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ALP Program Report

2017 Spring - Cycle 32

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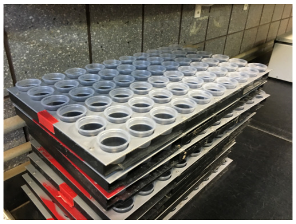
Special points of interest:

- Soil homogeneity assessment indicate ALP reference materials were highly uniform for Cycle 32.
- Sixty-one Laboratories provided soil pH (1:1) H_2O results and medians ranged from 5.32 - 8.12.
- Cycle 32 soil Bray P1 ranged from 1.7 to 540 mg kg^{-1} with MAD values ranging 0.2 - 42 mg kg^{-1} across the five soils.
- Lab results for Mehlich-3 Mg were inconsistent on two of five proficiency soils for cycle 32.
- Botanical P, ranged from 0.186 - 0.360% with one of thirty-eight labs noted for high bias.
- Botanical Zn results showed high consistency across the four samples for thirty-one of thirty-six labs for PT Cycle 32.
- Water EC content showed very high consistency by sixteen of seventeen labs across all samples.

Inside this issue:

ALP Overview

The Agriculture Laboratory Proficiency (ALP) Program spring 2017 Round Cycle 32 was completed May 12, 2017, with one-hundred eight labs enrolled from the United States, Canada, South Africa, Italy, Honduras, Serbia, Ukraine, Philippines and Guatemala. Proficiency samples consisted of five soils, four botanical and three water samples. Analytical methods evaluated are base on those published by AOAC, regional soil work groups, the Soil Plant Analysis Council and Forestry Canada. ALP has completed ten years of service to Ag laboratory industry.



Data was compiled for each method (test code) and proficiency material. Data analysis of each material include: the number results; grand median value; median absolute deviation (MAD), (95% Confidence Interval); method intra-lab standard deviation (*s*); lab mean, and standard deviation. Additional information on methods and statistical protocols can be found at the program web site.

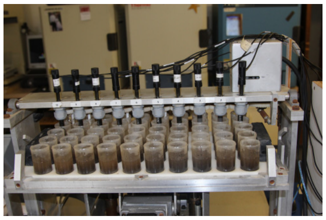
Proficiency Materials

Standard Reference Soils (SRS) materials utilized for cycle 32 were: SRS-1701 is a clay loam collected near Wilson, Alberta, Canada; SRS-1702 a Unadilla silt loam, from Franklin Cty, MA; SRS-1703 a Darrouzett clay loam collected Ochitree Cty, TX; SRS-1704 a Oshtemo sandy loam collected Kalamazoo Cty, MI; and SRS-1705 a Rin silt loam collected Fremont Cty, ID. Chemical properties of the SRS materials ranges: pH (1:1) H_2O 5.32 - 8.12; NO_3-N 6.5 - 75.8 mg kg^{-1}; Bray P1 (1:10) 1.0 - 519 mg kg^{-1}; K NH_4oAc 105 - 718 mg kg^{-1}; SO_4-S 7.1 - 17.6 mg kg^{-1}; Mehlich 3 P (ICP) 9.8 - 469 mg kg^{-1}; DTPA-Zn 0.69 - 4.40 mg kg^{-1}; SOM-LOI 1.60 – 3.00%; CEC 4.7 - 20.9 cmol kg^{-1}; clay 8.1 - 30.6% and soil available H_2O 9.1 - 18.6 %.

Standard Reference Botanical (SRB) materials for Cycle 32 were: SRB-1701 a pistachio leaf composite from CA; SRB-1702 grape leaf composite from CA; SRB-1703 cilantro from CA; and SRB-1704 alfalfa composite from MI. SRB material median analytes ranged: NO_3-N 36 - 1615 mg kg^{-1}; Dumas N 2.78 - 5.15%; total P 0.186 - 0.37%; total K 1.02 - 3.32%; total Mg 0.35 - 0.53%; total S 0.17 - 0.77 %, total Zn 24.0 - 152 mg kg^{-1}; and total Pb 0.04 - 7.4 mg kg^{-1}.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-1701 a water sample collected from a canal near American Falls, ID; SRW-1702 from Fremont Lake, Pindale, WY; and SRW-1703 from Windsor, CO. SRW median concentrations ranged: pH 7.06 - 7.65; EC 0.02 - 0.24 dSm^{-1}; SAR 0.19 - 0.79; Ca 0.11 - 1.06 mmolc L^{-1}; Mg 0.028 - 0.91 mmolc L^{-1}; SO_4 0.037 - 0.67 mmolc L^{-1} ; and NO_3 0.008 - 0.013 mmolc L^{-1}.

