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

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Introduction

- Liquid and soil wastes enter the environment
  - Quantity and diversity of wastes increasing
  - Contaminate soils and waters

- U.S. EPA Method 6020 developed to address contaminated soils and waters
  - Updated several times throughout the years
  - Applies to both waters and soils
  - Latest iteration is 6020B, which includes
    - New elements – 23 in total
    - New detection limit criteria
    - New QC criteria

Elements

Analyte	Symbol	Recommended Mass (amu)
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	Cu	63
Iron	Fe	56
Lead#	Pb	208

Analyte	Symbol	Recommended Mass (amu)
Magnesium	Mg	24
Manganese	Mn	55
Mercury	Hg	202
Molybdenum*	Mo	95
Nickel	Ni	60
Potassium	K	39
Selenium	Se	78
Silver	Ag	107
Sodium	Na	23
Thallium	Tl	205
Vanadium	V	51
Zinc	Zn	66

- B, Mo: Not part of 6020B; analyzed for “information only”
- Pb: Sum Pb206 + Pb207 + Pb 208 isotopes

Why Sum the Pb Isotopes?

- Pb occurs naturally with 4 isotopes:

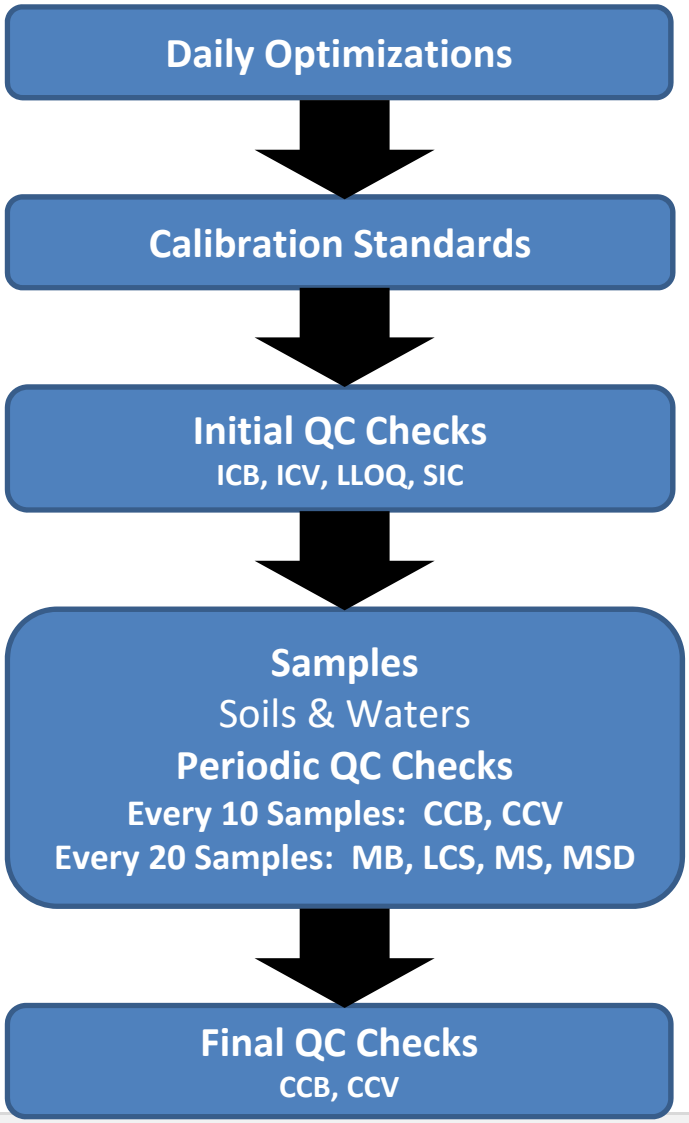
Pb Isotope	Natural Abundance
204	1.4%
206	22.4%
207	22.1%
208	52.4%

- Other elements undergo radioactive decay and turn into Pb
  - Th 232 → Pb 208 → Decay time = 1.4 billion years
  - U 235 → Pb 207
  - U 238 → Pb 206

  } Decay Time = 4.46 billion years

- For highest accuracy, the Pb isotopes must be summed

Daily Work Flow



Confirm instrument is performing as expected

Establish Calibration Curves

Verify calibration curve
Establish performance for methodology

Run Samples
QC verifies instrument performance during analysis & sample preparation

