Table 8.

Instrument drift performance was evaluated by monitoring the internal standard and CCV recoveries during a 12-hour sample analysis run. The internal standard recovery results, shown in Figure 1, are within ±30% limits, in agreement with EPA Method 6020B. CCV recoveries, shown in Figures 2 and 3, are within ±10% over a period of at least 8 hours, which means valid data can be achieved from the method setup without recalibration over an 8 hour period. The CCVs rise out of specification over time due to physical effects, such as evaporation from the vial while loaded in the autosampler. Combined with the internal standard recoveries, it is clear that the instrument stays within specification after the calls for recalibration, so recalibration and continuing sample analysis is possible.

Table 8. Concentrations and recoveries for simulated samples and spiked samples.

	SIC Solution conc.	Simulated Sample conc.	Measured Simulated Sample conc.	Sample Recovery	Spiked conc.	Measured Spike conc.	Spike Recovery
	µg·L^{-1}	µg·L^{-1}	µg·L^{-1}	%	µg·L^{-1}	µg·L^{-1}	%
^{9}Be	0.040	N/A	N/A	N/A	50	45	90
^{24}Mg	-	20000	20619	103	50	N/A	N/A
^{27}Al	-	50000	51604	103	50	N/A	N/A
^{39}K	-	15000	16018	107	50	N/A	N/A
^{44}Ca	-	120000	125986	105	50	N/A	N/A
^{51}V	0.229	250	295	118	50	59	119
^{52}Cr	1.226	500	463	93	50	41	81
^{55}Mn	0.606	2000	2003	100	50	46	92
^{57}Fe	-	85000	86863	102	50	N/A	N/A
^{59}Co	0.370	N/A	N/A	N/A	50	59	118
^{60}Ni	0.593	250	280	112	50	50	99
^{63}Cu	0.224	2000	2003	100	50	47	93
^{66}Zn	0.578	4000	3727	93	50	55	109
^{75}As	0.138	25	29	116	50	58	117
^{82}Se	0.050	50	44	88	50	45	90
^{107}Ag	0.187	300	257	86	50	43	87
^{111}Cd	0.617	50	50	100	50	52	104
^{121}Sb	0.211	N/A	N/A	N/A	50	52	105
^{137}Ba	1.148	2000	1824	91	50	60	119
^{202}Hg	0.179	10	10	99	N/A	N/A	N/A
^{205}Tl	0.032	N/A	N/A	N/A	50	53	105
^{206}Pb	0.240	600	619	103	50	55	110
^{207}Pb	0.241	600	629	105	50	53	107
^{208}Pb	0.237	600	629	105	50	55	109

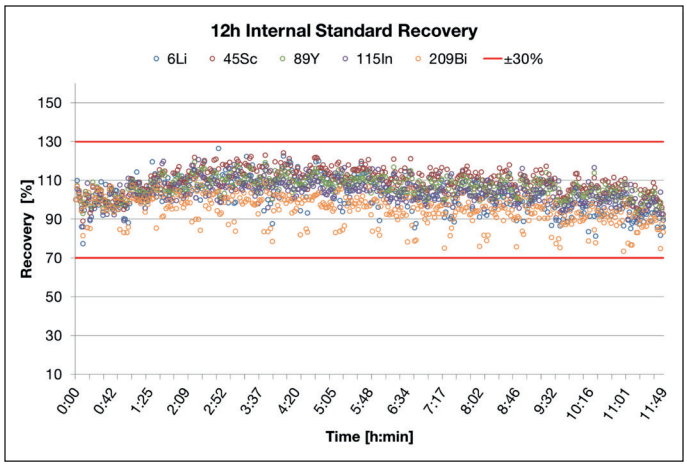

Figure 1. Internal standard recovery data, collected over 12 hours.

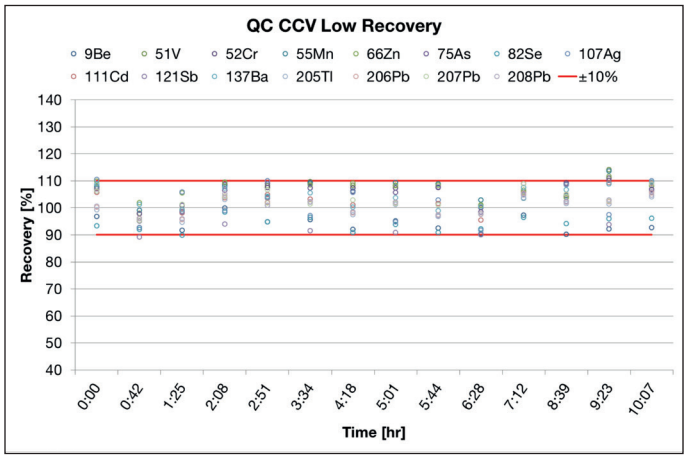

Figure 2. QC CCV-low recovery data.

