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PERCHLORATE IN FERTILIZERS

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FOR THE DIRECTOR

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This report documents an inter-laboratory collaborative study on the performance on ion chromatography (IC) methods for perchlorate analysis in lawn and garden fertilizers. Seven government, private, and commercial laboratories participated in the analysis of 34 aqueous suspensions of the test materials, using similar ion chromatography systems. Two method variants (AS-11 and AS-16) were evaluated. Statistical evaluations by paired t-test for the means analysis found good agreements in each of the methods variants and excellent agreement between the methods. The study also found no significant defferences in the performance of the microbore column with respect to the standard bore column. This report also evaluates and compares the performance of IC with respect to capillary eletrophoresis (CE), Raman spectroscopy (RS), and titration for perchlorate analysis. The study found excellent agreement between the ion chromatography and CE results, and little or no agreement between IC and RS or titration. As expected, compared to the IC results, titration is biased high.

14. SUBJECT TERMS

Ion chromatography	Capillary electrophoresis	Parts per billion
AS-16	Raman spectroscopy	
AS-11	Fertilizer	

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PREFACE

This report summarizes research that begun in February 1999. Research was completed in August 1999 under Department of the Air Force Contract No. F41624-96-C-9010. This study was a collaborative effort between the Department of the Air Force representing the Inter-Perchlorate Steering Committee, the Perchlorate Study Group, and the United States Environmental Protection Agency National Exposure Research Laboratory, Ecosystems Research Division (EPA/NERL/ERD).

Laboratories who participated in the study were Chemical Testing Service (Diamond Bar, CA), Del Mar Analytical Laboratories (Irvine, CA), American Pacific Corporation (Cedar City, UT), United Technologies Corporation (San Jose, CA), Montgomery Watson Laboratories (Pasadena, CA), Thiokol Corporation (Brigham City, UT), EPA/NERL/ERD (Athens, GA), and AFRL/HEST (Wright-Patterson AFB, OH).

Tommy Blackman (Lockheed Martin, Corporate Environment, Safety and Health, Burbank, CA) and Richard Scott (TRC Environmental Solutions Inc., Irvine, CA) served as the coordinator for the Perchlorate Study Group. MacArthur Long served as the coordinator for EPA/NERL/ERD. Major Steve Channel served as Contract Technical Monitor for the United States Air Force, AFRL/HEST.

LIST OF ABBREVIATIONS

α	probability of Type I error
ASRS	Anion Self Regenerating Suppressor
CDHS	California Department of Health Services
CE	capillary electrophoresis
CCD	charge coupled device
CV	cycle voltammetry
EOF	Electro-osmotic flow
HPLC	high performance liquid chromatography
i.d.	inner diameter
IC	ion chromatography
g	gram
kV	Kilo-volts
ISE	ion selective electrode
L	Liter
μg	microgram
μL	micro-liter
mL	milliliter
mm	millimeter
min	minutes
mΩ	mega-Ohm
mW	milli-watt
mM	milli-molar
mmol	milli-mole
mV	milli-volt
nL	Nanoliter
nm	nanometer
o.d.	outer diameter
ppm	parts per million

ppb	parts per billion
%CV	percent coefficient of variation
RS	Raman spectroscopy
S_d	Stdev, standard deviation
S_{di}	standard deviation of the sample measurements between laboratories
TDS	total dissolve solids
UV	ultra violet
V	volts

PERCHLORATE IN FERTILIZERS

1.0 INTRODUCTION

Perchlorate is a powerful oxidizer used in solid-rocket propellant mixtures, fireworks, and munitions. Inorganic salts of the perchlorate anion are relatively soluble in water. The presence of trace level perchlorate in drinking water poses a potential health risk, due to the interference of perchlorate with the uptake of iodide necessary to produce hormones in the thyroid gland. The EPA's current recommended acceptable level for perchlorate in drinking water is 18 parts per billion (ppb) [1-10]. Heightened awareness of perchlorate as a potential health risk has led to increased activities in the investigation of perchlorate occurrence in the environment [11-12]. Since perchlorate and the ammonium, sodium, and potassium salts of perchlorate are better known in their commercial and industrial applications, studies of occurrence have focused on surface and ground water sources near regions where munitions, aerospace components, and fireworks were manufactured, developed, and tested. However, reports have suggested that naturally occurring perchlorate is present in fertilizers, nitrate deposits from northern Chile (caliche), and minerals from arid environments with chloride deposits [15-17]. These new findings have sparked intense efforts in the study of natural perchlorate occurrence in non-aqueous matrices and the application of existing methodologies to accurately determine perchlorate levels.

The determination of perchlorate at trace (ppb) levels is a difficult analytical task. Early techniques for perchlorate analysis in aqueous and solid matrices, such as gravimetric analysis [18-22], titration [19, 20, 23-25], and liquid-liquid extraction/spectrophotometry [26-31], explored the formation of water insoluble ionic complexes of perchlorate with organic dyes, such as nitron, brilliant green, tetraphenylstibonium, and methylene blue. Because organic dyes are not specific for perchlorate and have preferential selectivity for perchlorate and similar anions, potential exist for those methods to over estimate perchlorate concentrations, leading to biased results.

More specific and selective methods, such as ion pair high performance liquid chromatography (HPLC) [32-33], capillary electrophoresis (CE) [34-40], ion selective electrode (ISE) [40-41], and Raman spectroscopy (RS) [42] have also been used in perchlorate analysis in complex matrices. However, the sensitivity of these methods is limited to the ppm levels.

For the determination of trace level perchlorate in aqueous matrices, ion chromatography coupled with a conductivity detector is the state of the art technology available to most analytical laboratories [43-47]. Several IC methods have been developed for the analysis of trace perchlorate levels. In 1997, the California Department of Health Services (CDHS) using the AS-5 anion separation column developed the so-called CDHS Method for the determination of trace level perchlorate in drinking water [44]. In April 1998, the Dionex Application Laboratory developed an improved IC method, using the AS-11 column, for perchlorate analysis [45-46]. The performances of both AS-5 and AS-11 methods for drinking water and groundwater were validated in an inter-laboratory collaborative study sponsored by the Interagency Perchlorate Steering Committee (IPSC). With respect to aqueous matrices having the same quality as drinking water and groundwater, the collaborative study found no differences between the two methods in terms of bias and accuracy [48]. In March 1999, California Department of Health Services Division of Sanitation Laboratory Services adopted both methods [49], and in July 1999 EPA proposed both methods for national drinking water and groundwater analysis [47].

Although both methods performed similarly, the AS-11 method has gained wider acceptance over the AS-5 because the AS-5 method is incompatible with the newer suppressors and is less rugged for matrices with high total dissolved solids (TDS). The p-cyanophenol organic modifier used in the AS-5 methods is electrochemically active. Incompatible with the newer electrochemical suppressor, the p-cyanophenol may de-grade the suppressor membrane and cause elevated baselines and lower IC performance [48-53]. High TDS effects perchlorate analysis by giving non-specific baseline rise that could mask the perchlorate peak. In a review sponsored by East Valley Water District, Shen and Harrington [54], showed that with respect to mixed water analysis containing TDS at greater 1,000 ppm, the performance of the AS-5 column is not as robust as the AS-11. Furthermore, in separate experiments, Eaton *et al.* and the IPSC analytical subcommittee demonstrated that although samples with high TDS pose a challenge to

both methods, the AS-11 column is more rugged than the AS-5. At greater than 2500 ppm TDS, the AS-5 method could not effectively resolve trace perchlorate at 5 ppb [48, 53-56].

