APPLICATION NOTE

ICP - Mass Spectrometry

Authors:

Cynthia Bosnak

Paul Krampitz

Stan Smith

Ewa Pruszkowski

Ken Neubauer

PerkinElmer, Inc.
Shelton, CT

Meeting the Requirements of U.S. EPA Method 6020B with the NexION 300X/350X

Introduction

The Resource Conservation and Recovery Act (RCRA) was implemented in 1976 to protect humans and the environment from liquid and solid wastes. In order to help labs comply with RCRA, the United States Environmental Protection Agency (U.S. EPA) published SW-846, titled "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" in 1980 as a guide for the analysis of multiple waste products. As such, SW-846 consists of numerous methods covering a broad range of sample types and analytes. Because wastes can impact the environment (and, ultimately, human health) through contamination of soil and/or water, both of these matrices are covered under RCRA and SW-846.

As industry has evolved, many new chemicals have been developed that can potentially make their way into the environment. Likewise, analytical instrumentation has also continued to advance, both with increased capabilities and new analytical techniques. As a result, SW-846 has required periodic updates.

PerkinElmer®
For the Better

The latest update (Update V) contains revisions to 23 of the methods, including Method 6020, which is referred to as 6020B in the newly updated form. Several changes have been made in 6020B, including the addition of new elements, new detection-limit criteria, and multiple new quality control (QC) parameters. Revision 2 of 6020B is anticipated to be updated yet again in the future based on public comments.

This work demonstrates how the PerkinElmer NexION® 300X/350X can meet the new requirements of Method 6020B in both water and soil matrices.

Experimental

Solutions

All reagents were prepared volume/volume (v/v) with 18 MΩ deionized (DI) water and Optima grade reagents (Fisher Scientific). Calibration, standard, and internal standard solutions were made from the Environmental Standard Kit for ICP-MS (PerkinElmer Part No. N9307111), whose pertinent components are shown in Table 1. Before making the final standards, the intermediate stock standards listed in Table 2 were prepared. The final calibration solutions were prepared with a diluent of 2% HNO_3 + 1% HCl and are shown in Table 3. To aid with Hg washout, 200 µg/L gold was added to each solution prior to analysis.

Water standard reference materials were purchased from NIST® (National Institute of Standards and Technology) and NRCC (National Research Council of Canada), and soil reference materials were purchased from High-Purity Standards™. Water samples were run without dilution; soil samples were diluted 10x.

Table 1. Environmental Standard Kit for ICP-MS.

PerkinElmer Part Number	Concentration (mg/L)	Elements
N9301721	100	Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Tl, V, Zn
N9307805	1000	Ca, Mg, Na, K
N9307806	1000	Al, Fe
N9300253	10	Hg
N9308592	100 50 1	Sc Ge In, Rh, Tb

Table 2. Intermediate Solutions.

PerkinElmer Part Number	Elements	Concentration (mg/L)	Diluent
N9301721	Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Tl, V, Zn	10	2% HNO_3
N9300253	Hg	1	2% HNO_3 + 1% HCl
N9308592	Sc Ge In, Rh, Tb	10 5 0.1	2% HNO_3 + 1% HCl + 10% MeOH

Table 3. Calibration Standards.

Elements	Units	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5
Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Tl, V, Zn	µg/L	1	10	50	100	200
Hg	µg/L	0.1	1	2.5	5	10
Ca, Mg, Na, K, Al, Fe	mg/L	0.1	1	5	10	20

Instrument and Hardware

All analyses were done on a PerkinElmer NexION 300X/350X operating in Standard and Collision modes. The instrumental and method conditions are shown in Tables 4 and 5, respectively. The autosampler rinse consisted of 2% HNO_3 + 1% HCl + 200 µg/L gold.

Table 4. Instrumental Conditions.

Parameter	Value
Sample uptake rate	250 µL/min
Nebulizer	Glass concentric (Meinhard C 0.5)
Spray chamber	Glass cyclonic (baffled)
Injector	Quartz, 2.5 mm i.d.
Nebulizer flow	Optimized for < 2% oxides
Plasma flow	16 L/min
Auxiliary flow	1.2 L/min
RF power	1600 W
Torch depth	+2 mm
Cones	Ni

Table 5. Method Parameters.

