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Unbalanced Nested Random Effects Estimation of Variance Components

February 2023

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Introduction

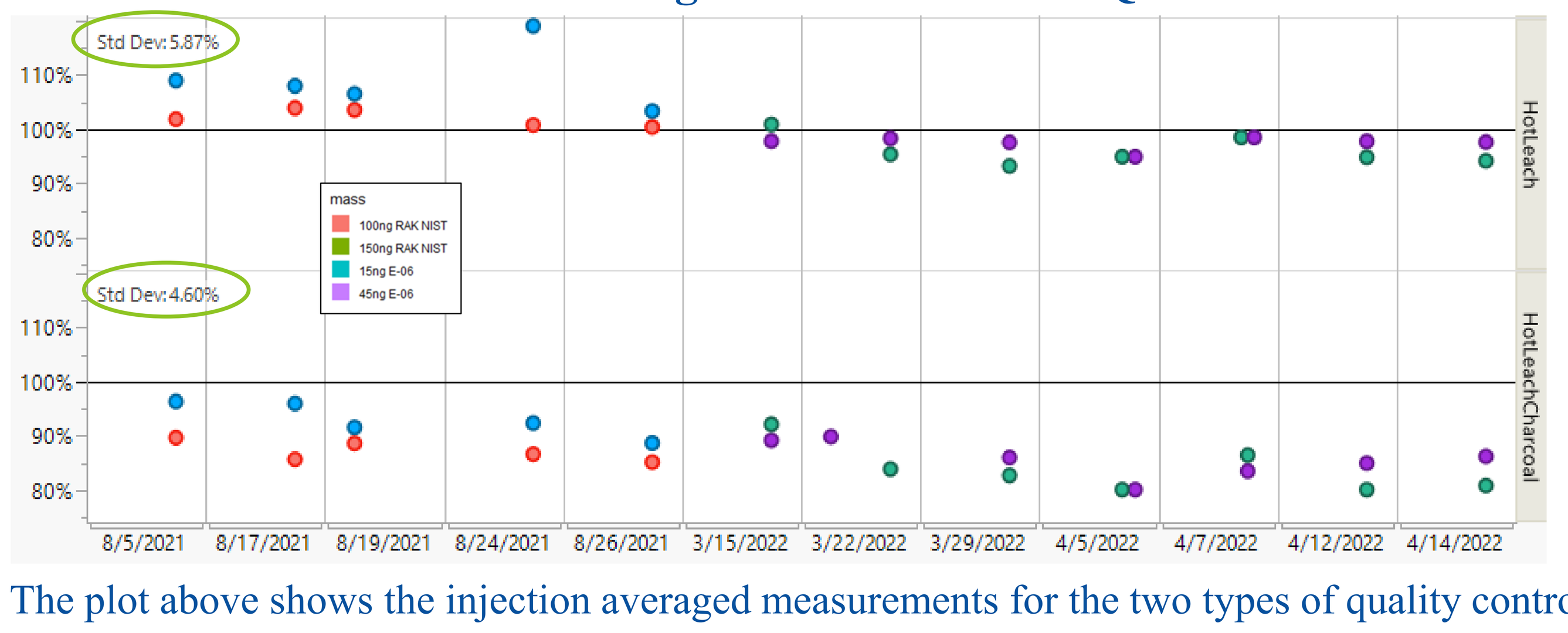
The current approach to uncertainty quantification of an Iodine isotope, ^{127}I, concentration measurement with an inductively coupled plasma mass spectrometry instrument (ICP-MS) is to combine known assay uncertainties with the variance calculated from multiple ICP-MS readings for a particular sample. This approach does not explicitly incorporate variance due to batch and run level processing because unknown samples are processed within one run in one batch (no replication). Here we use measurement results of standards with known concentrations, which are measured along side unknown samples during each processed batch and run, to quantify the uncertainty of the ^{127}I measurement with a random effects variance components analysis.

Objective:

Assess the validity of current uncertainty estimates for the measurement of ^{127}I obtained by forward uncertainty propagation and assay uncertainties.

- Compare to a variance components analysis using replicate measurements of standards.
- Determine largest sources of variance contributing to uncertainty in measurements and identify where improvements in precision can be made.
- Compare variance of process standard measurements with instrument calibration standard measurements.