To accommodate samples with high TDS, the AS-16 column was introduced, and an extensive methods development study based on the AS-16 column was completed in May 1999 [52, 53]. The optimized AS-16 method calls for a Dionex IonPac® AS-16 column with a 35-mM mobile phase flowing at 1.25 mL/min. The reported AS-16 method detection limit is 1 ppb, with a 1,000-µL injection loop volume and an ASRS-Ultra suppressor. The AS-16 column, with significantly higher column capacity and more hydrophilic functional groups than the AS-11 column, was developed to accommodate matrices with higher TDS and provide better separation for perchlorate. Whereas the AS-11 is limited in resolving 50-ppb perchlorate at around 6,800 ppm TDS, the AS-16 is capable to resolving 50-ppb perchlorate at TDS levels as high as 20,000 ppm. Shortly after this study began, the EPA proposed the AS-16 column as a replacement for both the AS-5 and AS-11 columns [57].

This report documents the results of a collaborative study conducted by the IPSC Analytical Sub-Committee with the EPA Office of Research and Development, National Exposure Research Laboratory, Ecosystems Research Division in Athens, GA. The objective of this collaborative (co-lab) study is to compare the performance of IC methods for the measurement of perchlorate in the liquid extracts of lawn and garden fertilizers containing high TDS. Additionally, this report evaluates the performance of capillary electrophoresis, titration, and Raman spectroscopy for perchlorate analysis.

2.0 METHODS AND MATERIALS

2.1 Test Materials

Test materials were purchased from various commercial and retail sources located in Missouri, New York, and California. Appendix A lists the test materials and corresponding sample number, manufacturer, and primary constituents appearing on the manufacture's labels.

All-Purpose Plant Food (Peters Inc.) having different lot numbers was purchased from three different locations: California (ps06), Kansas City, MO (ps05), and Long Island, NY (ps16). Samples ps17 and ps24 are duplicate samples of Fall Fertilizer (Johnathan Green Co.) purchased in Long Island, New York. Samples ps15 and ps21 are duplicate samples of Lawn Restorer (Ringer Inc.) purchased in Long Island, New York. Samples ps02 and ps09 are duplicate samples of Supreme Gardens (Ringer Inc.) purchased from Kansas City, MO. Samples ps08 and ps12 are duplicate samples taken from one lot of Vegetable and Bedding Plant Food bought in Kansas City, MO and sample ps19 was taken from another lot purchased in Long Island.

The caliche sample (ps34, Chilean nitrate) was collected from Region I of the Soquimich Nitrate Works located in Calama, Chile. The langbeinite ore sample (ps30) was obtained from IMC Minerals (Albuquerque, NM). The potassium nitrate used in the Champion (sample number ps31) and Best K-Power (ps32 and ps33) and Chilean Nitrate fertilizers were also collected from the Soquimich Nitrate Works.

Important to note, these raw test materials were heterogeneous. Regardless of mixing time and mesh quality, dividing the raw test materials for laboratory analysis represented sub-sampling of the test materials and the result for each sub-sample is inherently different from another. Although not a factor in the liquid extracts shipped in this study, shipment and storage of bagged fertilizer could bias the results due to changes in moisture content.

Consistent with the preliminary nature of this round robin, a homogenous suspension of subsamples of a nonrepresentative subsample of each fertilizer and raw test material was prepared and shipped to seven laboratories for blind analysis. The suspension was prepared by

mixing the solid sample with deionized water. The mixing ratio was 1 gram of solid sample per 10 mL of de-ionized water. De-ionized water used in this study was Type I reagent grade, with a resistance of 18 mΩ or better. The mixture was shaken over 48 hours, and the liquid phase was removed after the suspension had settled. Approximately 50 mL of the liquid phase from each of the thirty-four test materials was transferred to an amber glass bottle and shipped to the cooperating laboratories for perchlorate analysis. Two 100-µg/L positive controls (LCS1 and LCS2) and one negative control accompanied each set of thirty-four liquid test samples. The 100-µg/L perchlorate controls were prepared gravimetrically from sodium perchlorate (Fisher Scientific, Inc., Lot # 78164) and de-ionized water. The negative control blank was prepared from de-ionized water alone.

2.2 Analytical Methods

Ion Chromatography.

All seven laboratories performed the ion chromatography analysis on similar ion chromatography systems manufactured by Dionex Corp. of Sunnyvale, CA. A system consists of AS-40 autosampler for sample injection, GP-40 gradient pump for eluent delivery, and CD-20 conductivity detector for detection. Method variations differed in the ion separation columns and eluent conditions; both AS-11 and AS-16 columns were used in this study. Appendix B lists the differences in eluent conditions among laboratories.

Laboratories 3, 4, 6, and 7 employed the AS-11 method with identical method conditions. Perchlorate was chromatographically separated on a Dionex ATC-1 anion trap column, AG-11 guard column (4 mm x 50 mm), and AS-11 anion separation column (4 mm x 250 mm), with 100 mM NaOH mobile phase flowing at 1.0 mL/min. as eluent. All four laboratories used the Anion Self-Regenerating Suppressor-II (ASRS-II) operating in the external water mode for eluent suppression. Laboratory 3 used a 1,000-µL injection volume loop; and labs 4, 6, and 7 used 100-µL injection volume loops.

Laboratory 2 used a micro-bore equivalent of the standard AS-11 method. Instead of the 4-mm guard and separation column, Laboratory 2 used a 2-mm x 50-mm AG-11 guard column and a 2-mm x 250-mm AS-11 column for perchlorate separation. Accordingly, the 100-mM NaOH eluent flow rate was reduced from 1 mL/min to 0.38 mL/min. To avoid overloading the column, the sample injection volume was reduced proportionally from 1,000 µL to 1 µL. Eluent suppression was achieved using an ASRS-Ultra suppressor operating in the external water mode.

Laboratories 1 and 5 used the AS-16 method for perchlorate analysis. For the AS-16 method, perchlorate separation was obtained on a Dionex IonPac AS-16 separation column (4 x 250-mm) with an AG-16 guard column (4 x 50 mm) and an ATC-1 anion trap column. Laboratory 5 used the recommended 1,000-µL sample loop volume and an isocratic program with 35-mM NaOH mobile phase flowing at a rate of 1.25 mL/min. Laboratory 1 used a 50-µL sample loop injection with a gradient program: 20 mM NaOH for 5 minutes and 100-mM NaOH for the remainder of the analysis.

Capillary Electrophoresis.

Laboratory 6 performed the CE analysis. A Beckman P/ACE 5000 capillary electrophoresis system was used for indirect UV-detection (214 nM) of perchlorate in fertilizer samples. All data analysis was performed on Beckman System Gold Software. Liquid test materials diluted 1:10 to 1:100 were injected hydrodynamically for 5 seconds on a 47-cm fused silica (40-cm end to detection, 300-µm outside diameter and 75-µm inside diameter). The column temperature and voltage were set at 23°C and 20 kV, respectively. The running buffer consisted of 40-mM phosphate (pH 7.0) containing 2.24-mM pyromellitic acid visualizing agent and 0.5-mM tetradecyl trimethyl ammonium bromide for reduction of the electroosmotic flow. Perchlorate is non-UV active [32]. The displacement of pyromellitic acid by analyte in the running buffer gives negative peaks as the analyte passes the detector. For quantitation, the detector polarity is reversed to give a positive peak. Between sample analyses, the capillary was flushed for 1 minute with deionized water, 4 minutes with 0.1 M NaOH, 4 minutes with water, and 4 minutes with the running buffer. Sample run time was 6 minutes.