Homogeneity Evaluation Soil



SRS material homogeneity was evaluated based on soil test codes pH (1:1) H_2O, EC (1:1), P Olsen, K Olsen, NO_3-N and SOM-WB on analysis of five jars, each in analyzed in triplicate by an independent laboratory. Homogeneity results were within acceptable limits for all soils, with the lowest noted for pH H_2O. Homogeneity was also evaluated on SRB and SRW matrix samples.

"..soil pH, EC and Olsen P analysis Stdev values for Cycle 32 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation Cycle 32, 2017.

Sample	pH (1:1) H_2O		EC (1:1) (dSm^{-1})		Olsen P ($mg\ kg^{-1}$)		NO_3-N ($mg\ kg^{-1}$)	
	Mean [1]	*Std*	Mean	*Std*	Mean	*Std*	Mean	*Std*
SRS-1701	7.88	*0.06*	0.34	*0.030*	8.7	*0.8*	7.3	*0.2*
SRS-1702	5.10	*0.04*	0.73	*0.055*	114	*10*	80.3	*2.3*
SRS-1703	6.65	*0.04*	0.62	*0.015*	33.2	*2.1*	42.1	*0.9*
SRS-1704	6.06	*0.02*	0.30	*0.027*	25.2	*2.3*	23.1	*1.1*
SRS-1705	5.35	*0.02*	0.29	*0.014*	41.9	*1.3*	23.9	*0.4*

[1] Statistics based on five soil replicates, each analyzed in triplicate ALP Cycle 32.

2017 Cycle 32 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis MAD values for Cycle 32 averaged 0.08 pH units across the soils. Median within lab pH standard deviation was 0.024 pH units. Soil displacement CEC ranged 4.8 to 21.0 cmol kg^{-1} across the five soils. Soil Solvtia CO_2 respiration (test code 191) results were provided by six laboratories with median results ranging from 44 - 87 mg kg^{-1} with MAD values averaging >15 mg kg^{-1} for three of five samples. Sample SRS-1701 had a large discrepancy in soil CEC values: Displacement 19.3 cmol kg^{-1} and Estimated CEC of 48 cmol kg^{-1} . Soil ammonium acetate K (Test code 140) MAD values ranged 12.7 - 45 mg kg^{-1} and ammonium acetate Mg MAD values ranged 5.7 to 32 mg kg^{-1} for the five soils. These results for K and Mg were improved relative to cycle 31 results in 2016 and are attributed to: (1) improved lab consistency; (2) soils generally higher in potassium; and (3) ICP operation.

Across the four botanical samples Dumas combustion N MAD values averaged 0.078% nitrogen with intra-lab s of 0.031%, 0.112%, 0.171% and 0.066%, respectively. There was a greater inter-lab variability (MAD) in total boron values than for combustion N, P, K, Ca, Mg, Zn, or Mn concentrations across all samples. Generally the pistachio leaf composite sample SRB-1701 had lower median concentrations of SO4-S, P, S, Ca, Na, Al, Ba, Cd, Ni, and Pb relative to the other four botanical samples. One observation on Cycle 32, intra-lab variability was higher for S than all other macro elements for all four botanical samples.

Water EC results showed high consistency across samples. Across the three water samples EC MAD values ranged from 0.001 to 0.003 dSm^{-1}. NO_3-N values ranged from 0.006 - 0.013 molc L^{-1} across the three water samples with MAD values ranging 0.003 to 0.007 molc L^{-1} .

SRS Results - pH

Sixty-one laboratories provided ALP results for soil pH (1:1) H_2O (test code 115). Soils ranged from acid to alkaline, median range 5.32 - 8.14. Lab results were ranked low to high based on sample SRS-1702 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-1702, SRS-1703 and SRS-1704 showed good consistency across labs. Labs #6, #33, #57, and #60 were inconsistent across soils. Labs #1 an2 showed low bias. Source of bias is likely associated with ISE performance and/or method compliance. Inconsistency could be result of extract carry-over.