Variation in Average Measurements of QC Standards



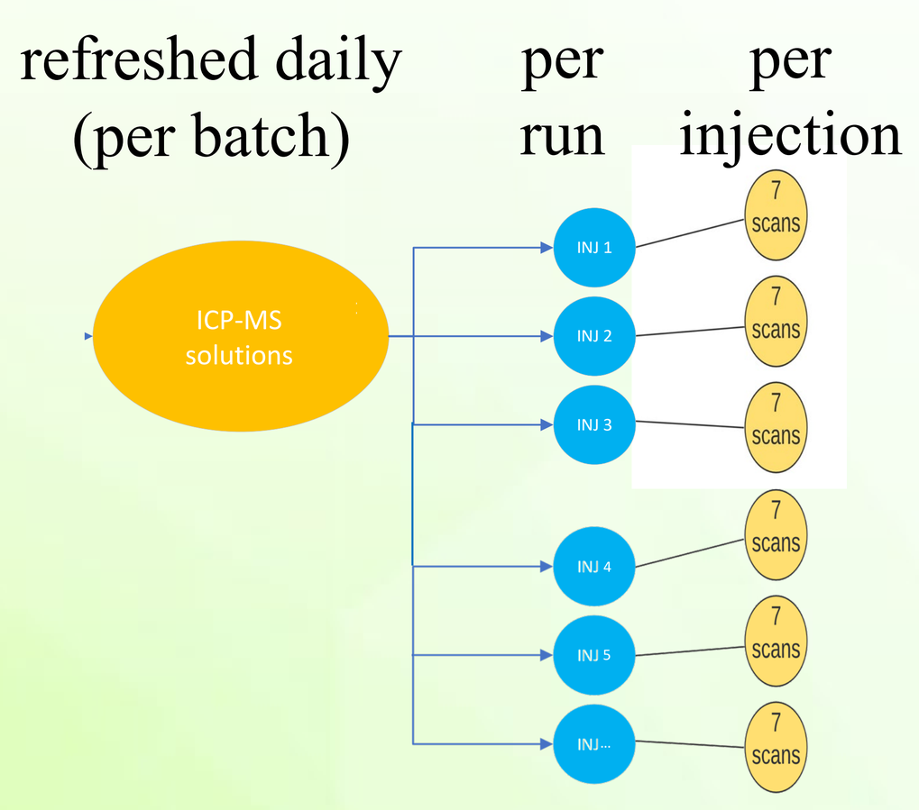
The plot above shows the injection averaged measurements for the two types of quality control (QC) standards from two experiments. This variation shown here gives an empirical estimate of the overall uncertainty (in standard deviation) which we expect to be similar to the uncertainty calculated from forward propagation and from the variance component analysis we present here.

Materials

The data used here are from two experiments from Idaho National Laboratory (INL). The data consist of two types of standards with known concentrations:

- Instrument calibration standards (1.0 ppb and 0.25 ppb).
  - Used only to calibrate instrument response for each ICP-MS run.
- QC standards (standards that go through hot-leach processing, and standards that are spiked on charcoal and then go through hot leach processing).
  - Used to monitor the entire measurement process.