Raman Spectroscopy Analysis.

Laboratory 6 also performed the RS analysis. For Raman spectroscopy analysis, 5-mL of the undiluted liquid test samples were analyzed on a Kaiser Optical Systems HoloProbe, using 785-nm laser excitation from a diode laser. The laser light was coupled to a remote probe head via a 1.9 meter-long fiber optic cable. The laser light was brought to focus with a series of lenses, at approximately 2.5 inches beyond the end of the probe head assembly. A standard quartz cuvette containing the sample was placed in the path of the beam such that the focus of the beam fell in the center of the cuvette. The power of the laser light at the sample was approximately 135 mW.

Raman scattered light from the sample was collected by the probe head along the same path as the excitation laser beam (i.e., 180° back scattering geometry). The probe head was coupled to a separate 1.9 meter-long fiber optic cable for delivery to the f /1.8 axial transmissive-type spectrograph. A holographic notch filter removed elastically scattered laser light from the probe head and a 50 μm slit focused Raman scattered light through a volume holographic transmissive grating. The dispersed Raman spectrum was collected by a charge coupled device (CCD) detector which allowed simultaneous acquisition of the entire Raman spectrum with useable Stokes Raman shift of about 3280 to 95 cm^{-1} in a single exposure (with spectral resolution of 5 cm^{-1}). The CCD detector used a back-illuminated, near-infrared optimized Princeton CCD-1024EHRB chip. The chip was thermoelectrically cooled at –65°C.

Tetraphenylstibonium Titration.

Chemical Test Service of Diamond Bar, CA performed tetraphenylstibonium titration of all samples. For titration, the suspension was transferred onto an ion exchange column containing 25 grams of Dowex-1 resin (VWR Inc.) and eluted with 100 mL of 0.01-M potassium bicarbonate solution (VWR Inc.) to remove nitrate, chloride, chlorite, and chlorate ions. The solutions were monitored using a perchlorate selective electrode (Orion Inc., Model 938101), to determine if a portion of the perchlorate eluted in the rinse. If the perchlorate selective electrode indicated over 10-ppm perchlorate, the sample preparation step was repeated with using a larger dilution. When perchlorate was no longer detectable in the effluent by the perchlorate selective electrode, the ion exchange column was rinsed first with 75 mL of 0.05-M sodium fluoroborate

solution followed by 25 mL of the same solution to de-sorb the perchlorate from the ion exchange column. Both rinses were collected. The combined sodium fluoroborate solution was then analyzed using the perchlorate selective electrode. To determine the efficiency of the extraction process, various control samples and duplicate samples were also extracted and analyzed. A 25-mL aliquot was removed from the combined sodium fluoroborate solution, diluted with 10 mL of de-ionized water and titrated with 0.01M (3.6 mg/mL) tetraphenylstibonium sulfate using six drops of bromocresol green as an indicator. The endpoint was clearly visible for each titration, with the bromocresol green color disappearing, producing a clear solution.

2.3 Statistical Method

Due to method variations, it would be erroneous to determine the variability in IC measurements by pooling the data from all seven laboratories. There are not enough data points to form a representative population for each method variation. Only three of the laboratories used the same methodology; the others used significant modifications to the method. Therefore, the first goal of this analysis was to investigate the consistency of Laboratories 3, 4, and 7, which used the unaltered AS-11 IC method.

The consistency of data from laboratories 3, 4, and 7 was tested using the paired t-test for a series of null hypotheses:

Ho: data from laboratories 3 and 4 are from the same population

Ho: data from laboratories 3 and 7 are from the same population

Ho: data from laboratories 4 and 7 are from the same population

The paired t-test was appropriate because most of the laboratories involved did not analyze replicates. The paired t-test statistic looks at the normalized differences between analyses of the same sample conducted by two different laboratories. For a given level of significance, the resulting t statistic is compared to zero to see if the difference is significantly different from zero. If the difference is not significantly different from zero, the two sets of

values are assumed to be from the same population, or in practical terms, the same to within a small probability of error.

To avoid undue weighting of the difference between large concentrations and the difference between small concentrations, the data were normalized. Lacking a clear definition of the probability distribution of the population of the measurements of the split samples, the normalization of dividing the measurements by the standard deviation of the sample measurements (values from laboratories 1, 2, 3, 4, 5, and 7) was applied. The normalized difference d_i is

$$d_i = \frac{x_i - M_i}{S_{Di}} - \frac{y_i - M_i}{S_{Di}} = \frac{x_i - y_i}{S_{Di}}$$

where x_i is the analysis of split sample i = ps01, ps02, ps03, ..., ps34 by laboratory x, y_i is the analysis of split sample i = ps01, ps02, ps03, ..., ps34 by laboratory y, M_i is the mean of the sample measurements between laboratories $i = x, y, z, \ldots, m$ in which m is the total number of laboratories in a pool of results (i.e., $m = 6$ for a pool of results from laboratories 1, 2, 3, 4, 5, and 7), and S_{Di} is the standard deviation of the sample measurements between laboratories for each split sample i = ps01, ps02, ps03, ..., ps34.

Since the only assumption necessary to use the paired t-test is that the d_i values follow a normal distribution, the Shapiro-Wilk test of normality was applied to ensure the set of pair-wise differences in the analysis between any two laboratories was normally distributed. The probability of 0.01 was selected to test normality of these differences. If the population of a set of differences was not normally distributed, the non-parametric Wilcoxon-Signed Rank test was used to test for consistency in measurement between laboratories instead of the paired t-test [57].

The probability α of making a Type I error of rejecting the null hypothesis that mean differences between laboratories is not significantly different from zero, when this is true, was selected as the 0.01 level of significance. Using the Bonferroni [58] approach, the individual pair-wise comparisons of the laboratories were made at α/k significance level, where k is the total number of pair-wise comparisons that need to be made. This limits the chance of making one mistake in the k different paired tests to $\alpha = 0.01$.

Based on these criteria, each test was conducted as follows:

Null Hypothesis	Ho: measurements from laboratory x are not significantly different from those of laboratory y
Alternative Hypothesis	Ha: measurements from laboratory x are significantly different from those of laboratory y
Test Statistic	$t = \frac{\sum_{i=1}^{n} d_i}{s_d / \sqrt{n}}$
Decision Rule	If probability of $\lvert t \rvert < \alpha/k$, then reject Ho

When none of the null hypotheses were rejected for the initial comparisons between laboratories 3, 4, and 7, then the measurements for each sample split from labs 3, 4, and 7 were pooled and a "golden mean" was obtained for comparison with other methods to determine consistency. Paired t-tests were conducted between the "golden mean" for the AS-11 method and each IC method variant to see if the hypothesis of measurement consistency can be rejected at the α/k level of significance. Then, the AS-11 mean was compared to CE, RS, and Titration, individually.

In the absence of adequate controls to determine accuracy in this round robin, the term "golden mean" reflects a practical choice of the most likely point of comparison, not necessarily the most accurate point of comparison. For example, other methods like ion chromatography using the new AS-16 column or capillary electrophoresis may prove to be more accurate than ion chromatography using the AS-11 column.