Verifies instrument performance

Samples & Sample Preparation

- Samples
  - Water & soil reference materials
  - NIST 1640a Trace Elements in Natural Water
  - HPS Soil Solution B
  - HPS River Sediment B

- Sample Preparation
  - Waters: Acidified to 2% HNO_3 + 1% HCl
  - Soils: 10x dilution with 2% HNO_3+ 1% HCl
  - 200 ppb Au added to aid with Hg washout

A Word on Soil Reference Materials

- Solid soil reference materials exist
  - For example NIST 2711a Montana II Soil

- The analytical results depend on sample preparation
  - Since soils contain Si, complete digestion requires HF
  - EPA methods for leaching soils, without the use of HF
    - Silicates not dissolved → not total metals
  - Various sample preparation methods available

HCl (mL)	HNO_3 (mL)
0	10
3	9
9	3

Will give different results

A Word on Soil Reference Materials

- NIST 2711 Montana II Soil as an example
  - Drying Samples
    - Recommended at 110°C for 2 hours
    - But don't dry for volatile elements (i.e. As, Hg, Se)
      - Need to correct for moisture content
  - Total Results
    - Many from solid-sampling techniques (i.e. XRF, INAA, etc.)
    - Analyses done by NIST and USGS
  - Leach Results
    - Determined with ICP-OES and Method 3050b (hot plate digestion)
    - 6 commercial labs
    - % Recoveries relative to total composition: 1.5% (Na) to 100% (Hg)

What is the correct, accepted concentration in solid soil reference materials?

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	5000	10000
Ga, Ge, In, Ir	Internal Standards			

- Prepared in 2% HNO_3 + 1% HCl
- 200 ppb Au added to aid with Hg washout
- External calibration curves – linear through zero

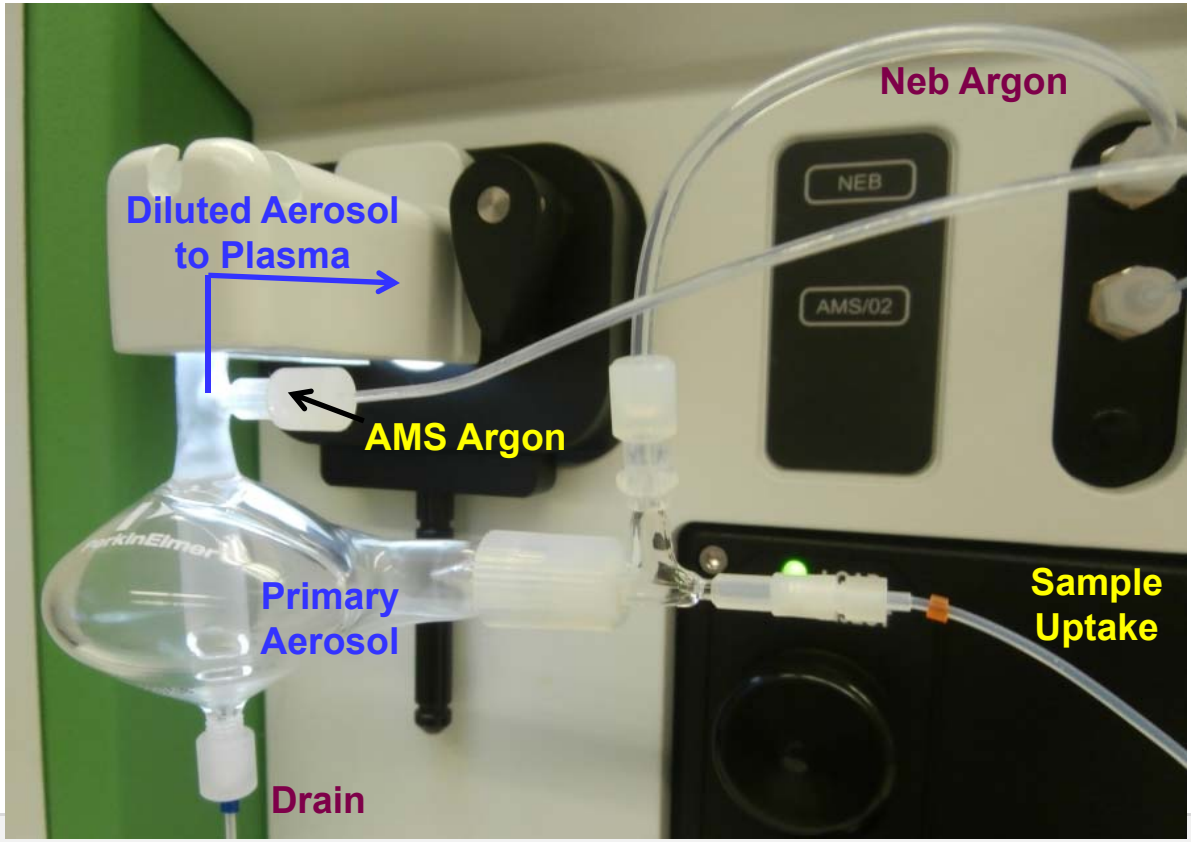
Instrumental Conditions: NexION® 2000 ICP-MS