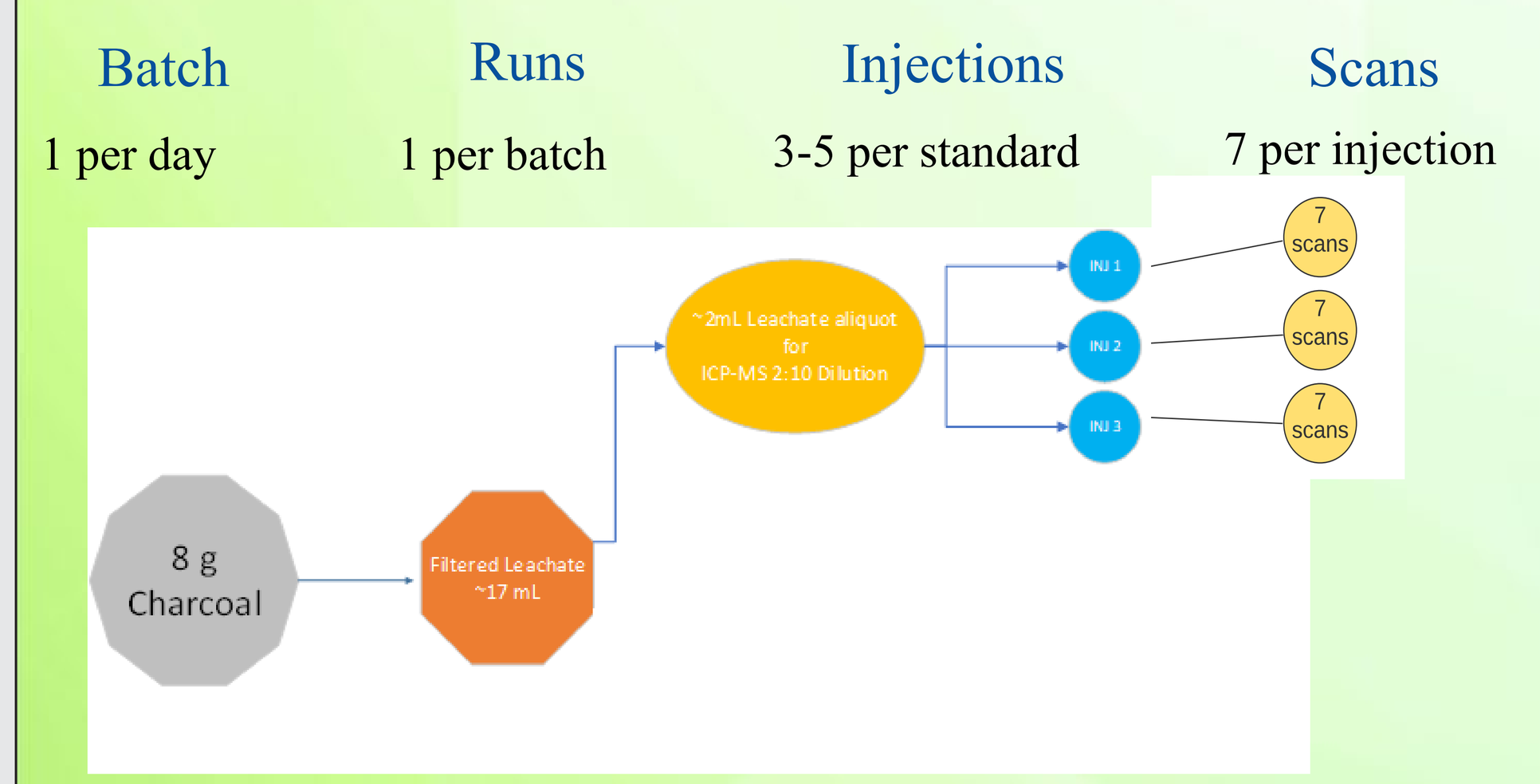
Instrument Calibration Standards



Calibration Standards measure variance of ICP-MS assay

- 12 days (batches), 2 ICP-MS runs per day
- 179 1.0-ppb-standard injections
- 119 0.25-ppb-standard injections