Element	Mass	Mode
Be	9	Standard
Na	23	Collision
Mg	24	Collision
Al	27	Collision
K	39	Collision
Ca	44	Collision
V	51	Collision
Cr	52	Collision
Mn	55	Standard
Fe	56	Collision
Co	59	Collision
Ni	60	Collision
Cu	63	Collision
Zn	66	Collision
As	75	Collision
Se	78	Collision
Mo	95	Standard
Ag	107	Standard
Cd	111	Collision
Sb	121	Standard
Ba	137	Standard
Hg	200	Standard
Tl	205	Standard
Pb	208	Standard

Results and Discussion

Quality Control Terminology

When using Method 6020B, the user must be familiar with and understand the Quality Control (QC) definitions and criteria, which are summarized in Table 6.

Figure 1 shows a flow chart of the daily operation scheme, including QC. First, instrument performance optimizations are performed automatically using SmartTune Express in Syngistix™ for ICP-MS software. Next, the calibration standards are analyzed, followed by the initial QC checks and samples, which consist of a mixture of soil and water certified reference materials, along with periodic QC checks (CCB, CCV, MB, LCS, MS, MSD). After all the samples have been analyzed, final QC checks are analyzed.

Table 6. Quality Control Parameters Used in Method.

Name	Definition	Limits	Reference*	Notes
ICB	Initial Calibration Blank	≤ 0.5 times the LLOQ	10.5.4	
ICV	Initial Calibration Verification	± 10% of true value	7.24, 10.5.1	Secondary source near (but not equal to) the mid calibration
LLOQ	Lower Limit of Quantification (Low Level Verification)	± 20% of true value	10.5.2	
SIC	Spectral Interference Check	< 2 times LLOQ	9.9	
CCB	Continuing Calibration Blank	≤ LLOQ	10.5.5	
CCV	Continuing Calibration Verification	± 10% of true value	10.5.3	Mid-level calibration read back
MS	Matrix Spike	± 25% of spike level	9.7.2	Run every batch of 20 samples
MSD	Matrix Spike Duplicate	≤ 20 relative percent difference	9.7.2	Run every batch of 20 samples
MB	Method Blank	< LLOQ	9.7.1	Alternates: - 50% of regulatory limit- 10% of lowest sample
LCS	Laboratory Control Sample	± 20% of true value	9.7.3	Run every batch of 20 samples
IS	Internal Standard	≥ 70% recovery	9.10	
CAL	Calibration	R ≥ 0.995	10.4	Lowest calibration standard must be at or below LLOQ
IDL	Instrument Detection Limit	Mean + 3SD	9.3	10 replicate analyses

** Refers to section of the Method 6020B where these are discussed*

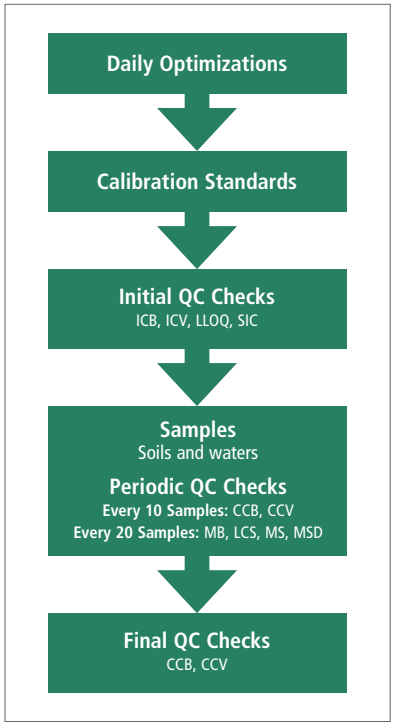

Figure 1. Daily workflow for running Method 6020B.

Analysis

Before analyzing samples, the LLOQs and IDLs of the method were established. The LLOQ (or low-level verification) was established using the low-level calibration standards. The low-level standard must recover within ± 20% of the true value. A new way of establishing IDLs is defined in Method 6020B: the mean of the blank is added to three times the standard deviation of ten replicate analyses of the reagent blank. The LLOQs and IDLs are shown in Table 7.

Table 7. LLOQs and IDLs.

Element	LLOQ (µg/L)	IDL (µg/L)
Be	0.2	0.004
Na	20	0.665
Mg	20	0.134
Al	20	0.689
K	50	5.57
Ca	100	9.04
V	0.5	0.074
Cr	0.2	0.040
Mn	0.2	0.025
Fe	20	0.486
Co	0.2	0.002
Ni	0.2	0.015
Cu	0.5	0.015
Zn	0.2	0.135
As	0.2	0.020
Se	0.2	0.083
Mo	0.2	0.007
Ag	0.2	0.003
Cd	0.2	0.005
Sb	0.2	0.001
Ba	0.2	0.003
Hg	0.2	0.007
Tl	0.5	0.048
Pb	0.2	0.005

The accuracy of the method was demonstrated with the analysis of multiple certified reference materials (CRM), as shown in Tables 8 and 9 for waters and Tables 10 and 11 for soils. All recoveries are within 10% of the certified values, except for those which result from common contaminants.