3.0 RESULTS AND DISCUSSIONS

3.1 Ion Chromatography

Analytical results obtained from ion chromatography analyses are summarized in Appendix C. Laboratory 6 did not report result for sample ps03 because the sample container arrived at Laboratory 6 damaged. Except for Laboratory 6, all laboratories that performed IC analysis submitted the results within a month after sample preparation. Laboratory 6 reported instrument and technical difficulties during the study. The initial set of data from Laboratory 6 showed obvious disagreement with the data from the rest of the laboratories and the data was rejected at the Lab's request. Laboratory 6 re-analyzed the samples three months after sample preparation; these will be evaluated separately.

All seven laboratories using ion chromatography for perchlorate analysis reported non-detects for samples ps10, ps13, and ps17. From individual laboratories, reported method detection limits perchlorate standard prepared in de-ionized water were 5 μg/L or lower. Table 3.1 lists the reported method detection limits in mg perchlorate per kg of test material, after adjusting for injection volume, dilution and extraction ratio. Laboratory 2 reported a higher adjusted detection limit because of the small injection volume required by the microbore column. Method detection limit from Laboratory 6 was unavailable.

TABLE 3.1 REPORTED IC METHOD DETECTION LIMITS FROM PARTICIPATING LABORATORIES

Laboratory	Adjusted Reported Detection Limit (mg/kg)
1	6.00
2	40.0
3	0.40
4	3.00
5	1.00
6	NA
7	4.00

Laboratories 3, 4, and 7 used the AS-11 method with the same instrument conditions and parameters; the results were compared by paired two sample tests, as described in Section 2.3. Individual hypothesis tests by paired two sample tests for means analyses are shown in Appendix D. In general, Laboratory 7's results were lower than Laboratory 3's, which were a little lower than Laboratory 4's. The hypothesis of agreement between Laboratory 7 and Laboratory 3 had a p-value of 0.0592, and therefore not rejected. A p-value smaller than $\alpha/3$ = 0.0033 leads to rejection of the null hypothesis. The hypothesis test of agreement between Laboratory 3 and Laboratory 4 had a p-value of 0.1874, and thus failed to reject also. In the last of the three pair-wise combinations, the hypothesis test of agreement between Laboratory 7 and Laboratory 4 had a p-value of 0.0031, which is right at the rejection point of $\alpha/3$ = .0033. Laboratory 4's result for sample ps30 was a statistical outlier, contributing to this difference. Removing the outlier resulted in good agreement between the two laboratories.

All three sets of the normalized differences were approximately normal as discussed in Section II, thus the paired t-test was used. Since the results from laboratories 3, 4, and 7 were not statistically different from each other, it was reasonable to average the three values to obtain a "golden mean" for AS-11 perchlorate concentration in each of the 34 samples. As shown in Appendix E, for each sample, the percent coefficient of variation (% CV) was less than ten, showing good precision and little variability among the laboratories using the standard AS-11 method.

Laboratory 2 used a 2-mm AS-11 microbore column instead of a 4-mm AS-11 standard bore column for perchlorate analysis. The Shapiro-Wilk test of normality was used to compare the sample split differences between the AS-11 "golden mean" results and the results from Laboratory 2. These differences were not normally distributed at a probability of less than 0.01. Therefore non-parametric analysis was used to show that the results from Laboratory 2 were not different from the "golden mean" using the standard AS-11 method. The non-parametric test statistic for the differences, p was 0.295 (Appendix E), indicating good agreement in perchlorate measurements using the AS-11 standard bore method and the microbore.

Laboratories 1 and 5 used an AS-16 column, but the eluent conditions were not the same. A comparison between Laboratory 1 values and AS-11 "golden mean" in a paired t-test is shown in Appendix E, and the results from Laboratory 1 were not different than the "golden mean"

using the AS-11 method. The hypothesis of consistency had a p-value of 0.0101, which when testing at the 0.01 confidence level, failed to reject the null hypothesis. Lab 5 results were also not significantly different from the AS-11 "golden mean" (p-value of 0.0560). Overall, Laboratory 5 reported smaller concentrations than Laboratory 1 in all but 8 of the 33 samples.

Averaging the two AS-16 laboratory measurements and comparing them to the AS-11 "golden mean" values gave the best match of any comparison conducted in this study. The p-value for paired t-test comparison between the mean AS-11 results and the average AS-16 data was 0.9248, indicating that the average of the AS-16 results was very close to the AS-11 results for each sample.

Although Laboratory 6 used the same AS-11 method, comparison of Laboratory 6 results to the AS-11 means did not show agreement. The p-value was 0.0001, indicating less than 0.01% chance that the data from Lab 6 agreed with the mean AS-11 data. Since Laboratory 6 also analyzed the samples by CE and RS, attempts were made to compare Lab 6's IC data to that of RS and CE, and there were no agreement among the data. Null hypothesis tests by paired two sample tests for means analysis for Lab 6' IC and RS data showed absolutely no agreement. Furthermore, there were no agreement between IC and CE, and CE and RS.

Results for the negative control blanks and positive (100-µg/L) perchlorate spikes are shown in Table 3.2. All seven laboratories reported non-detect for the blank negative control. Except for Laboratory 6, all labs reported results within 94 to 104% of the expected value, showing excellent agreement and accuracy. Laboratory 6 did not report results for the spiked controls.

TABLE 3.2 ION CHROMATOGRAPHY RESULTS OF BLANKS AND 100-µg/L PERCHLORATE SPIKED CONTROLS

Laboratory	Blank	Reported LCS1	Expected LCS1	Reported LCS2	Expected LCS2
1	ND	96	100	104	100
2	ND	99	100	94	100
3	ND	100	100	99	100
4	ND	94	100	97	100
5	ND	99	100	98	100
6	ND	NA	100	NA	100
7	ND	99	100	99	100

Although the laboratories reported excellent duplicate recoveries for the spiked controls, duplicate sample analyses were shown to vary widely. The disparity in duplicate sample analyses reflected intra-lot and inter-lot variability. Table 3.3 showed the AS-11 mean values for duplicate sample analyses. Duplicate samples from a same lot of All Natural Lawn Restorer ps15 (5,827 mg/kg) and ps21 (2,767 mg/kg) showed an absolute difference of 58%. The absolute difference for duplicate Supreme Gardens fertilizer sample ps02 (3180 mg/kg) and the duplicate ps09 (4,193 mg/kg) was about 24%. For duplicate Fall Fertilizer samples, 2,360 mg/kg was reported for ps17 and non-detect (ND) for ps24. Three samples taken from three different lots of All-Purpose Plant Food had perchlorate concentrations ranging from 3,093 to 7,303 mg/kg. Samples ps08 (937 mg/kg) and ps12 (550 mg/kg) taken from a same lot of Vegetable Bedding Plant Food showed an absolute difference of 43%. Both ps08 and ps12 were significantly different than the reported result for sample ps19 (2,620 mg/kg) which taken from a different lot of Vegetable/Bedding Plant Food.