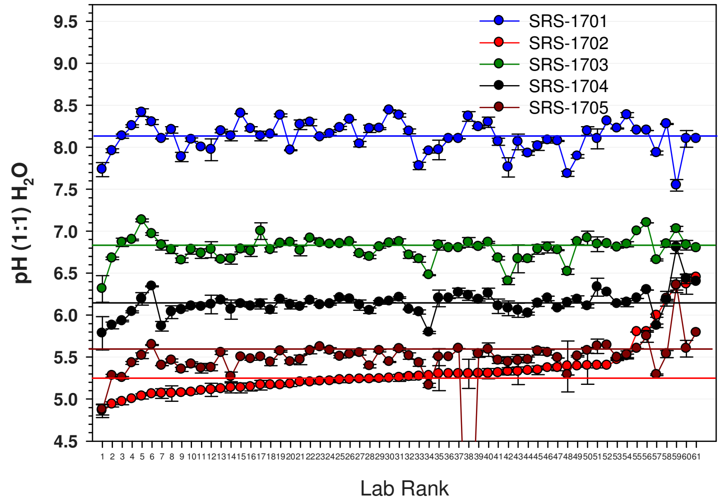


Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2017 Cycle 32.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (s) values ranging from 0.021 to 0.028 pH units, the lowest noted for SRS-1704. For specific labs poor precision was noted for four laboratories, exceeding by three times that noted for consensus median intra-lab s. Specifically s for lab #12 and #35 exceeded 0.10 pH units for three of five soils. Soil SRS-1614 was the least variable with respect to intra-lab variance for Cycle 32.

SRS - Phosphorus: Bray P1, Bray P2, Olsen, Modified Morgan, M1, and M3

Bray P1 results were reported by twenty-eight labs. M3-P ICP was reported by 32 labs. Median soil Bray P1 values ranged from 1.7 - 540 mg kg^{-1} PO_4-P; Olsen P 7.6 to 133 mg kg^{-1} P and Bray P2 ranged from 1.7 to 695 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-1701, median Bray P1 ICP concentrations are shown in indicated in Figure 2. A saw tooth trend was noted for soils SRS-1704 and SRS-1705 associated with the moderate P concentrations. Soil SRS-1701, lowest in concentration, showed low intra-lab variability with a range of 1.0 - 6.0 mg kg^{-1}. Lab #1 showed low bias on three samples. Labs #8, #12, #18, and #25 were inconsistent. Inconsistency is likely related to extraction, analysis instrument and/or method compliance.

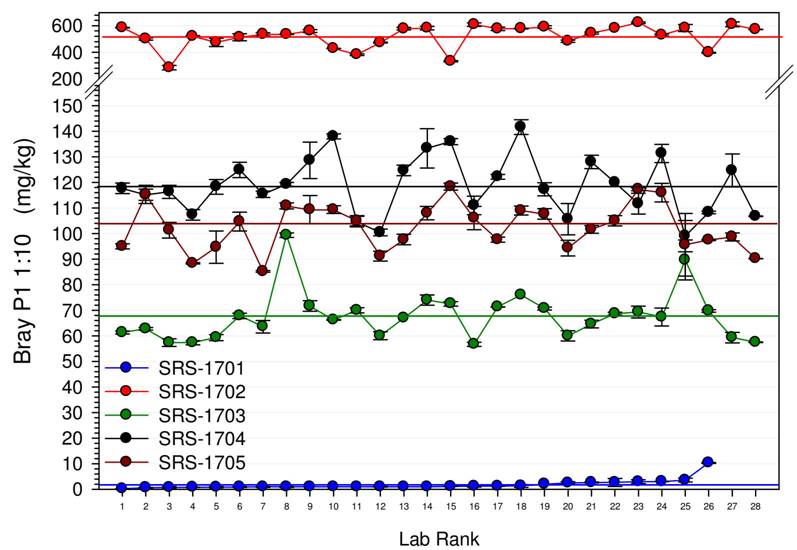


Figure 2. Bray P1 distribution plots for SRS materials, ALP 2017 Cycle 32.

Three laboratories provided ALP results for Mehlich 1 P, with medians ranging from 1.6 to 156 mg kg^{-1} PO_4-P . Bray P1 (1:7) median concentrations were 6 to 90 mg kg^{-1} PO_4-P reported by five labs. Modified Morgan was reported by four laboratories ranging from 14.6 - 35.7 mg kg^{-1} PO_4-P with the highest concentration noted for SRS-1703.

SRS - Potassium

Forty-eight laboratories provided ALP results for soil K (test code 141) results. Results were ranked low to high based on sample SRS-1704 (see Figure 3). Soils SRS-1701 and SRS-1705 were the most inconsistent across labs. Lab #1 showed low bias on 4 of 5 five soils. Labs #9, #11, #23, #24, #25, #28 and #46 were inconsistent across the five soils for K. Source of inconsistency is likely related to sample extraction, analysis instrument and/or method compliance.