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

- All elements measured in Collision mode
  - Increases confidence in results when matrices & interferences can vary from sample to sample

Instrumental Conditions: NexION® 2000 ICP-MS

- On-line aerosol dilution
  - Decreases matrix suppression
  - Set to 2.5x



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Instrumental Conditions: NexION® 2000 ICP-MS

- 7-port switching valve with 1 mL sample loop
  - Increases sample throughput
  - Minimizes sample uptake and washout
- On-line addition of internal standards through switching valve
  - Increased productivity
  - Less chance of error
  - Enhanced mixing

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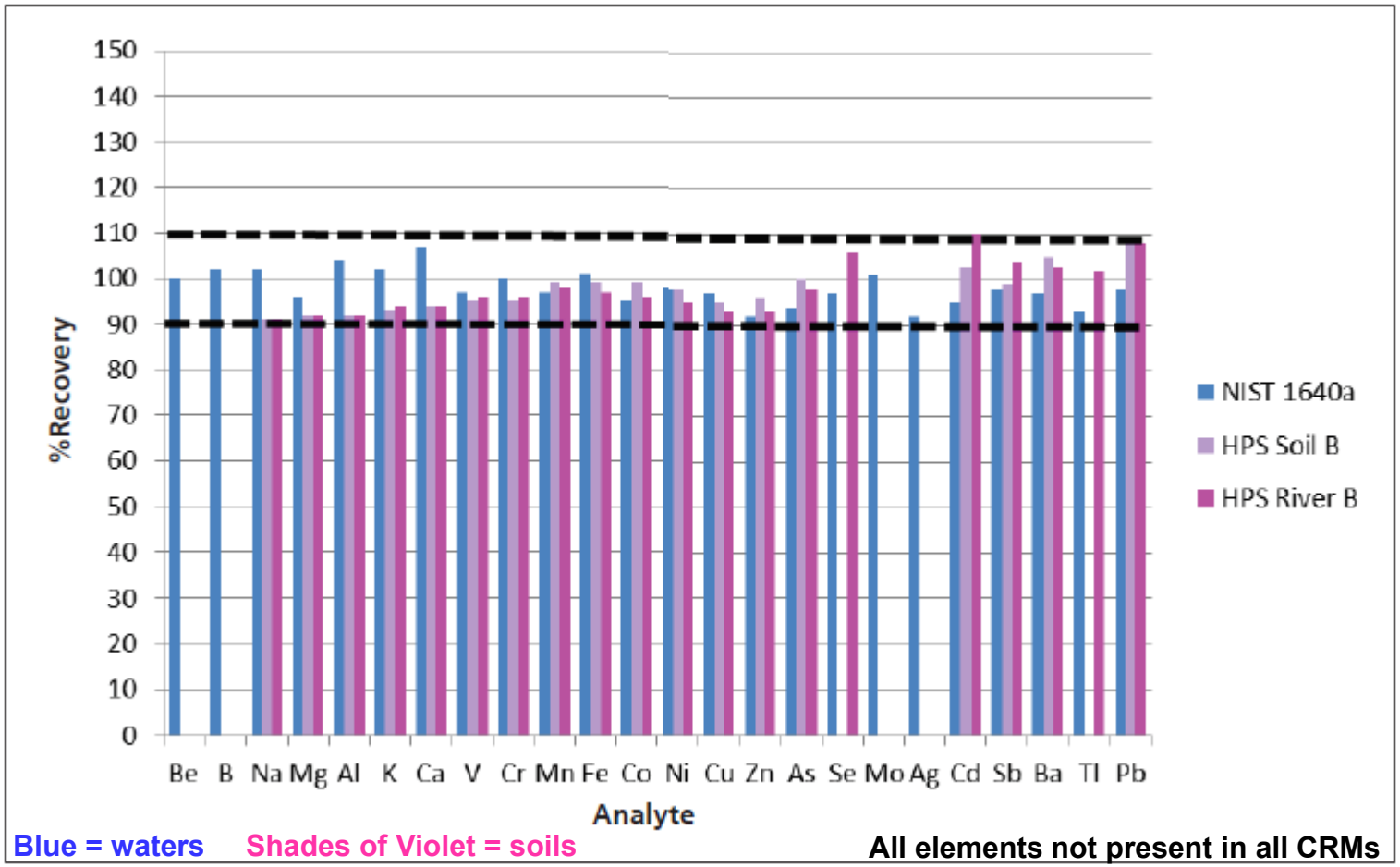
Results: Reference Materials