Hot Leach QC Standards



Experiment A

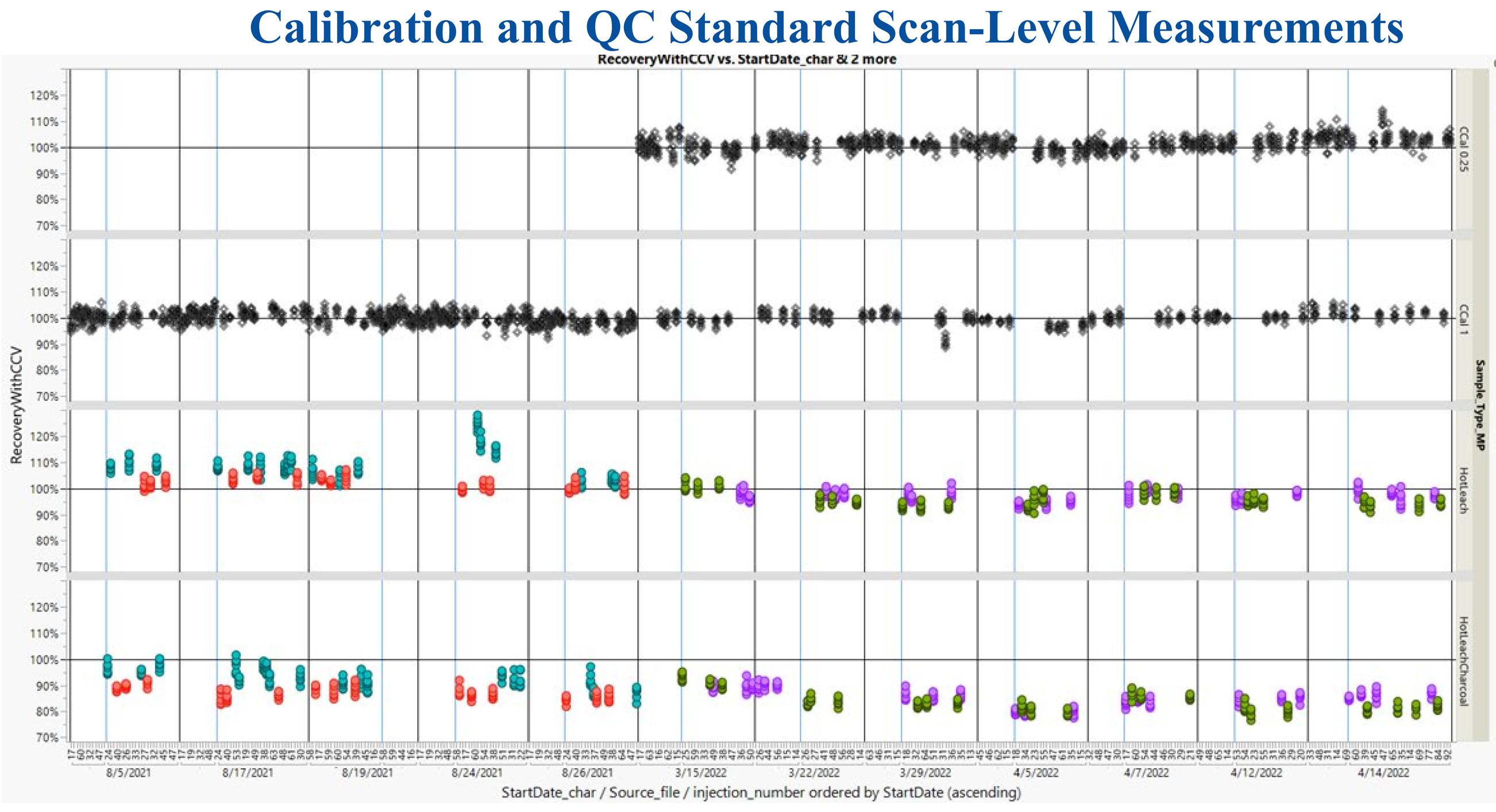
- 5 days, ~1 ICP-MS run per day
- 18 15-ng-standard injections
- 15 100-ng-standard injections

Experiment B

- 7 days, ~1 ICP-MS run per day
- 22 45-ng-standard injections
- 22 150-ng-standard injections

	Variance Mechanism		
Variance component	ICP-MS 'Continuing Calibration (CC)' Standards	QC Standards – No Charcoal	QC Standards – Charcoal
Scans within injections	Instrument	Instrument	Instrument
Injections within runs	Instrument	Instrument	Instrument
Runs within days	Instrument	Instrument	Instrument
Among days (hot leach batches)	• Instrument • ICP-MS solutions (standards, diluent, rinse,…)	• Instrument • ICP-MS solutions • Chemical processing • *Solution spiking process*	• Instrument • ICP-MS solutions • Chemical processing • *Charcoal spiking process* • Leaching process • Charcoal

Calibration and QC Standard Scan-Level Measurements



The plot above shows (from top to bottom) the 0.25 ppb and 1.0 ppb calibration standards, QC leached standards, and QC spiked on charcoal and leached standards' scan-level data. The colors of the points indicate different masses, the black vertical lines indicate batches, and the blue vertical lines indicate runs.