Potassium intra-lab *s* values were lowest for soil SRS-1612, with a median intra-lab value of 1.7 mg kg^{-1} Kg and highest for SRS-1614 with a value of 9 mg kg^{-1} Kg. Potassium within-lab precision across the ALP soil materials indicates very good precision, generally, for soils with less than 150 mg kg^{-1} K. Precision was poor (based on intra-lab *s*) for labs #23, #25, #40, and #42 which exceeded 10 mg kg^{-1} K on SRS-1611; and labs #25, #29, and #36 the value exceeded 20 mg kg^{-1} K for SRS-1613. Poor precision is attributed to extraction and/or analysis instrument operation.

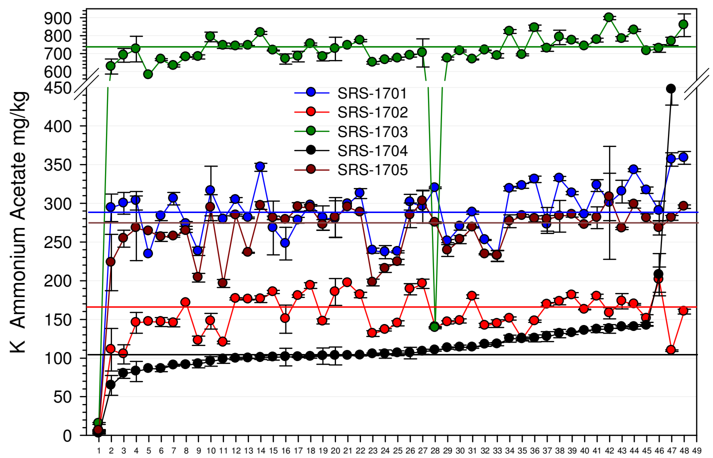


Figure 3. Extractable K distribution plots for SRS materials, ALP 2017 Cycle 32.

SRS SOM-LOI

Forty-two laboratories provided ALP results for soil SOM-LOI (test code 182). Soil Median SOM-LOI values ranged from 1.78 to 5.47%. Results were ranked based on sample SRS-1704 (see Figure 4). Labs #1, #10, #15, #29, #37, #41 and #42 were noted having inconsistency three of five soils. Sample SRS-1703 shows high inconsistency likely associated with 2.8 % SOM content. Bias was noted in eight lab results. Source of bias is likely related to muffle furnace operation and/or method compliance.

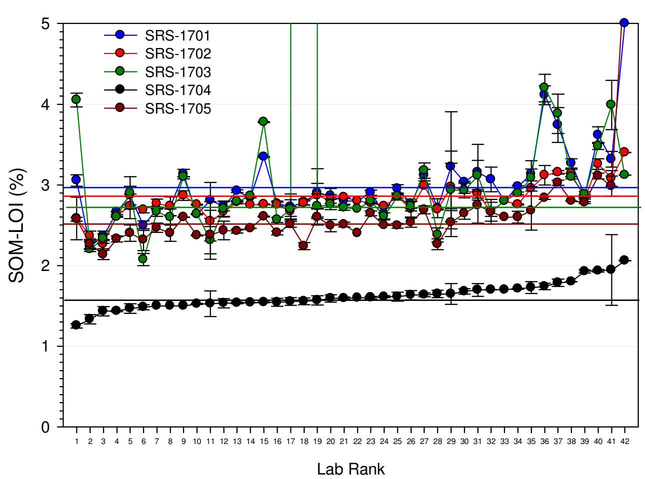


Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2017 Cycle 32.

SOM-LOI precision across the five materials indicates high intra-lab precision, with median *s* values ranging from 0.04 to 0.08% SOM-LOI, the highest for SRS-1614. Across labs, *s* values for SRS-1613 ranged from 0.01 - 0.35 %. Across soil materials low precision was noted for several laboratories. Specifically *s* for labs #1, #9, #13, #14, #23 and #37, exceeded 0.20 % SOM for SRS-1611. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

SRS - Mehlich 3 Mg

Thirty-five laboratories provided ALP results for Mehlich 3 Mg (M3-Mg, test code 161). Results were ranked low to high based on sample SRS-1702 (see Figure 5). Soil SRS-1701 was the highest in concentration and the most in consistent across labs. Across soils, labs #1 #2, #13, #32, #33, #33 and #34 were inconsistent across soils and #35 had high bias. Source of this inconsistency is likely related to instrument calibration or method compliance.