Table 8. Results for NIST 1643e Trace Elements in Water.

Element	Certified (µg/L)	Measured (µg/L)	% Recovery
Be	13.98	13.05	93
Na	20740	20021	97
Mg	8037	7769	97
Al	141.8	154.7	109
K	2034	2090	103
Ca	32300	31508	98
V	37.86	37.21	98
Cr	20.4	21.0	103
Mn	38.97	35.94	92
Fe	98.1	97.6	100
Co	27.06	26.71	100
Ni	62.41	62.18	100
Cu	22.76	23.16	102
Zn	78.5	75.3	96
As	60.45	59.12	98
Se	11.97	11.89	99
Mo	121.4	118.9	98
Ag	1.062	1.012	95
Cd	6.658	6.175	93
Sb	58.3	54.7	94
Ba	544.2	564.2	104
Hg	n/c	n/c	n/c
Tl	7.445	7.400	99
Pb	19.63	20.04	102

n/c = not certified

Table 9. Results for NIST 1640a Trace Elements in Natural Water.

Element	Certified (µg/L)	Measured (µg/L)	% Recovery
Be	3.026	2.879	95
Na	3137	2859	91
Mg	1058.6	1038.0	98
Al	53	56	105
K	579.9	605.7	104
Ca	5615	5763	103
V	15.05	14.66	97
Cr	40.54	39.79	98
Mn	40.39	35.53	88
Fe	36.8	36.6	100
Co	20.24	20.01	99
Ni	25.32	24.80	98
Cu	85.75	88.24	103
Zn	55.64	55.94	101
As	8.075	7.979	99
Se	20.13	20.20	100
Mo	45.6	44.3	97
Ag	8.081	7.978	99
Cd	3.992	3.999	100
Sb	5.105	4.853	95
Ba	151.8	149.7	99
Hg	n/c	n/c	n/c
Tl	1.619	1.663	103
Pb	12.101	12.652	105

n/c = not certified

Table 10. Results for Soil Solution A (certified material from High Purity Standards).

Element	Certified (µg/L)	Measured (µg/L)	% Recovery
Be	n/c	0.14	n/c
Na	70000	65053	93
Mg	70000	67778	97
Al	500000	492818	99
K	200000	203823	102
Ca	350000	332435	95
V	100	97	97
Cr	n/c	2.83	n/c
Mn	100	97	97
Fe	200000	202367	101
Co	n/c	3.83	n/c
Ni	300	289	96
Cu	300	320	107
Zn	1000	963	96
As	200	193	97
Se	10	10	101
Mo	n/c	1.62	n/c
Ag	n/c	0.88	n/c
Cd	n/c	4	n/c
Sb	30	30	100
Ba	5000	5022	100
Hg	n/c	0.09	n/c
Tl	n/c	1.41	n/c
Pb	400	412	103

n/c = not certified

Table 11. Results for Soil Solution B (certified material from High Purity Standards).

Element	Certified (µg/L)	Measured (µg/L)	% Recovery
Be	n/c	0.13	n/c
Na	100000	90469	91
Mg	80000	76842	96
Al	700000	697175	100
K	210000	213085	102
Ca	125000	120772	97
V	800	780	98
Cr	400	404	101
Mn	100000	95582	96
Fe	350000	360264	103
Co	100	103	103
Ni	200	200	100
Cu	3000	2934	98
Zn	70000	67177	96
As	6000	5779	96
Se	n/c	0.08	n/c
Mo	n/c	4.88	n/c
Ag	n/c	0.86	n/c
Cd	200	199	100
Sb	400	387	97
Ba	7000	6896	99
Hg	n/c	0.17	n/c
Tl	n/c	1.64	n/c
Pb	60000	66682	111

n/c = not certified

Table 12 shows recoveries from a river water CRM, as well as the results from one of the matrix spikes and matrix spike duplicates. The CRM recoveries are generally within 10% of the certified values, consistent with the other CRMs analyzed. In addition, both the matrix spike and matrix spike duplicate pass the method-defined acceptance criteria, as shown in Table 6.