Methods

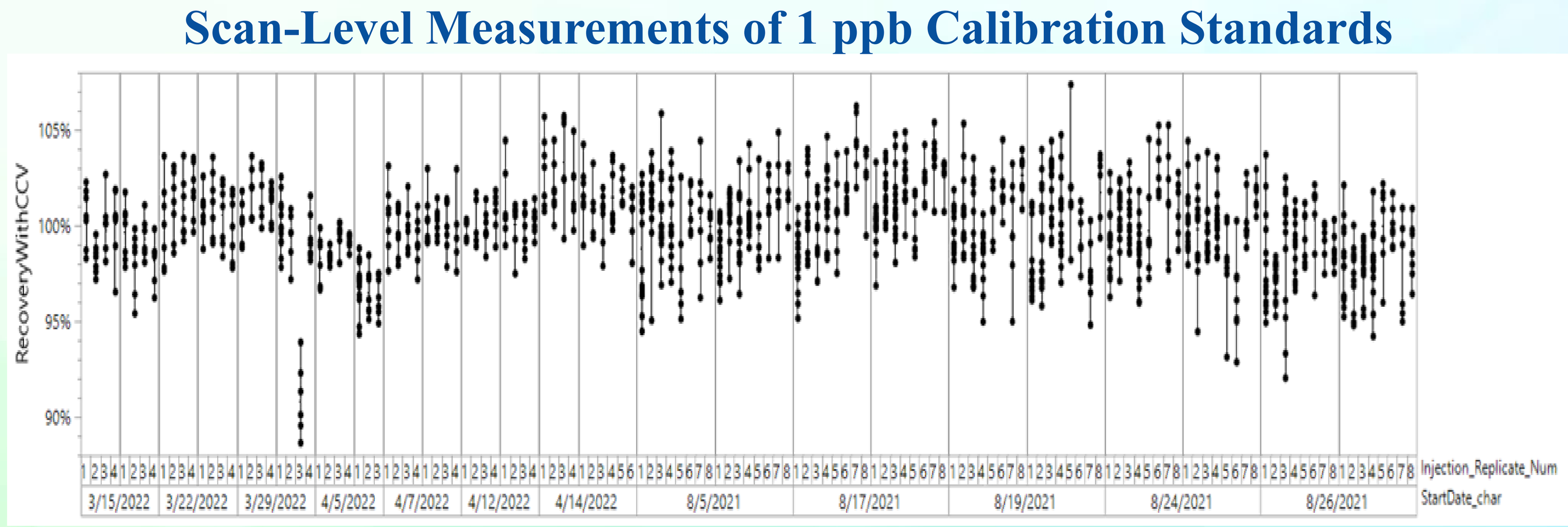
We implemented an unbalanced, nested, random effects analysis of variance (ANOVA) to estimate the variance components for the different levels of the data using SAS Enterprise Guide version 7.15 Procedure VarComp with Restricted Maximum Likelihood (REML). We then derived a formula to calculate the uncertainty of a measurement from a single batch, single run, and average of three (or more) injections with seven scans per injection using the estimated variance components. The design was unbalanced because the number of injections varied among observations (calibration standards typically had more injections than QC standards).

Source of Variation	Degrees of Freedom	Mean Square	Expected Mean Square
Total	abcd - 1	—	—
Batch	a – 1	MSA	$\sigma^2_{c(b)} + c\sigma^2_{b(a)} + bc\sigma^2_a$
Injection within Batch	a(b – 1)	MS(B/C)	$\sigma^2_{c(b)} + c\sigma^2_{b(a)}$
Scans within Injection	ab(c – 1)	MS(C/D)	$\sigma^2_{c(b)}$

The three variance components are estimated by equating the mean squares to the expected mean squares in the ANOVA table above and solving by to obtain each of the σ^2 terms.

Variance of mean of b injections: $\sigma^2_{\bar{y}_{b_{inj}}} = \frac{\sigma^2_{c(b)}}{bc} + \frac{\sigma^2_{b(a)}}{b} + \sigma^2_a$