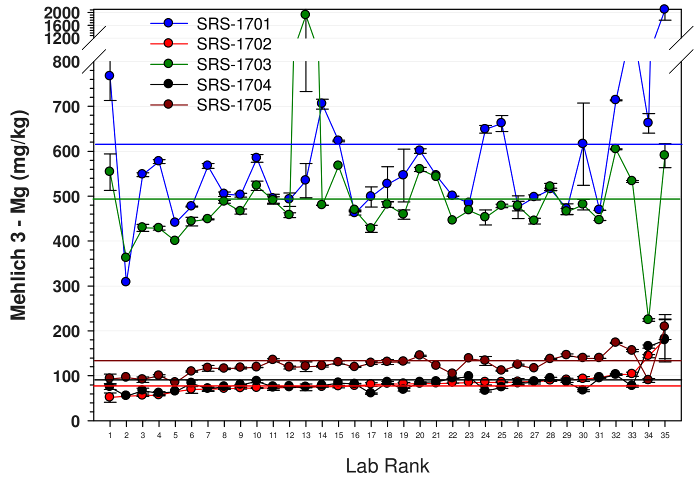


Figure 5. Soil M3-Mg distribution plot, ALP 2017 Cycle 32.

M3-Mg median intra-lab *s* values were lowest for ALP soil SRS-1702 with an intra-lab median value of 2.0 mg kg^{-1} and highest for SRS-1701 with a value of 5.8 mg kg^{-1} . Individual lab precision across the ALP soil materials indicates very high precision, generally, with the exception of soil SRS-1701. Intra-lab precision was poor for labs #10, #12, #21, #25, #27, and #35 on three of five soils. Poor precision maybe associated with M3 extraction and/or ICP-OES instrument operation. Five labs were flagged for poor precision.

SRB Nitrate-Nitrogen

Nineteen laboratories provided ALP results for NO_3-N by cadmium reduction (test code 202 203 and 204). Median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-1702 (see Figure 6). The data plot shows labs #17, #18 and #19 had high bias for SRB-1702. Labs #1, #9, #15, and #16 were inconsistent.

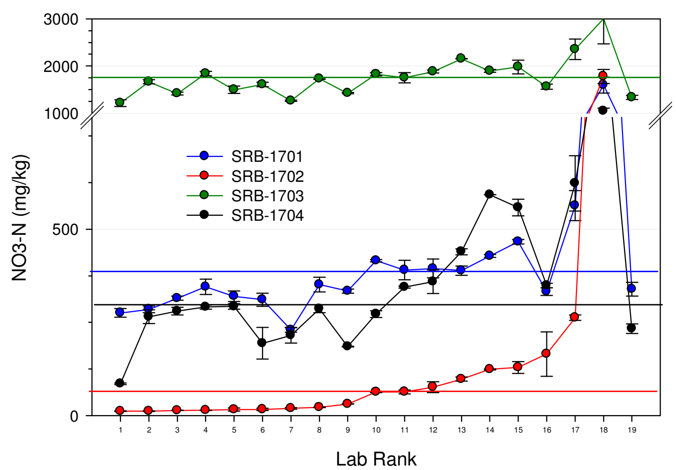


Figure 6. Nitrate distribution plots for SRB materials, ALP 2017, Cycle 32.

Botanical NO_3-N (test code 202) results for Cycle 32 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 2.6 to 46 mg kg^{-1} for the four samples. Individual lab NO_3-N by cadmium reduction (test code 202) intra-lab *s* values for SRB-1701 ranged from 5 – 25 mg kg^{-1}; SRB-1702 ranged from 0.3 - 59 mg kg^{-1} , SRB-1703 ranged from 11 – 107 mg kg^{-1} and SRB-1704 ranged from 2 - 42 mg kg^{-1} Lab #16 had consistently high standard deviations for two of four samples. Five labs were flagged for poor precision.

SRB - Dumas Nitrogen and TKN

Thirty laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and nine labs for TKN (Test code 209) for Cycle 32. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-1701 (see Figure 7). It is note worthy that TKN was lower than Dumas for all four samples. Labs #1 and #2 showed low bias for Dumas N for three samples, whereas labs #9 and #24 showed inconsistency across the all four botanical samples.

Dumas N and TKN results indicate very high precision across all labs for all samples. Individual lab Dumas N lab *s* values for SRB-1701, ranged 0.003 to 0.07% N, SRB-1702 ranged from 0.003 to 0.61% N, SRB-1703 ranged from 0.005 to 0.86 % N, and SRB–1704 from 0.001 to 0.31 % N. Lab #24 had consistently high standard deviations. Lab TKN *s* values for SRB-1701 ranged from 0.07 to 0.12%, SRB-1702 ranged from 0.01 to 0.16% TKN, SRB-1703 ranged from 0.01 to 0.24% TKN nitrogen and SRB-1704 ranged from 0.007 to 0.12% TKN nitrogen.

