APPLICATION NOTE

ICP - Mass Spectrometry

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The Analysis of Soils and Waters in Accordance with U.S. EPA Method 6020B using the NexION 2000 ICP-MS

Introduction

With the continued growth in global population and industry, liquid and solid wastes from a variety of sources are being generated and making their way into the environment. Although there is an increase in the implementation of recycling, green energy sources, and waste treatment technologies, waste continues to enter the environment.

In order to protect humans and the environment from liquid and solid wastes, the Resource Conservation and Recovery Act (RCRA) was implemented in 1976. Four years later, the United States Environmental Protection Agency (U.S. EPA) published “Test Methods for Evaluating Solid Waste, Physical/Chemical Methods” (also known as SW-846) to help labs comply with RCRA. Because of its breadth, SW-846 contains many methods covering a wide range of sample types and analytes. Since wastes can impact the environment through contamination of soil and/or water, both matrices are covered under RCRA and SW-846.

Through the years, both industry and analytical instrumentation have advanced. With the development of new chemicals and processes, new pollutants may enter the environment. However, the capabilities of analytical instruments have also increased, allowing the measurement of ever lower levels of environmental contaminants, as well as new pollutants.

To meet these new demands and capabilities, SW-846 has required periodic updates throughout the years, with the latest being Update V. This most recent version contains revisions to 23 of the methods, including Method 6020, which is now referred to as 6020B. Method 6020B includes the addition of new elements (as shown in Table 1), new detection limit criteria, and multiple new quality control (QC) parameters.

This work demonstrates that PerkinElmer's NexION® 2000 ICP Mass Spectrometer (ICP-MS) can be used as a simple Collision cell instrument to meet the needs of analytical laboratories involved in the analysis of waters and soils in accordance with Method 6020B, while offering the future proofing capability of three gas channels for the use of Controlled Reaction mode should the limits or the list of elements change.

Experimental

Samples and Sample Preparation Since waters and soils fall under Method 6020B, both were analyzed.

The water samples were acidified to 2% HNO3 + 1% HCl (v/v), while the soil solutions were diluted 10x with a mixture of 2% HNO3 + 1% HCl (v/v). To aid mercury (Hg) washout, 200 µg/L gold (Au) was added to all samples and standards. Calibration standards were also prepared in the same acid mixture at the levels shown in Table 2, along with the addition of 200 µg/L Au. All standards and internal standards were made from stock solutions shown in the Consumables Used table at the end of this document.

Internal standards were added on-line to all standards and samples, eliminating the need for manual addition. Although a variety of internal standards may be used, the four listed in Table 2 were found to be effective for all elements by spanning both the mass range and ionization potentials of the analytes.

In order to verify the accuracy of the technique, both water and soil certified reference materials (CRMs) were analyzed. The water CRM is representative of a natural water (NIST 1640a Trace Elements in Natural Water, National Institute of Standards and Technology, Rockville, Maryland, USA), which is most likely to be affected by waste discharges. The soil reference materials mimicked digested contaminated soils: Soil Solution B and River Sediment B, both from High Purity Standards™ (Charleston, South Carolina, USA).

Instrumental Conditions

To simplify analysis and increase sample throughput, all analyses were performed on a NexION 2000 ICP-MS, which comes equipped with both a SMARTintro™ High Throughput/High Matrix sample introduction module which includes an All Matrix Solution (AMS) system. The High Throughput/High Matrix system consists of a 7-port switching valve and 1 mL loop, which increases sample throughput by minimizing sample uptake and washout. The AMS system uses on-line aerosol dilution to decrease matrix suppression normally seen with aqueous dilutions. Specific conditions are listed in Table 3.

To further increase productivity and confidence in the data, as well as simplify the analysis, all analyses were carried out in Collision mode, which greatly reduces the effects of polyatomic interferences. This is an important consideration in environmental analyses where the interferences can vary from sample to sample, depending on matrix differences and/or containing different wastes.

Table 1. Complete List of Elements Defined in Method 6020B with Recommended Analytical Masses.