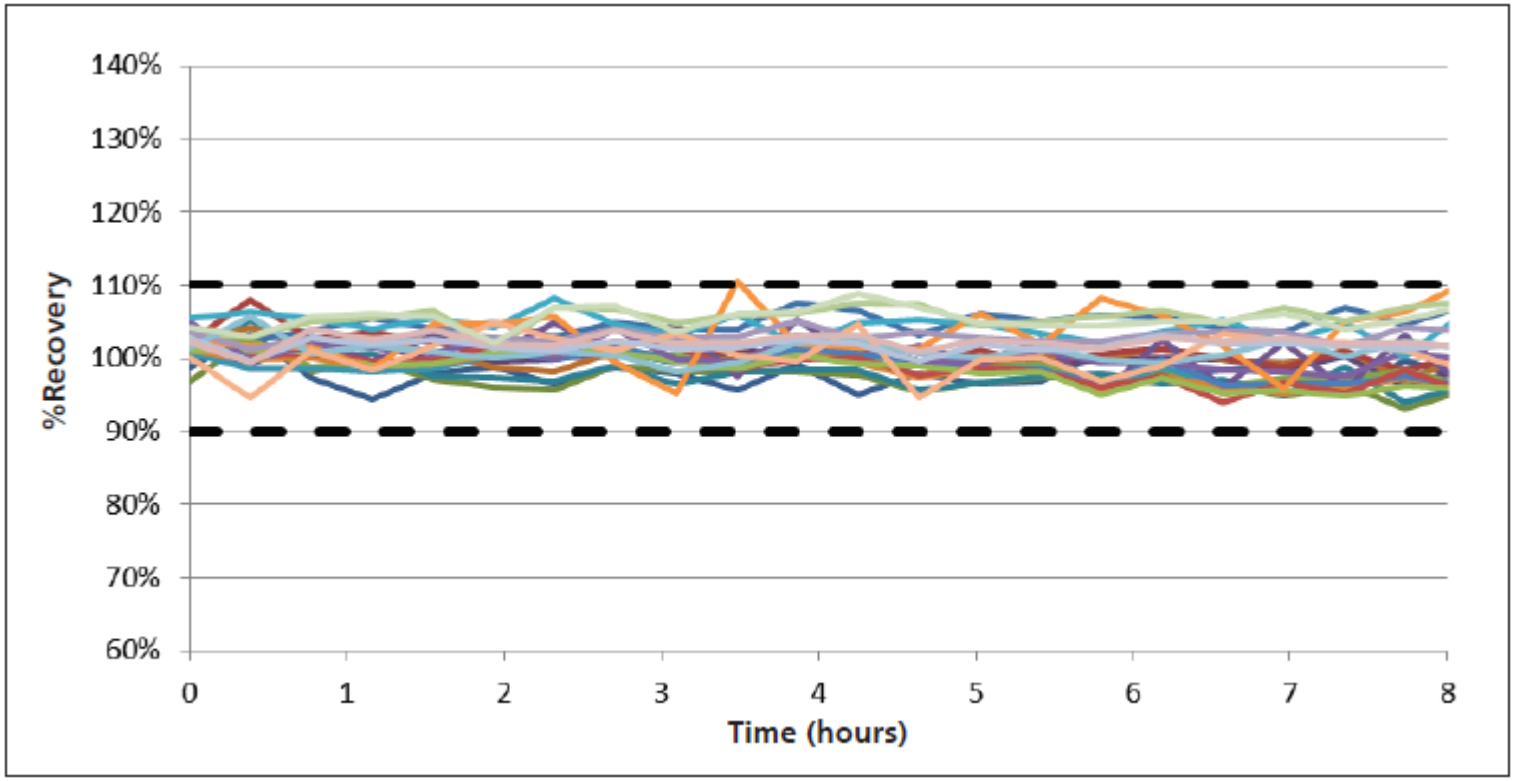


All Recoveries within 10% of Certified Values

Accuracy Established

Results: Stability – CCV

- 8 hour analysis of soil samples
- Calibration check standard analyzed every 10 samples
- No recalibration, no extra rinsing