TABLE 3.3 DUPLICATE ANALYSIS OF TEST MATERIALS BY AS-11 METHOD

Samples	Brand Name	Purchase Location	Perchlorate Concentration (mg/kg)
ps15	All Natural Lawn Restorer	Long Island	5827
ps21	All Natural Lawn Restorer	Long Island	2767
ps02	Supreme Gardens	Kansas City	3180
ps09	Supreme Gardens	Kansas City	4193
ps17	Fall Fertilizer	Long Island	ND
ps24	Fall Fertilizer	Long Island	2360
ps08	Vegetable/Bedding Plant Food	Kansas City	973
ps12	Vegetable/Bedding Plant Food	Kansas City	550
ps19	Vegetable/Bedding Plant Food	Long Island	2620
ps06	All-Purpose Plant Food	California	3093
ps05	All-Purpose Plant Food	Kansas City	6287
ps16	All-Purpose Plant Food	Long Island	7303

3.2 Capillary Electrophoresis

For capillary electrophoresis, a calibration curve was generated by plotting the concentrations of aqueous sodium perchlorate standards (in deionized water) versus absorbance. Solutions of 3, 7, 10, 15, 20, 30, 40, 50 and 60 mg/L sodium perchlorate were used to prepare the standard curve. The correlation coefficient for regression of the calibration curve was better than 0.9973. The limit of detection based on a signal-to-noise ratio of 3:1 for perchlorate was about 3 mg/L (3 ppm). Each solution was analyzed twice and the resulting absorbance values were averaged. Migration times for the perchlorate peak in all 18 analyses used for the standard curve ranged from 3.73 to 3.81 min.

Liquid samples were analyzed as received or diluted 1:10 to 1:100 to avoid interference from a large peak with a migration time matching that of the sulfate anion. Dilution reduced the sulfate signal to the level where the perchlorate peak was easily distinguished and integrated by the instrument if it was present above the detection level. Spike recovery analyses ensured proper peak identifications. Each sample was analyzed in triplicate and an average of triplicate analyses are reported and shown in Appendix C. The average %CV for the 30 samples in which perchlorate was detected by CE was 4.4%, based on triplicate analysis of each sample. No results were reported for ps03 because the sample arrived in a damaged container. No CE data were reported for LCS1 or LCS2. Individual hypothesis testing between the AS-11 mean and capillary electrophoresis by paired two sample tests for means analysis is shown in Appendix F, where agreement is shown with p-value = 0.0225 at the 0.01 level of significance.

3.3 Raman Spectroscopy

The Raman spectra for the perchlorate standard showed four bands at 462, 629, 934, and 1113 cm^{-1}, consistent with the predicted results using group theory for a tetrahedral molecule [42, 43]. The (3N – 6) rule indicated nine normal vibrational modes. The weak lower frequency band at 462 cm^{-1} was attributed to doubly degenerated deformation modes, *e*. The intense line (a_1) at 934 cm^{-1} was assigned to the symmetric stretching and contraction of the Cl-O bonds. This band

was only observed in the isotropic spectrum but not in the anisotropic spectrum. The two remaining week bands were assigned to two triply degenerated modes, f_2. The band at 1113 cm^{-1} was attributed to the anti-symmetric Cl-O stretching modes, and the other at 629 cm^{-1} was attributed to the deformation of the anti-symmetric modes. The assignment of the major and minor peaks was consistent to reference values [42, 60].

Interference experiments were conducted to see if the 934 cm^{-1} peak of perchlorate could be obscured by the presence of fertilizer components that are Raman active. Standards of nitrate, sulfate, phosphate, urea, and a mixture of these anions were analyzed with or without perchlorate. Except for phosphate, none of these common components were found to interfere with Raman analysis. Phosphate was found to interfere with perchlorate when pH was above 10.5, as a peak at 937 cm^{-1} was present. However, protonating PO_4^{3-} species to HPO_4^{2-} by lowering the pH to 10.5 or below removed the interference. The pKa of PO_4^{3-} is 12.32. Below the pH of 10.5, less than 1.5% of the phosphate exists as the PO_4^{3-} species. All of the fertilizer samples had pH's below 9.0. Therefore, interference from common fertilizer components is not expected. A few small peaks, not attributed to nitrate, sulfate, phosphate, and urea, were observed also, but they were all far removed from 934 cm^{-1}. Confidence level of the 934 cm^{-1} peak of perchlorate at below pH 10.5 is high.

The intense 934 cm^{-1} peak was used for quantitation. Quantification was performed by comparing the ratio of the area of the 934 cm^{-1} peak of perchlorate to the 2329 cm^{-1} peak of atmospheric nitrogen that is observed in all spectra recorded with adequate laser power and exposure time. This approach allowed spectra collected under different conditions to be adequately normalized, and also corrected for minor changes in instrument performance, such as laser power fluctuations. Two sets of 18 perchlorate standards prepared in de-ionized water covering the range from 20 to 3,000 ppm were prepared, and 36 data points were used to generate the calibration line. The calibration line was linear and typically described by the equation $Y = 434 * X - 36.82$; where Y is the perchlorate concentration and X is the ratio of perchlorate and nitrogen peaks. The correlation coefficient value is 0.9980 or better.

Each sample was first run with an exposure time of 20 sec and 5 accumulations co-added, resulting in a total analysis of 7 min per sample. Results obtained by Raman spectroscopy are shown in Appendix C. The reported RS method detection limit is 20 ppm. No result was

reported for ps03 because the sample arrived damaged. The Lab did not report results for LCS1 and LCS2 because they were below their detection level. Additionally, sample ps34, which is supposed to be Chilean Nitrate, does not exhibit a peak for nitrate in the Raman Spectrum.

The t-test comparison shows strong disagreement between the AS-11 means and the RS results with the p-value at 0.0000. Over seventy percent of the RS values were lower than the AS-11 means. The disparity might have been caused by Tyndall scattering from the micro-particles in the solution and fluorescent interference from the organic components of the test materials [42].

Six of the 34 samples exhibited excessive fluorescence; the Raman spectrum could not be observed at the 20-second exposure time. For all but one of the six samples, the problem was overcome by lowering the exposure time until the spectrum background near the 934 cm^{-1} peak fell below 15,000 counts. At or below this level of fluorescence, perchlorate could be observed if present in the sample at above 20 ppm or more. In ps28, the fluorescence was so severe that the baseline could not be lowered below 15,000 counts without decreasing the exposure to such a low level that the atmospheric nitrogen peak used as quantification standard was not observable. In this sample, the sample was shaken with activated charcoal (~50 mg/mL) in order to remove fluorescent interference. After filtering, the extract was clear and was analyzed at a 20-sec exposure with no noticeable fluorescence. Use of activated charcoal is a common technique employed to remove trace-level, high molecular weight organics.

It was suspected that treatment with charcoal would also reduce the level of perchlorate in ps28. This was investigated by analyzing perchlorate standards in distilled water and in other fertilizers with varying levels of perchlorate. In each case, the level of perchlorate was determined before and after charcoal treatment. Charcoal treatment was found to lower the level of perchlorate, but by a constant amount. It was demonstrated that 36 (± 13) percent of the perchlorate was removed, regardless of the nature of the matrix. Thus, the value of the perchlorate reported in Appendix C for ps28 is 1.36 times that actually measured in the charcoal-treated sample.

3.4 Tetraphenylstibonium Sulfate Titration

For tetraphenylstibonium sulfate titration, a calibration curve was generated from perchlorate standards at 100, 500, 1,000, and 5,000 ppm. Results obtained from titration are shown in Appendix C. The reported titration method detection limit was 50 ppm (mg/kg). For the positive 100-µg/L LCS1 and LCS2 controls, titration reported 90 and 104 µg/L, respectively. Non-detect was reported for the negative blank. As shown in Appendix E, titration results were significantly different from the AS-11 means with a p-value of 0.0002.