Analyte	Symbol	Recommended Mass (amu)	Elemental Equation
Aluminum	Al	27	
Antimony	Sb	121	
Arsenic	As	75	
Barium	Ba	137	
Beryllium	Be	9	
Boron*	B	11	
Cadmium	Cd	111	
Calcium	Ca	44	
Chromium	Cr	52	
Cobalt	Co	59	
Copper Iron	Cu	63	
Lead #	Fe	56	
Magnesium	Pb	208	+1 * Pb206 + 1 * Pb207
Manganese	Mg	24	
Mercury	Mn	55	
Molybdenum	Hg	202	
* Nickel	Mo	95	
Potassium	Ni	60	
Selenium	K	39	
Silver Sodium	Se	78	
Thallium	Ag	107	-0.030461 * Kr83
Vanadium	Na	23	
Zinc	Tl	205	
	V	51	
	Zn	66	

* Information only (not part of Method 6020B)
# Sum of isotopes provides more accurate results due to radioactive decay of higher mass elements

Table 2. Calibration Standards.

Analytes	Standard 1 (µg/L)	Standard 2 (µg/L)	Standard 3 (µg/L)	Standard 4 (µg/L)
Be, B, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sb, Ba, Tl, Pb	1	10	50	100
Hg	0.1	1	5	10
Na, Mg, Al, K, Ca, Fe	100	1000	5 0 0	0 10000
Ga, Ge, In, Ir	Internal Standards			

Table 3. Instrumental Conditions.

Parameter	Description/Value
Sample Delivery Rate	350 µL/min
Nebulizer	MEINHARD® plus Glass Type C
Spray Chamber	Glass cyclonic (baffled), 2 °C
Injector	2.0 mm i.d.
Nebulizer Flow	Optimized for < 2% oxides
RF Power	1600 W
Cones	Ni
Replicates	3
Aerosol Dilution	Set to 2.5x

Results and Discussion

Accuracy of the methodology was established through the analysis of the three reference materials described above. The analyte recoveries appear in Figure 1, showing that all recoveries are within 10% of the certified values, thus validating the accuracy of the NexION 2000 methodology.

With the accuracy of the methodology established, the stability was verified during an eight-hour analysis of soil samples. A continuous calibration verification (CCV) standard (representing the mid-point of the calibration curve) was measured every 10 samples. Figure 2 demonstrates the stability of the NexION 2000 system: over eight hours, the CCV recovery remained within 10% of the true value for all elements. This data was acquired without recalibration or excessive rinsing between samples: the analysis mimics a run in a commercial lab, emphasizing the robustness and stability of both the methodology and the NexION 2000 system.

During the same analytical run, the internal standard recoveries relative to the calibration blank were also monitored, as shown in Figure 3. All internal standards recover within 15% of their values in the calibration blank, further validating the robustness of the methodology. This performance is the direct result of NexION 2000's instrumental design considerations (including the solid state, free-running RF generator, Triple Cone Interface, and Quadrupole Ion Deflector), the use of AMS and the SMARTintro High Throughput/ High Matrix sample introduction system.

With the accuracy and stability of the methodology established, the method detection limits (MDLs) and lower limits of quantitation (LLOQs) were determined. The MDLs were calculated by multiplying the standard deviation of seven replicate measurements of a blank by 3.14, while the LLOQ is the lowest concentration standard that reads within + 35% of its true value when measured against the calibration curve. The values for both the MDLs and LLOQs appear in Figure 4.

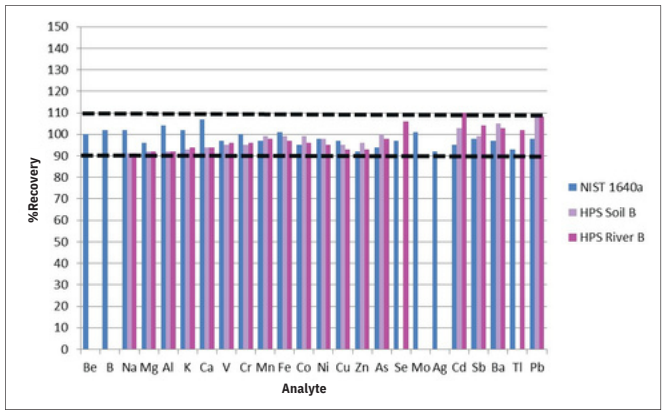

Figure 1. Analyte recoveries in reference materials: blue represents the water, shades of violet represent soils. Not all elements were certified in all reference materials.