Table 12. SLRS-4 River Water: Analyte, Matrix Spike and Matrix Spike Duplicate Recoveries.

Element	Certified (µg/L)	Measured (µg/L)	Recovery (%)	Spike Concentration (µg/L)	Matrix Spike (% Recovery)	Matrix Spike Duplicate (Relative % Difference)
Be	0.007	< LLOQ	*	50	94.3	6.34
Na	2400	2090	87.1	5000	85.0	0.05
Mg	1600	1590	99.5	5000	92.2	0.05
Al	54	55	102	5000	95.3	0.06
K	680	710	105	5000	99.5	0.05
Ca	6200	5840	94.2	5000	93.5	0.03
V	0.32	< LLOQ	*	50	91.2	6.37
Cr	0.33	0.36	109	50	93.3	6.89
Mn	3.37	2.97	88.1	50	97.3	5.77
Fe	103	104	101	5000	99.0	0.06
Co	0.033	0.037	112	50	92.5	6.33
Ni	0.67	0.72	108	50	92.5	6.21
Cu	1.81	1.87	104	50	95.1	5.91
Zn	0.93	1.08	116	50	106	5.52
As	0.68	0.68	100	50	95.5	6.07
Se	n/c	< LLOQ	*	50	97.6	6.22
Mo	0.21	0.18	85.7	50	92.9	6.45
Ag	n/c	< LLOQ	*	50	98.0	6.22
Cd	0.012	0.011	91.7	50	99.4	5.90
Sb	0.23	0.25	109	50	95.2	6.29
Ba	12.2	12.7	104	50	97.3	4.85
Hg	n/c	n/c	n/c	0.5	107	0.00
Tl	n/c	< LLOQ	*	50	102	5.90
Pb	0.086	0.091	106	50	103	5.84
n/c = not certified			** = < LLOQ*			

The robustness of the method was determined by running samples for ten hours using the workflow scheme in Figure 1 and monitoring the internal standard recoveries over time. The results are shown in Figure 2 and indicate that internal standard recoveries are well within the 30% required by Method 6020B.

Conclusion

This work has demonstrated the ability of the NexION 300X/350X, running in both Standard and Collision modes, to easily meet the requirements of U.S. EPA Method 6020B for both water and soil samples. Unique instrument design characteristics minimize instrument maintenance, daily tuning/optimization, and increase stability, thereby allowing the analysis of more samples.

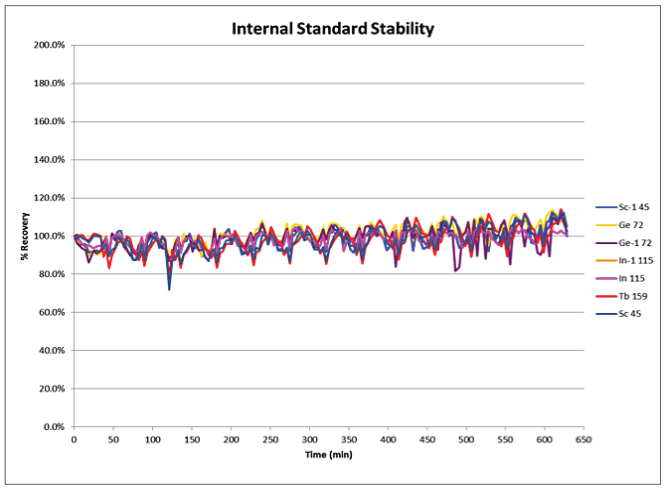

Figure 2. Internal standard recoveries over 10 hours.

Consumables Used

Peristaltic Pump	Component	Description	Part Number
MP2	Sample uptake tubing	0.64 mm id (orange/white), flared, 2-stop	N8145201
	Internal standard addition tubing	0.19 mm (orange/red), flared, 2-stop	N8145194
	Drain tubing	1.30 mm id (gray/gray), Santoprene, 2-stop	N8145173
	Internal standard addition tee	Tee for adding internal standard on-line	N0777294
Standard	Sample uptake tubing	0.38 mm id (green/orange), flared, 2- stop	N0777042
	Internal standard addition tubing	0.19 mm (orange/red), flared, 2-stop	N0773111
	Drain tubing	1.30 mm id (gray/gray), Santoprene, 2-stop	N0777444
	Internal standard addition tee	Tee for adding internal standard on-line	N0777294

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

PerkinElmer®

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

011973_01 PKI