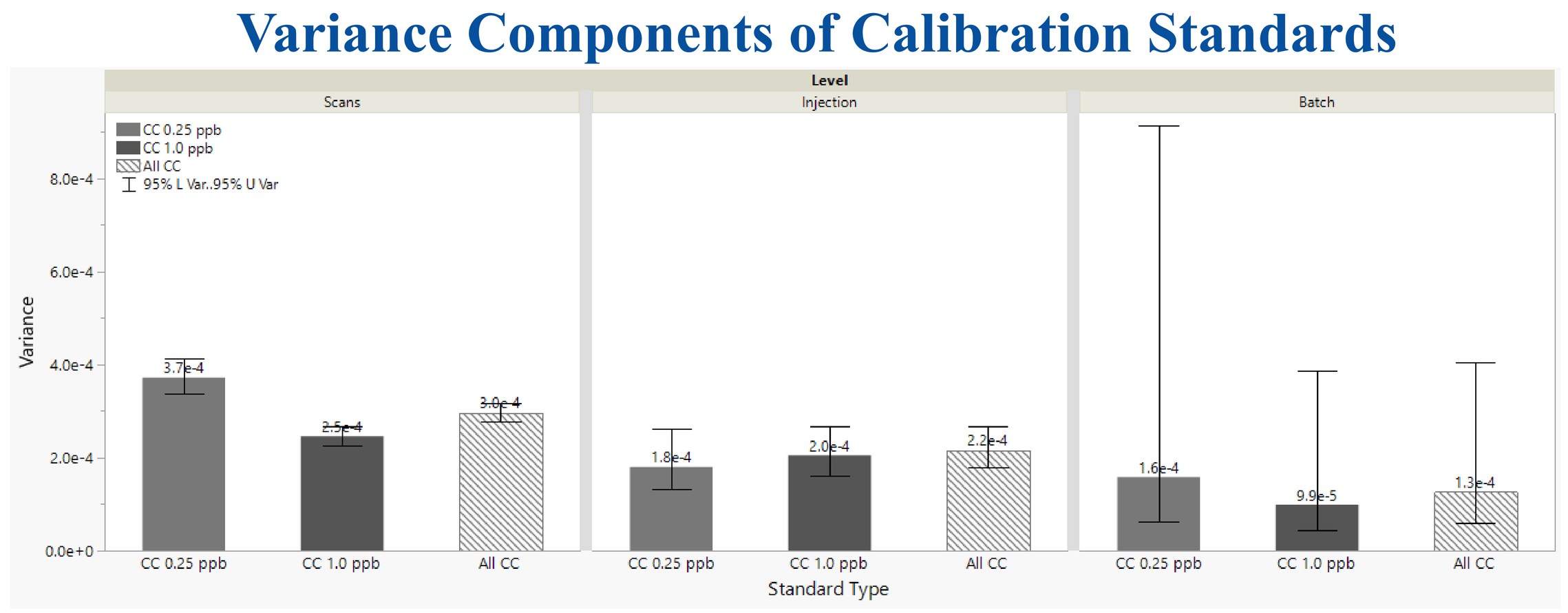
Scan-Level Measurements of 1 ppb Calibration Standards



This plot shows the variation in scans, injections, and batches for the 1 ppb calibration measurements. The connected dots represent the seven scans from on injection, and the vertical lines represent runs, and the dates indicate batches. Also note the number of injections varies among runs.