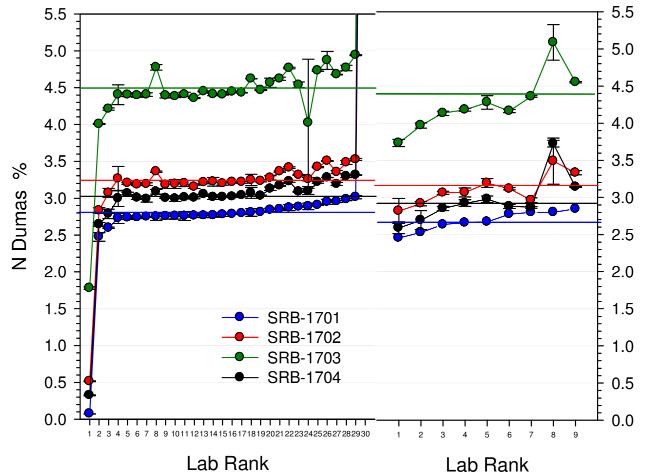


Figure 7. N distribution plots for SRB materials, ALP 2017 Cycle 32.

SRB - Potassium

Thirty-eight laboratories provided ALP results for potassium (K) (test code 213). Results median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-1702 (see Figure 8). Laboratories #1 and #2 showed low bias. Labs #4, #20, #27 and #34 were inconsistent. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical K results indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 0.022 to 0.080 %K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-1701, ranged from 0.005 to 0.57 % K; SRB-1702, 0.001 — 0.24 % K; SRB-1703, 0.015 - 0.29 % K; and SRS-1704, 0.010 to 0.39 % K. Four labs had high standard deviations exceeding 0.20 %K for SRB-1703. Seven labs were flagged for poor K precision.

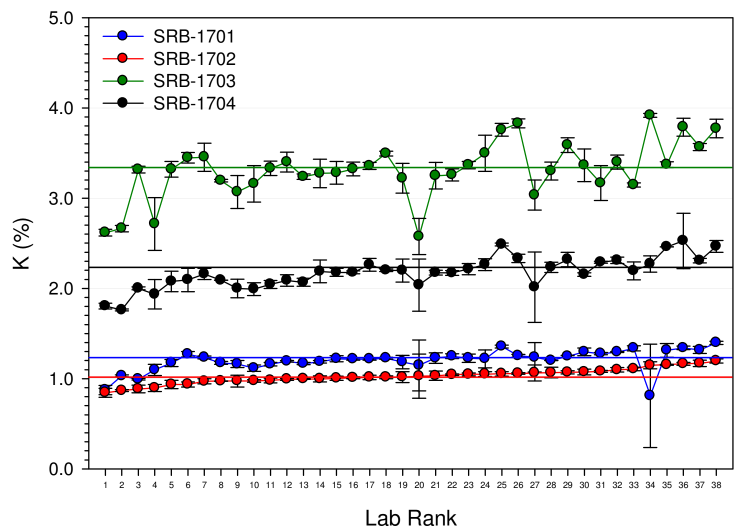


Figure 8. Potassium (code 213) plots for SRB materials, ALP 2017 Cycle 32.

SRB - Phosphorus

Thirty-eight laboratories provided ALP results for Cycle 32 phosphorus (P) combined (test codes 212). Botanical results median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-1701 (see Figure 9). Consistent high bias was noted for labs #37 and #38. Labs #5 and #21 showed inconsistency. Source of inconsistency is likely related to sample extraction, analysis instrument and/or method compliance.

Botanical P results indicate very high precision, with median intra-lab standard deviation (*s*) values ranged 0.005 to 0.010 % P for test code 212 across the four botanical samples. Individual lab intra-lab *s* values for SRB-1701; ranged from 0.001 - 0.023 % P; SRB-1702 ranged from 0.001 – 0.032 % P and SRB-1703 0.001 - 0.046 % P; and SRB-1704 0.0004 - 0.044 % P. Labs #21 had a high standard deviation exceeding 0.012 % P on all four botanical samples. Six labs were flagged for poor precision for botanical P.