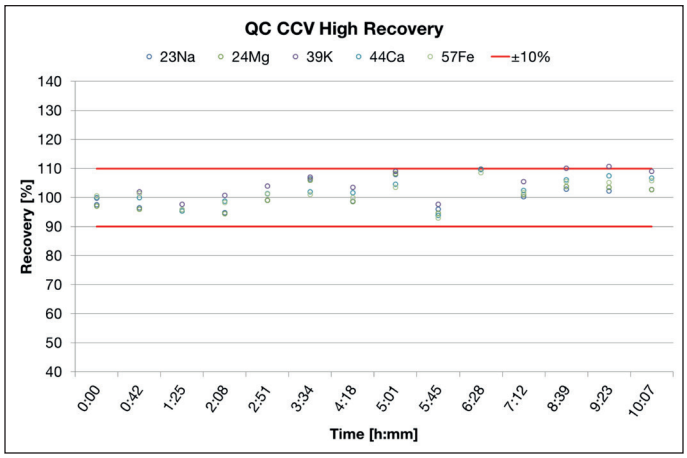

Figure 3. QC CCV-high recovery data.

Conclusion

The iCAP RQ demonstrates SW-846 method 6020B compliant analysis and easily copes with the stringent interference checks and the QC requirements of the method. A combination of specifically designed hardware and software tools enables and simplifies analysis as outlined below. Mass calibration and resolution checking is made simple with custom performance reports, and analysis peaks are easily set to the required width using the variable resolution function. Any deviations from acceptable performance are clearly flagged and the report ends with an unambiguous Pass or Fail statement.

The unique interface design produces low background equivalent concentrations, resulting in very low instrument detection limits (as seen in Table 6). It enhances stability when analyzing solutions containing high levels of matrix components, e.g. Ca, Na, Fe, Mg, K. This is demonstrated by the stability of the internal standards (shown in Figure 1) and the consistent CCV results (as shown in Figures 2 and 3). The Qtegra ISDS software has a built-in QC checking capability that is specifically designed to meet the requirements of EPA methods. Each QC type (ICV, CCV, etc.) is available as a default in the QC set-up page and the user can define their own QC tests, as required.

Results in the software are visually flagged if they are outside the allowed range, which makes validation a simple process. Sample and spike recoveries are automatically calculated for any QC standard or spiked sample and percentage recoveries can be calculated for DUP and SER samples. A variety of user-selectable automated actions can be set up to ensure fully compliant analysis is achieved during an unattended run (see Figures 4 to 6).

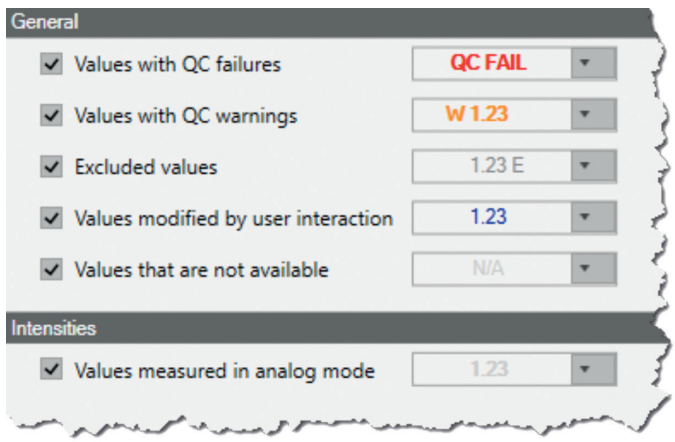

Figure 4. Global, user definable data flags can be set in Qtegra ISDS Software for easier data visualization.