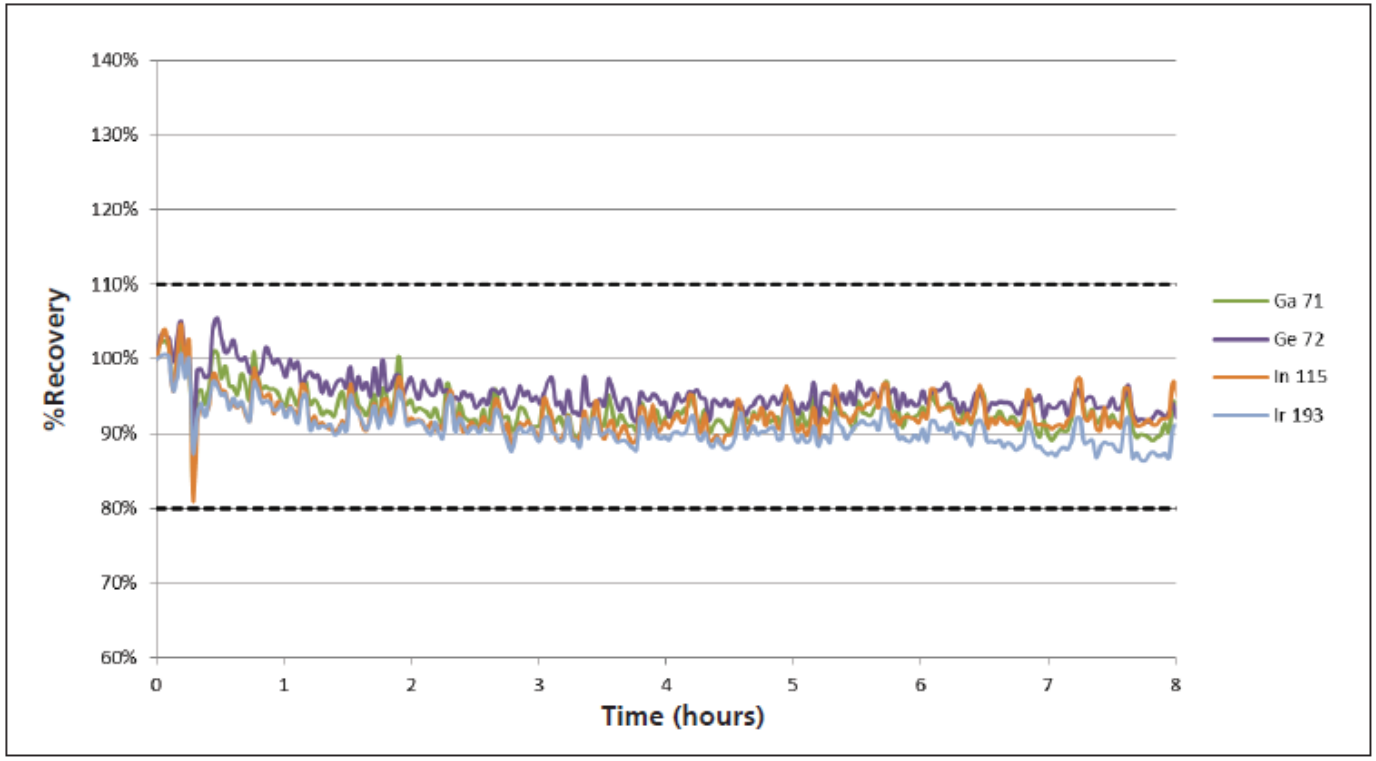


Variations within ± 10% over 8 hours

Stability Established

Results: Stability – Internal Standards

- 8 hour analysis of soil samples
- Monitor internal standard intensities for all samples
  - Recoveries relative to calibration blank