In fitting a model to the AS-11 perchlorate concentration means, the model given below is reasonable. However, the model only explains 51.4% of the variability in the perchlorate numbers, based on phosphorous, nitrogen, and potassium. Sample numbers ps22 and ps31 were having too much influence on the model, so they were removed. A model should be robust, but if small amounts of data are pulling the model around, their effect should be removed. After these samples were removed, the model met all assumptions of the normal error model:

$$\text{Predicted } [ClO_4] = 3057.54 + 205.93*[NO_3^-] - 456.98*[PO_4^{3-}] + 14.69*[PO_4^{3-}]^2$$

What this model illustrates is that NO_3^- is related to the perchlorate level in a linear fashion with a positive slope, so a unit increases in the NO_3^- level results in a 205.93 ppm increase in the sample's ClO_4^- concentration, while holding the PO_4^{3-} level constant. Notice that PO_4^{3-} exhibits a quadratic relationship with ClO_4^-, where the predicted ClO_4^- level in a sample decreases as PO_4^{3-} goes from 0 to 15.55, but then the ClO_4^- level increases as PO_4^{3-} increases above 15.55. K^+ is not in the model because K^+ did not show a direct relationship with ClO_4^-. K^+ concentration has no predictive capability over ClO_4^- concentration.

This choice of variables in the model appeared robust no matter which Laboratory or method was being modeled. Only the coefficients changed, when, for instance, predicting the perchlorate values for the Titration method, which were significantly different than the AS-11 means. The model had the same variables but the coefficients were:

$$\text{Predicted Perchlorate} = 3454.25 + 219.09*[NO_3^-] - 487.26*[PO_4^{3-}] + 15.76*[PO_4^{3-}]^2$$

The difference in coefficients makes the prediction steeper, so agreement with the AS-11 means is not good. The Y-intercept changed from 3057.54 to 3454.25, indicating that Titration method is generally larger than the AS-11 values even when NO_3^- and PO_4^{3-} levels were at zero.

4.0 Conclusions

A successful inter-laboratory collaborative study on the performance of ion chromatography methods for perchlorate analysis in aqueous fertilizer suspensions was conducted. The study included seven government, private and commercial laboratories, and evaluated two method variants (AS-11 and AS-16). Three of the laboratories employed the widely used AS-11 IC method for perchlorate analysis; the paired t-tests for the means analysis showed acceptable agreement with little variability (<10% CV) among the data sets. Two laboratories employed the AS-16 method; the statistical evaluation of the results showed acceptable agreement. This study also showed good agreement between the microbore and the standard bore AS-11 columns, rendering credibility in using the microbore column for perchlorate in limited applications where the analyses are restricted by the sample size.

Furthermore, the study found excellent agreement between two method variants (AS-11 and AS-16). At 99 percent confidence level, the p-value for the means analysis of AS-11 and AS-16 results by paired t-test comparison was 0.9248. The large p-value indicates that there was a very high probability of finding the AS-11 and AS-16 mean values were the same. The good precision between the two methods was also evidenced by the low percent relative deviations in all five labs' results. The average relative standard deviations from the laboratories for all samples were less than seven percent, consistent to that observed in the groundwater and drinking water study [59]. At the conclusion of that study, EPA adopted the AS-16 method as Method 309.0 for perchlorate analysis in groundwater and drinking water; the EPA method 309.0 is currently being recommended for promulgation [57].

This study found poor agreement between ion chromatography and tetraphenylstibonium titration results. Overall, compared to ion chromatography, tetraphenylstibonium titration tends

to over estimate the perchlorate titration values by about fourteen percent. Reasons accounting for the over-estimations have been discussed elsewhere [24]. This study found good agreement between capillary electrophoresis and IC but poor agreement between Raman and IC.

This study found good agreement between capillary electrophoresis (CE) and IC quantitative results. The precision of CE is also good; the average %CV for the 30 fertilizer samples in which perchlorate was detected was 4.4%, based on triplicate analyses. CE, like IC, has no fingerprinting capability for qualitative analysis such as does Raman spectroscopy; however, the precision for peak migration, shown by the %CV of <1, is good enough to provide confidence in peak identify if questionable samples are spiked with perchlorate and the peak area/height increase proportionately with no peak splitting. In summary, this CE method is accurate, precise and moderately fast; a total sample analysis requires less than 20 min. IC is a preferred method because of its greater sensitivity. However, for most of the fertilizer samples CE was sensitive enough for the detection of perchlorate, with a detection limit of about 3-ppm in the fortified matrix. If a laboratory possesses both IC and CE instrumentation, the CE would be very useful for initial screening to determine the dilution factor need for IC analysis. Additionally, the CE is useful for confirmation of IC results, since it is based on an entirely different separation principle and complimentary to IC.

The disparity in the duplicate sample analyses reflected the inherent heterogeneity of the fertilizer samples. As expected for any heterogeneous sample, the lawn and garden fertilizer samples examined in this report exhibited both intra-lot and inter-lot variability. Each sample tested in this study was essentially a sub-sampling of a fertilizer lot, and a single sub-sampling datum taken from a heterogeneous sample can not represent the sample as a whole. Hence, the values as presented in this report were the perchlorate concentrations in the extract of each sub-sample for a given fertilizer, but the values did not necessarily represent the true concentrations in the fertilizer brands examined in this study.

The determination of a true perchlorate concentration for a given type or brand of fertilizer is beyond the scope of this project, since the purpose of this study was to verify methods performance with respect to matrices having the same quality as the test materials. It would be economically unfeasible for the collaborative study group to find the true perchlorate concentration for all 27 brands of fertilizers examined in this study. Because multiple sampling

data are required per sample batch, per lot, and per brand, the number of data points and analyses desired to generate statistically sound values for all of the 27 fertilizer brands would have increased exponentially and overwhelmed the resources available to this collaborative study group. This round robin effort was not to establish or define the occurrence of perchlorate for the final risk assessment. The purpose was to standardize analytical approaches for gaining insight into the occurrence of perchlorate in fertilizers.

Modeling efforts in correlating the perchlorate concentrations to that of potassium, nitrate, and phosphate were unsuccessful. Multiple linear regression model found no correlation between perchlorate and potassium, and the model was only able to predict 51.4% of the variability ($R^2 = 0.5140$) in correlating perchlorate concentration to that of nitrate and phosphate. The poor prediction in the variability was attributed to data quality. Since fertilizers were shown to be heterogeneous, the actual N-P-K values, similar to the perchlorate value, were expected to differ from sub-sample to sub-sample. The N-P-K values used in the predictive modeling effort were provided by the manufacturers and were not experimentally determined for each sub-sample. Manufacturers' N-P-K values were statistical values determined based on multiple sampling. The actual N-P-K values for each sub-sample may have been higher or lower than the values provided the manufacturers.

Although the predictability was low, the model was robust. Regardless of the lab or the method, only the magnitudes or the coefficients changed. The variables (i.e. nitrate and phosphate) having influence on the predictability of variability did not change. This is interesting because the presence of perchlorate has been identified in nitrate and phosphate ores [15, 61-63]. Future perchlorate occurrence study design should carefully incorporate matrix characterization measurements for pH, anions, and cations.