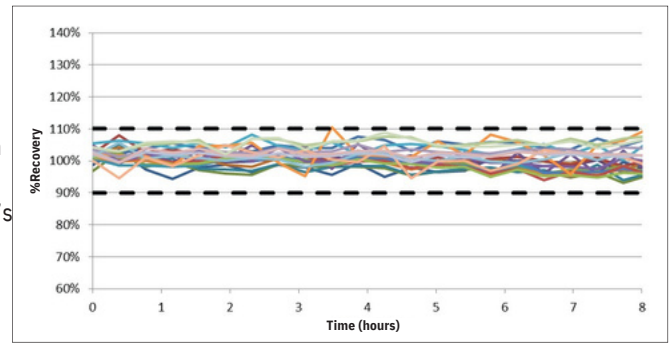

Figure 2. CCV recoveries over an eight-hour soil analysis.

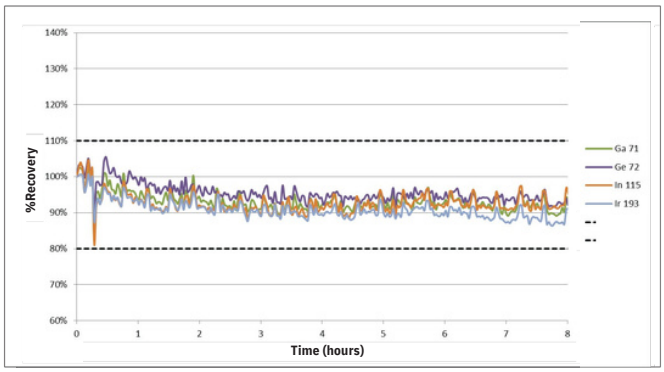

Figure 3. Internal standard stability over eight hours of soil analysis.

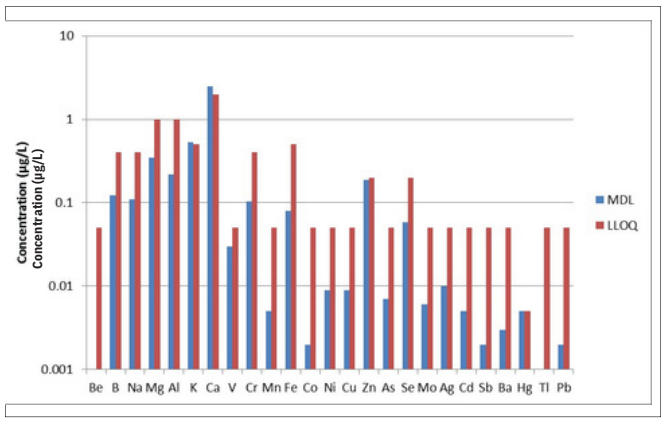

Figure 4. MDLs (blue) and LLOQs (red).

Conclusion

This work has demonstrated the ability of PerkinElmer's NexION 2000 ICP-MS to easily meet the requirements of U.S. EPA Method 6020B. Excellent accuracy and stability are achieved through distinctive features of the NexION 2000, including the Triple Cone Interface, Quadrupole Ion Deflector, Universal Cell Technology, a unique solid-state free-running RF generator, and All Matrix Solution system. With the use of the standard SMARTintro High Throughput/High Matrix sample introduction module, productivity is increased without sacrificing performance.

The NexION 2000 ICP-MS provides a complete solution to the challenges of U.S. EPA Method 6020 for dealing with liquid and solid wastes in the environment.

Consumables Used

Component	Description	Part Number
Sample Uptake Tubing	Green/orange (0.38 mm id), flared, PVC, package of 12 Gray/gray	N8145197 (MP2 peristaltic
Spray Chamber Drain Tubing	Santoprene (1.30 mm id), package of 12	pump) N8145160 (MP2
Instrument Calibration Standard 2	100 mg/L Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni,	peristaltic pump) N9301721 (125 mL)
Environmental Standard Mix 2	Pb, Sb, Se, Sn, Sr, Ti, Tl, V, Zn	N9307805 (125 mL)
Environmental Standard Mix 3	1000 mg/L Na, Mg, K, Ca	N9307806 (125 mL)
Environmental Standard Mix 4	1000 mg /L Al, Fe	N9307807 (125 mL)
Mercury Standard	100 mg/L B, Th, U	N9300253 (125 mL)
Internal Standard Mix	10 mg/L Hg	N9307738 (125 mL)
Germanium Standard	Sc = 200 mg/L; Ga = 20 mg/L; Rh, In, Ir, Tm = 10 mg/L 1000 mg/L	N9303774 (125 mL) N9300120 (500 mL)
Gold Standard	1000 mg/L	N9303759 (125 mL)
Autosampler Tubes	Metal-free, racked, white caps, 500 per package	N0776118 (15 mL) N0776116 (50 mL)

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