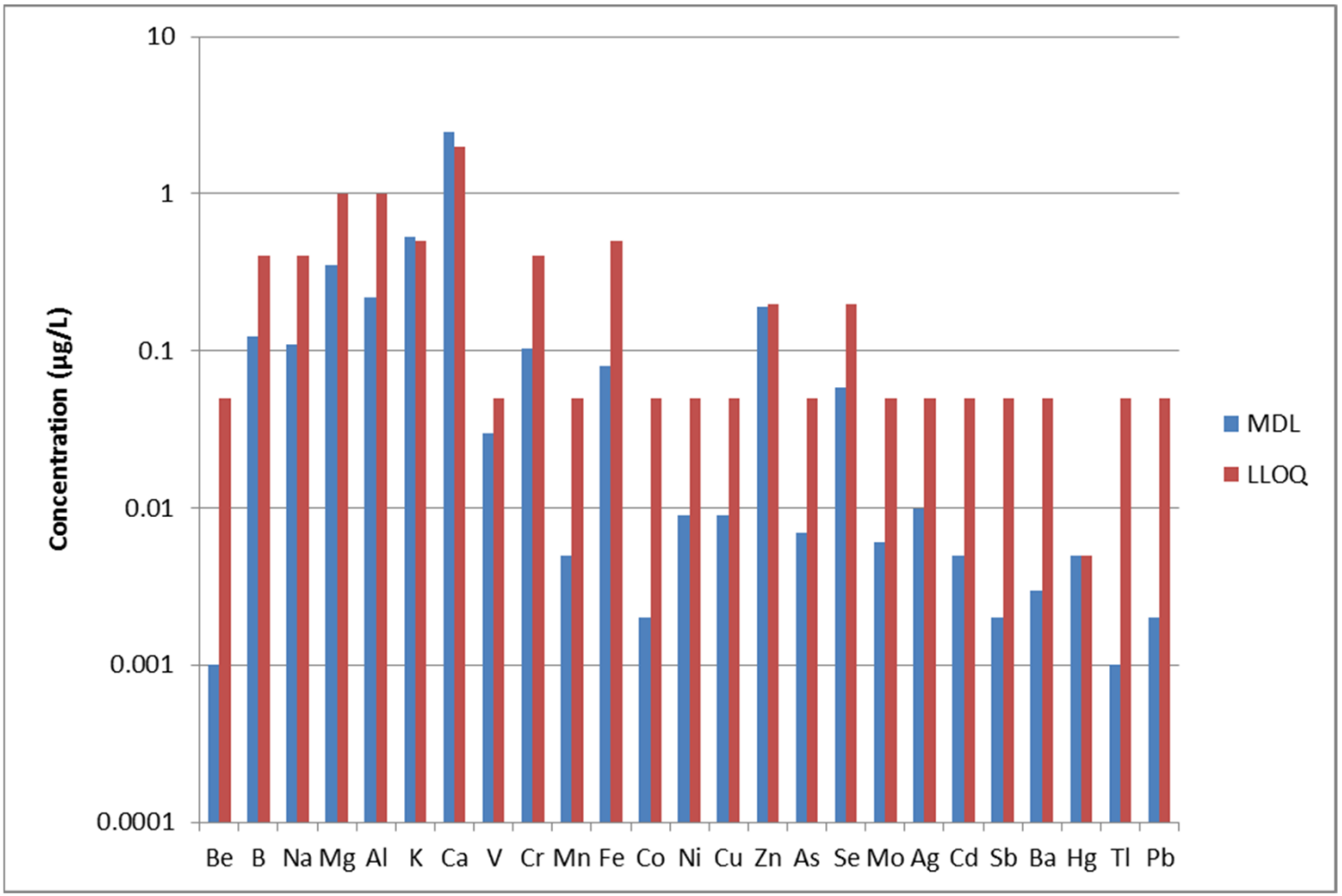
Well within method-defined criteria over 8 hours

Stability Established

Results: MDLs & LLOQs

- Method Detection Limits
  - 7 replicate measurements of a blank
  - Multiply standard deviation by 3.14
- Lower Limit of Quantitation
  - Lowest concentration standard that can be read within 35% of its true value against the calibration curve

Results: MDLs & LLOQs



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Summary

- Criteria of U.S. EPA Method 6020B met
  - Accuracy
  - Stability
  - Matrix effects
- Same methodology applied to both waters and soils
- Everything run in Collision mode
  - More confidence in results as samples can vary significantly