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APPENDIX A:

TEST MATERIALS, PURCHASED LOCATIONS, AND MANUFACTURES' INFORMATION

Samples	Manufacturer	Brand Name	Primary Constituent	Purchase Location	N	P	K
ps01	Fertilome	Start-N-Grow Plant Food	Potassium Nitrate	Kansas City, MO	18	6	12
ps02	Ringer	Supreme Gardens	Nitrate of Soda	Kansas City, MO	7	7	7
ps03	Peters	Lawn Food and Iron	Potassium Nitrate	Kansas City, MO	38	4	4
ps04	Hi-Yield	Nitrate of Soda	Nitrate of Soda	Kansas City, MO	16	0	0
ps05	Peters	All Purpose Plant Food	Potassium Nitrate	Kansas City, MO	20	20	20
ps06	Peters	All Purpose Plant Food	Potassium Nitrate	California	20	20	20
ps07	Sudbury	Fertilizer Potash	Potassium Chloride	Kansas City, MO	0	0	44
ps08	Osmocote	Vegetable and Bedding Plant Food	Ammonium Nitrate	Kansas City, MO	14	14	14
ps09	Ringer	Supreme Gardens	Nitrate of Soda	Kansas City, MO	7	7	7
ps10	Acme	Stump Remover	Potassium Nitrate	Kansas City, MO	NA	NA	NA
ps11	Scott's	Miracle-Gro Lawn Food	Potassium Nitrate	Kansas City, MO	36	6	6
ps12	Osmocote	Vegetable and Bedding Plant Food	Ammonium Nitrate	Kansas City, MO	14	14	14
ps13	Shulte	Rose Plus	Potassium Nitrate	Kansas City, MO	19	24	24
ps14	Jobe's	Plant Food Spikes	Potassium Nitrate	Kansas City, MO	16	2	6
ps15	Ringer	All Natural Lawn Restorer	Nitrate of Soda	Long Island, NY	10	2	6
ps16	Peters	All Purpose Plant Food	Potassium Nitrate	Long Island, NY	20	20	20

Samples	Manufacturer	Brand Name	Primary Constituent	Purchase Location	NO_3^+	PO_4^-	K^+
ps17	Johnathan Green	Winter Survival Fall Fertilizer	Muriate of Potash	Long Island, NY	10	18	20
ps18	Osmocote	Outdoor and Indoor Plant Food	Ammonium Nitrate	Long Island, NY	18	6	12
ps19	Osmocote	Vegetable and Bedding Plant Food	Ammonium Nitrate	Long Island, NY	14	14	14
ps20	Frank's	All Purpose Concentration Plant Food	Muriate of Potash	Long Island, NY	15	30	15
ps21	Ringer	All Natural Lawn Restorer	Nitrate of Soda	Long Island, NY	10	2	6
ps22	Scott's	Miracle-Grow Lawn Food	Potassium Nitrate	Long Island, NY	31	3	9
ps23	Vigoro	Tomato and Vegetable Plant Food	Muriate of Potash, Sul Po Mag	Long Island, NY	10	8	14
ps24	Johnathan Green	Winter Survival Fall Fertilizer	Muriate of Potash	Long Island, NY	10	18	20
ps25	Best	All Purpose Triple Sixteen	NA	California	16	16	16
ps26	Bandini	Sul Po Mag	NA	California	0	0	22
ps27	Plant Marvel	Matriculture	KNO_3	California	12	31	14
ps28	Orchid	Premium Orchid Food – Bloom Formula	NA	California	6	30	30
ps29	Dexol	Stump Remover	KNO_3	California	NA	NA	NA
ps30	IMC	Langbeinite Ore	Sul Po Mag	New Mexico	NA	NA	NA
ps31	CNC - Champion	Potassium Nitrate	Potassium Nitrate	Albequerque, NM	14	0	45
ps32	Best, K-Power	Prill	Chilean Nitrate	Chile	14	0	46
ps33	Best, K-Power	Prill	Chilean Nitrate	Chile	14	0	46
ps34	NA	Caliche	Sodium Nitrate	Chile	NA	NA	NA

APPENDIX B:

SUMMARY OF ION CHROMATOGRAPHY METHODS

Laboratory Code	1	2	3	4	5	6	7
Separation Column	AS-16	AS-11	AS-11	AS-11	AS-16	AS-11	AS-11
Guard Column	AG-16	AG-11 (1)	AG-11	AG-11	AG-16	AG-11	AG-11
Column Size	4 mm	2 mm	4 mm	4 mm	4 mm	4 mm	4 mm
Anion Trap Column	ATC-1	None	ATC-1	ATC-1	ATC-1	ATC-1	ATC-1
Suppressor	ASRS-Ultra	ASRS-Ultra	ASRS-II	ASRS-II	ASRS-Ultra	ASRS-II	ASRS-II
Suppressor Mode	Ext. Water	Ext. Water	Ext. Water	Ext. Water	Ext. Water	Ext. Water	Ext. Water
Regenerant	H_2O	H_2O	H_2O	H_2O	H_2O	H_2O	H_2O
Regenerant Flow Rate	10 mL/min	12 psi	10 mL/min	10 mL/min	5 mL/min	25 psi, 3 mL/min	10 mL/min
Autosampler	AS-40	AS-40	AS-40	AS-40	AS-40	AS-40	AS-40
Pump Type	GP-40	GP-40	GP-40	GP-40	GP-40	GP-40	GP-40
Detector Type	CD-20	CD-20	CD-20	CD-20	CD-20	CD-20	CD-20
Sample Size	50 µL	1 µL	1000 µL	100 µL	1000 µL	100 µL	100 µL
Mobile Phase	(2)	100 mM NaOH	100 mM NaOH	100 mM NaOH	35 mM KOH	100 mM NaOH	100 mM NaOH
Flow Rate	1.0 mL/min	0.38 mL/min	1.0 mL/min	1.0 mL/min	1.25 mL/min	1.0 mL/min	1.0 mL/min

(1) 2-mm x 50-mm AF-11 guard column instead of the 4-mm guard column and separation column

(2) 20 mM NaOH for 5 minutes, 100 mM NaOH for remainder

APPENDIX C:

RESULTS OF FERTILIZER ANALYSIS BY TITRATION, ION CHROMATOGRAPHY, CAPILLARY ELECTROPHORESIS (CE), AND RAMAN SPECTROSCOPY (RS)