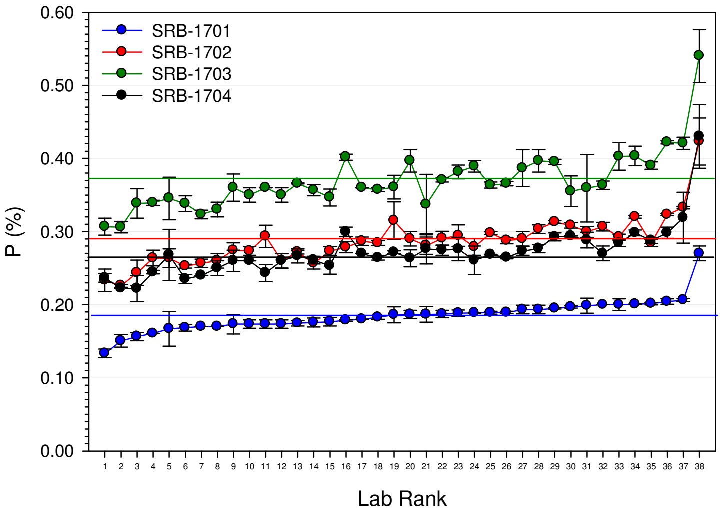


Figure 9. Phosphorus distribution plots for SRB materials, ALP 2017 Cycle 32.

SRB - Zinc

Thirty-six laboratories provided ALP results for zinc (Zn) (test code 220). Result median values are designated by horizontal lines for each botanical material and individual labs results are ranked low to high based on sample SRB-1704 (see Figure 10). Labs #3 showed low bias on all samples. Labs #2, #15, #26, #34 and #36 were inconsistent and data suggests that samples may have switched during analysis. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical Zn results indicate very high precision, with median intra-lab standard deviation (*s*) values ranged from 0.88 to 4.4 mg kg^{-1} Zn for across the four botanical samples. Individual lab intra-lab *s* values for SRB-1701; ranged from 0.11 - 4.6 mg kg^{-1} Zn; SRB-1702 ranged from 0.47 – 14.2 % Zn; SRB-1703 0.16 - 8.2 mg kg^{-1} Zn; and SRB-1704 0.02 - 5.7 mg kg^{-1} Zn. Labs #25 and #34 had consistently high standard deviations for two of four botanical samples.

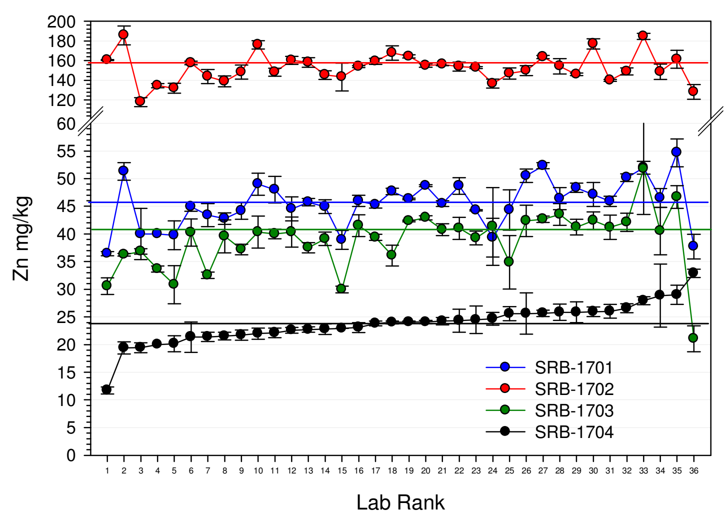


Figure 10. Zinc distribution plots for SRB materials, ALP 2017 Cycle 32.

SRW - Water EC

Sixteen laboratories provided ALP results for water EC (test code 302). Lab result were ranked low to high based on sample SRW-1701 (see Figure 11). Sample SRW-1701 had the lowest EC ever recorded in the ALP Program. Lab #16 indicated consistent high bias on SRS-1702. Lab #6 showed inconsistently across the three samples. Source of bias is likely associated with EC probe performance and/or calibration.

EC precision across the three water materials indicates good high precision, with intra-lab median Std values of 0.003, 0.0005 and 0.0001 dSm^{-1}, respectively. Precision for sample SRW-1703 was the most consistent across the sixteen participating laboratories. Intra-lab s values for lab #16 exceeded 0.004 dSm^{-1} on SRW-1703. Highest precision was noted for lab #8 with intra-lab s values of < than 0.0001 dSm^{-1}.