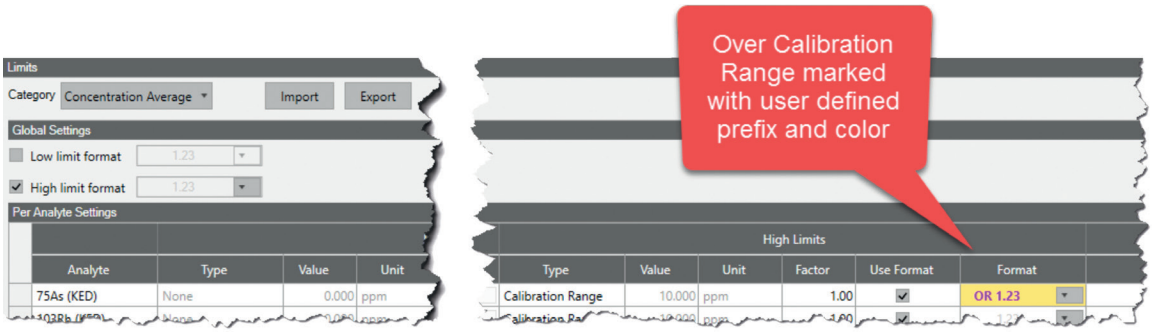

Figure 5. User definable data flags can be set with limits for each analyte in Qtegra ISDS Software for easier data visualization.

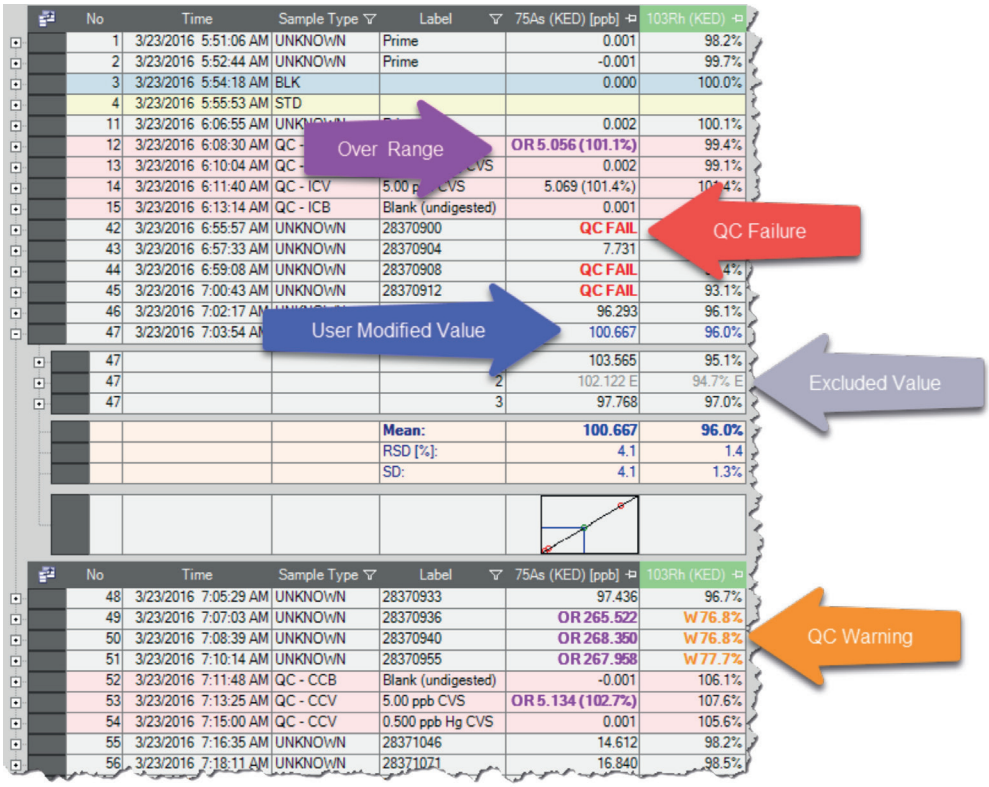

Figure 6. Data display with data flags for easier data visualization in Qtegra ISDS Software.

Samples in this study were processed at a speed of 1 sample every 1 minute and 39 seconds, or 36 analyses per hour. Instrument stability has been demonstrated to be within EPA limits over a period of 12 hours, and method stability has been demonstrated for 8 hours without recalibration. This equates to over 280 analyses without the need for recalibration, making the iCAP RQ the ultimate ICP-MS for cost-effective elemental analysis.

References

1. *Method 6020B.* (United States Environmental Protection Agency, 2014).
2. *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.* (United States Environmental Protection Agency, 2016).

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