Samples	Titration (mg/kg)	Lab1 (mg/kg)	Lab2 (mg/kg)	Lab3 (mg/kg)	Lab4 (mg/kg)	Lab 5 (mg/kg)	Lab 6 (mg/kg)	Lab 7 (mg/kg)	CE (mg/kg)	RS (mg/kg)
ps01	5900	4680	5150	5300	4710	4872	5703	4700	5557	4637
ps02	2950	3490	2360	3100	3240	3077	3954	3200	3752	2569
ps03	9900	8950	7730	9400	8860	7678	NR	8600	NR	NR
ps04	6800	7620	6300	8000	7660	6908	9023	7400	4255	7186
ps05	7150	6700	4760	6200	6360	6898	7760	6300	6535	4677
ps06	3400	3220	3680	3000	3090	3128	3563	3190	4399	2169
ps07	5440	4730	8830	5000	4920	4369	5554	4800	5821	4979
ps08	1250	1090	968	970	1010	903	1034	940	917	726
ps09	5200	4380	5120	4300	4380	4049	4949	3900	4039	3836
ps10	< 50.0	< 6.0	< 40.0	< 0.4	< 3.0	< 1.0	< 4.0	< 0.4	< 3.0	< 20.0
ps11	8600	8160	6260	8800	8290	7068	8559	7400	7592	7673
ps12	750	636	597	530	580	526	593	540	707	286
ps13	< 50.0	< 6.0	< 40.0	< 0.8	0.6	< 1.0	ND	13	< 3.0	< 3.00
ps14	10350	9480	8640	9000	9920	6896	9688	8100	9476	8514
ps15	6140	6060	5190	6100	6080	4673	6278	5300	6146	5867
ps16	6980	7510	5640	7400	7210	6194	7439	7300	7196	6079
ps17	< 50.0	< 6.0	< 40.0	< 2.2	< 3.0	< 1.0	< 4.0	< 0.4	< 3.0	< 3.00
ps18	740	733	832	750	690	904	682	600	495	342
ps19	3100	2650	3270	2700	2660	2053	2648	2500	2687	2408
ps20	6250	5380	10000	4800	5560	7098	5768	5400	5470	4070
ps21	3400	2960	2560	2900	3000	2376	2943	2400	2918	2617
ps22	1700	1549	2646	1400	1530	1995	1433	1300	1894	1153
ps23	450	464	738	340	430	514	391	360	707	< 3.00
ps24	2850	2590	2840	2200	2480	2530	2600	2400	3493	2618
ps25	5250	4223	3680	4000	4310	3727	4586	4200	4528	4343
ps26	3550	3073	4810	3200	3160	2834	3474	3000	3722	3391
ps27	6300	6680	7120	5500	6450	6246	6816	5300	7117	4650
ps28	2800	2599	3623	2200	2490	3135	2840	2500	3185	1690
ps29	5800	5189	5290	5400	5420	4576	4819	4900	7186	4699
ps30	15600	14300	20090	14000	16400	13649	17397	13000	15644	15734
ps31	16800	13290	14380	13000	15100	11749	15603	12000	13817	14120
ps32	8200	6381	6300	6100	6560	5862	5477	6300	7416	6214
ps33	8250	7563	2600	7400	7870	7201	8018	7100	8302	7278
ps34	32800	26310	32980	27000	30900	26120	32454	30000	26013	28183

NR = Not Reported

APPENDIX D:

PAIRED TWO SAMPLE TESTS FOR MEANS ANALYSIS ON AS-11 METHOD

Lab 7 Vs. Laboratory 3	$\alpha = 0.01$
Shapiro-Wilk Normality test	W=0.96324
Prob(<W)	0.3793
Paired t-test	
Mean Difference	-0.30738
Std Error	0.157135
Df	32
t-Stat	-1.95605
p-value > |t|	0.0592

Laboratory 7 Vs. Laboratory 4	$\alpha = 0.01$
Shapiro-Wilk Normality test	W=0.93970
Prob(<W)	0.0828
Paired t-test	
Mean Difference	-0.53432
Std Error	0.166783
Df	32
t-Stat	-3.20367
p-value > |t|	0.0031

Laboratory 3 Vs. Laboratory 4	$\alpha = 0.01$
Shapiro-Wilk Normality test	W=0.933269
Prob(<W)	0.0532
Paired t-test	
Mean Difference	-0.22695
Std Error	0.168475
Df	32
t-Stat	-1.34711
p-value > |t|	0.1874

APPENDIX-E:

PERCHLORATE IN GARDEN AND LAWN FERTILIZERS BY AS-11

Samples	Lab 7 (mg/kg)	Lab 3 (mg/kg)	Lab 4 (mg/kg)	Average (mg/kg)	Standard Deviation	Percent Coefficient of Variation
ps01	4700	5300	4710	4903	344	7 %
ps02	3200	3100	3240	3180	72	2 %
ps03	8600	9400	8860	8953	408	5 %
ps04	7400	8000	7660	7687	301	4 %
ps05	6300	6200	6360	6287	81	1 %
ps06	3190	3000	3090	3093	95	3 %
ps07	4800	5000	4920	4907	101	2 %
ps08	940	970	1010	973	35	4 %
ps09	3900	4300	4380	4193	257	6 %
ps11	7400	8800	8290	8163	709	9 %
ps12	540	530	580	550	26	5 %
ps14	8100	9000	9920	9007	910	10 %
ps15	5300	6100	6080	5827	456	8 %
ps16	7300	7400	7210	7303	95	1 %
ps18	600	750	690	680	67	10 %
ps19	2500	2700	2660	2639	106	4 %
ps20	5400	4800	5560	5253	401	8 %
ps21	2400	2900	3000	2767	71	3 %
ps22	1300	1400	1530	1410	115	8 %
ps23	360	340	430	367	37	10 %
ps24	2400	2200	2480	2360	144	6 %
ps25	4200	4000	4310	4170	157	4 %
ps26	3000	3200	3160	3120	106	3 %
ps27	5300	5500	6450	5750	141	2 %
ps28	2500	2200	2490	2397	170	7 %
ps29	4900	5400	5420	5240	295	6 %
ps30	13000	14000	16400	14467	1747	10 %
ps31	12000	13000	15100	13367	1485	11 %
ps32	6300	6100	6560	6320	231	4 %
ps33	7100	7400	7870	7457	388	5 %
ps34	30000	27000	30900	29300	2042	7 %

APPENDIX - F

PAIRED TWO SAMPLE TEST FOR MEANS ANALYSIS ON AS-11 VERSUS AS-16, CAPILLARY ELECTROPHORESIS, RAMAN SPECTROSCOPY, AND TITRATION

AS-11 Average Vs. Laboratory 2	$\alpha = 0.01$
Shapiro-Wilk Normality test	W=0.859024
Prob(<W)	0.0004
Paired t-test (Nonparametric)	
Df	32
t-Stat	-59.500
p-value > |t|	0.295

AS-11 Average Vs. Laboratory 1 (AS-16)	$\alpha = 0.01$
Shapiro-Wilk Normality test	W=0.948665
Prob(<W)	0.1516
Paired t-test	
Mean Difference	-0.33115
Std Error	0.121099
Df	32
t-Stat	-2.73457
p-value > |t|	0.0101

AS-11 Average Vs. Laboratory 5 (AS-16)	$\alpha = 0.01$
Shapiro-Wilk Normality test	W=0.96364
Prob(<W)	0.3882
Paired t-test	
Mean Difference	0.35321
Std Error	0.178093
Df	32
t-Stat	1.9833
p-value > |t|	0.0560

AS-11 Average Vs. Lab 6 - IC Analysis	$\alpha = 0.01$
Shapiro-Wilk Normality test	W=0.882071
Prob(<W)	0.0029
Paired t-test (Nonparametric)	
Df	29
t-Stat	-182.5
p-value > |t|	0.0001

AS-11 Average Vs. CE Analysis	$\alpha = 0.01$
Shapiro-Wilk Normality test	W=0.914288
Prob(<W)	0.0211
Paired t-test	
Mean Difference	-1.024154
Std Error	0.424712
Df	29
t-Stat	-2.411409
Prob > |t|	0.0225

AS-11 Average Vs. RS Analysis	$\alpha = 0.01$
Shapiro-Wilk Normality test	W=0.888470
Prob(<W)	0.0043
Paired t-test (Nonparametric)	
Df	29
t-Stat	179.5
p-value > |t|	0.0000

AS-11 Vs. Titration	$\alpha = 0.01$
Shapiro-Wilk Normality test	W=0.927197
Prob(<W)	0.0350
Paired t-test	
Mean Difference	-1.422302
Std Error	0.341295
Df	32
t-Stat	-4.167373
Prob > |t|	0.0002