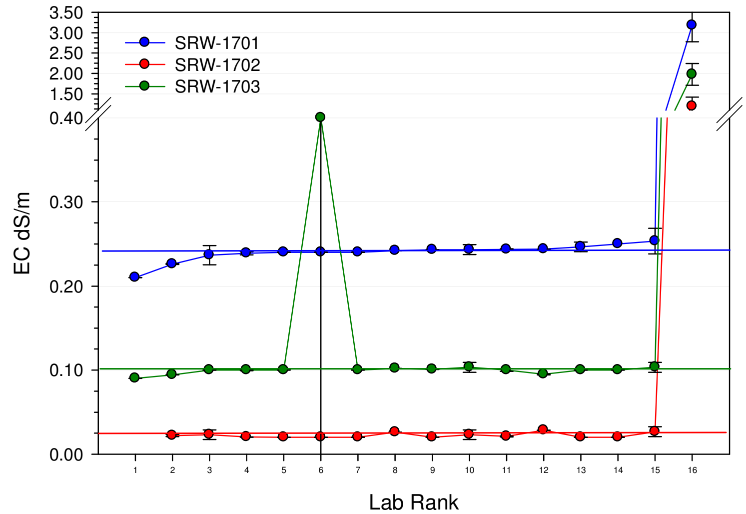


Figure 11 . Water EC distribution plots for SRW materials, ALP 2017 Cycle 32.

SRW - Ca Results

Fifteen laboratories provided ALP results for water Mg (test code 303). Lab results were ranked low to high based on sample SRW-1701 (see Figure 12). Median values are designated by horizontal lines. Lab #3 had high bias. Labs #1 and #15 showed inconsistency across samples.

Mg precision across the three water solution matrices indicates excellent precision, with intra-lab s values of 0.057, 0.009, and 0.011 meq L^{-1} for SRW-1701, SRW-1702, and for SRW-1703, respectively. Water Mg precision was excellent for all individual labs with only lab #13 exceeding 0.20 meq L^{-1} on one of the three samples. Across samples intra-lab s was less than 0.025 meq L^{-1} for lab #4. Four labs were flagged for poor precision on ALP Cycle 32 for Mg content.

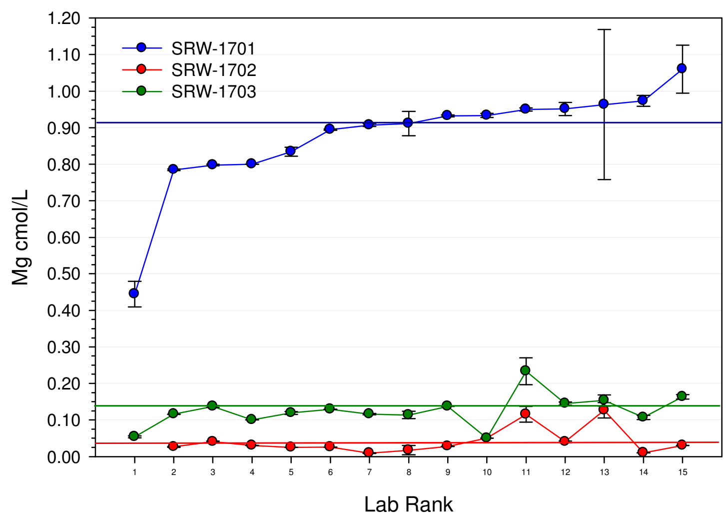


Figure 12. Water Ca distribution plots for SRW materials, ALP 2017 Cycle 32.

Announcements

- Improved soil homogeneity. Soils for the ALP program are processed to achieve 100% 0.7 mm minus. Specific soils with SOM > 1.0% are now double sieved to 0.7 mm minus to removed fine root fragments and improve SOM homogeneity. Soils are blended in two successive operations to assure optimum uniformity.

- New ALP soils were collected in April, with nine from central and northern California from vineyards, almond orchards and a sweet corn field. One soil was collected from near Iowa City, Iowa in February.

- A laboratory tour is scheduled of soil/plant testing labs in the Pacific Northwest the week of August 28th 2017. The tour will include four testing labs and an Ag industry facility. Tour is space is limited. Email rmiller@colostate.edu for more information.

- The Soil and Plant Analysis Council (SPAC) is developing a national certification program for botanical analysis. The program will be based on proficiency testing data and evaluate on a yearly basis. The program is under review.

- If there is a specific soil type, soil properties or botanical sample materials that you believe should be considered for the proficiency program please contact the ALP Program Technical Director, rmiller@lamar.colostate.edu.

Summary

ALP is celebrating ten years of service with the completion of Cycle 32. Since 2006 ALP has completed the analysis of 160 soils, 100 plant samples and 96 water samples providing comprehensive proficiency data on inter and intra laboratory performance across a range of analytical methods.

We thank all laboratories who participated in Cycle 32. As the coordinators of the program we appreciate your consideration and participation in the proficiency program. We continually seek feedback from laboratory participants to improve the service and function of the program. Please forward all comments to info@cts-interlab.com.

Cycle 33 Ship

June 22, 2017

"Skepticism enables us to distinguish fancy from fact, to test our speculations."

— Carl Sagan , 1980

ALP
Agricultural Laboratory Proficiency Program