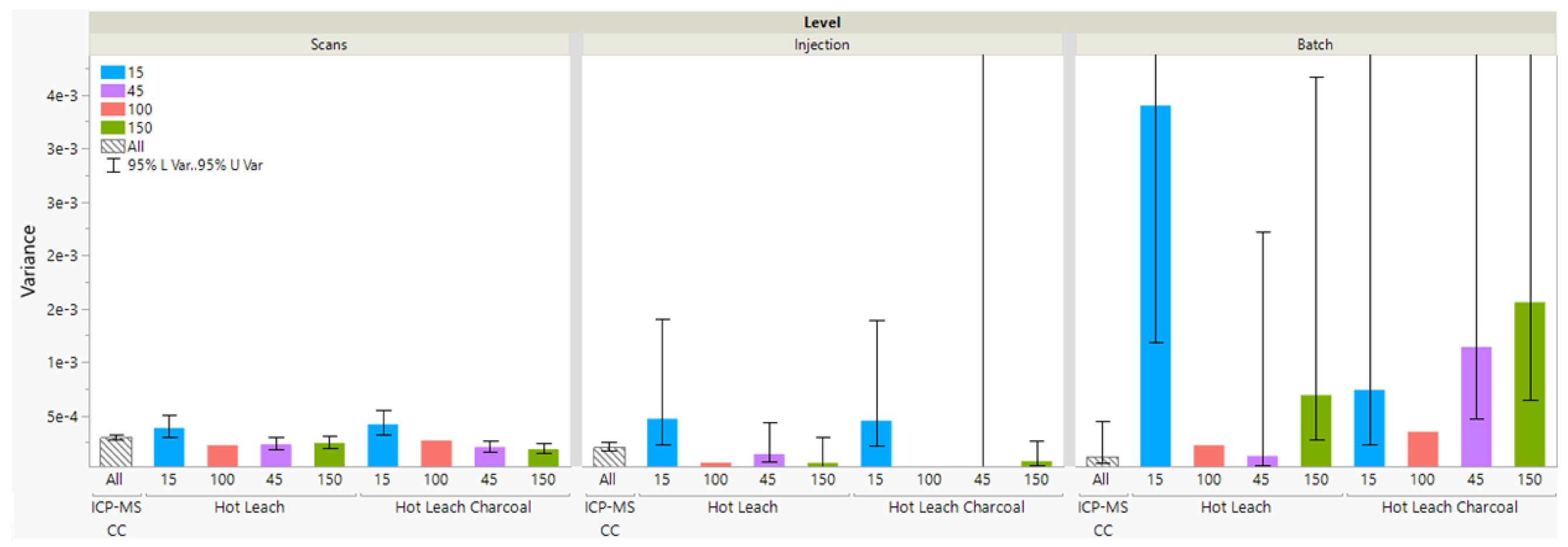
Results

Variance Components of Calibration Standards



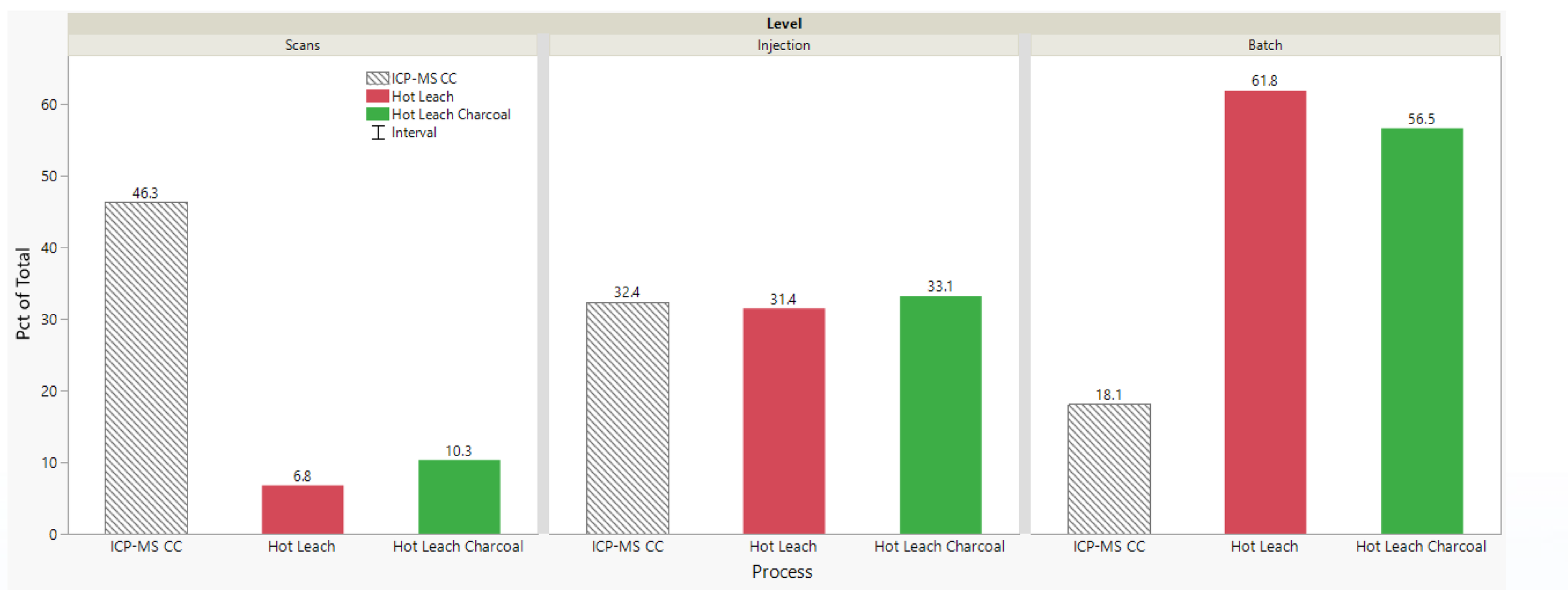
- Variance Components ordered by magnitude:
  - Scan > Injection > Batch (Day)
    - QC standards are only in one run per batch

→ Combined run and batch as one level

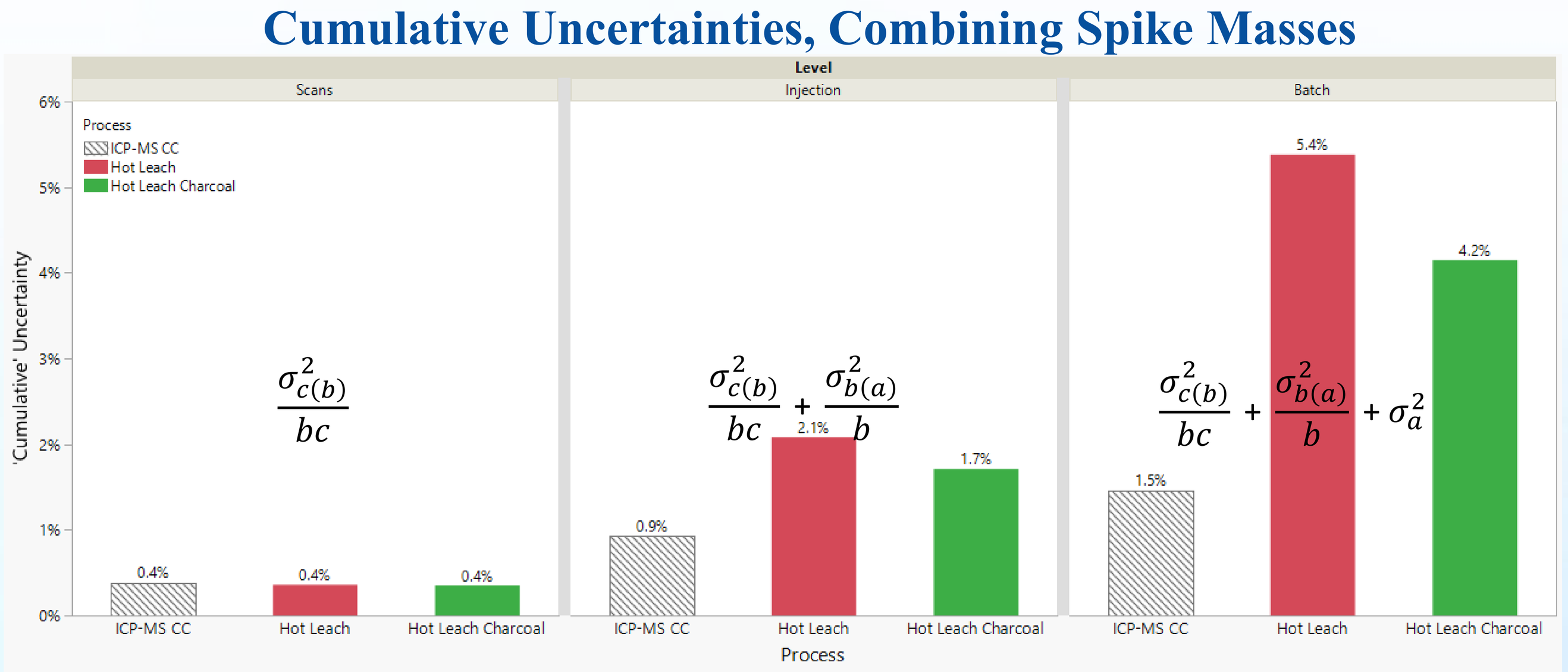


- Comparing variance components of leached solutions to calibration data:
  - Scan- and Injection- level variances similar
  - Batch-level variance, while more uncertain, is significantly greater for leached solutions
  - 15-ng stands out as having greater overall variance
  - No obvious relationship between spike mass and variance

Variance Fraction of hot leach QC Standards Combining Masses



Cumulative Uncertainties, Combining Spike Masses



Conclusion

- Overall uncertainties in 127I recovery, of hot-leach-processed solutions, is ~5% of mass (which is consistent with current reported uncertainties from forward propagation).
- Uncertainties in 127I 'recovery' of ICP-MS CC standards is ~1%.
- Batch- Injection- level variance, while more uncertain, is significantly greater for processing solutions.
- Scan- level variances seem consistent across ICP-MS- and hot-leach- standards.
- Though based on limited data, concentration dependence is not evident in variances.
- Run-level and batch-level variance estimates were most imprecise (small N).

• Future Work

- Upcoming replicated measurements experiment should improve these estimates.
- Compare these Type A uncertainties to those generated by forward propagation:
  - Mass & volume measurement uncertainties
  - ICP-MS intensity variance
  - Calibration parameter uncertainty
  - 128Te IPA correction uncertainty.

References

Kuehl R. O. *Design of Experiments : Statistical Principles of Research Design and Analysis*. 2nd ed. Duxbury/Thomson Learning. 2000.

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