Interlaboratory Study of the Canadian Council for Ministers of the Environment (CCME) Method for the Analysis of Petroleum Hydrocarbons in Soil

Prepared by
Harold Malle
Environment Canada
National Laboratory for Environmental Testing
National Water Research Institute
Burlington, Ontario
L7R 4A6

Prepared for
Canadian Association for Environmental Analytical Laboratories (CAEAL)

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SUMMARY

The National Laboratory for Environmental Testing (NLET) , Information and Quality Management (IQM) was contracted to provide an interlaboratory study of the CCME Method for the Analysis of Petroleum Hydrocarbons in Soil by the Canadian Association for Environmental Analytical Laboratories (CAEAL). As part of the contract NLET was to design the study, provide samples, data analysis and distribute a final report.

There were two phases to the study. The first phase consisted of designing the study and monitoring the stability of the hydrocarbon samples and verifying bottle to bottle homogeneity. The second phase consisted of the interlaboratory study. Laboratories across Canada received solid and liquid samples to evaluate the Canada-wide Standard (CWS) for petroleum hydrocarbons (PHC).

The sample sets were shipped to participating laboratories May 2002 with a reporting assigned in mid-July 2002.

The interlaboratory study was commissioned to determine if the CWS for PHC would be suitably addressed by laboratories and if the outcome would satisfy the requirements of the CAEAL PT program for their implementation.

It is possible to produce solid interlaboratory test samples that are sufficiently homogenous and stable to be used in interlaboratory studies.

The laboratory producing the solid samples is able to produce large quantities (>200 bottles) of a specific sample at one time and the stability of the solid samples makes them useful as long term reference materials.

The interlaboratory data shows that method is inherently sound and can be used with sufficient precision.

It is possible for quality data to be generated from 75% of the participating laboratories using the CWS.

CCME PHC INTERLABORATORY STUDY

1.0 Introduction

This study was done at the request of Canadian Association for Environmental Analytical Laboratories (CAEAL) and financed by the CCME. Study samples were shipped in May 2002. Solid samples and hydrocarbon test solutions were prepared by Environment Canada's National Laboratory for Environmental Testing (NLET), Information and Quality Management section (IQM). Environment Canada's Wastewater Technology Centre Analytical Laboratory was responsible for analyzing samples for homogeneity and stability. Participating laboratories were identified through the CAEAL performance testing program. 61 sets of samples were distributed to 41 laboratories. A total of 39 sets of data were returned, although some data sets were incomplete.

CAEAL determined that a study was needed to generate an estimate of the uncertainty in the determination of PHC fractions. This estimate of uncertainty could be used as a starting point for future performance testing studies. This interlaboratory study would also be used to establish study design criteria that could be used as a model for possible future proficiency testing studies. The results of this study would also be used to confirm that the Canada Wide Standard (CWS) for Petroleum Hydrocarbons could be applied with adequate precision and accuracy. In support of the CAEAL performance testing program there was a need to produce proficiency testing samples with demonstrated stability of approximately 10 weeks.

At the end of the study it was hoped that there would exist a source of standards and reference materials available for distribution to Canadian researchers, consultants and laboratories.

The study was designed to promote the widespread use of the analytical method in support of the CWS for PHC's by making samples available in sufficient quantity so that various method modifications could be explored by participating laboratories.

2.0 Selection of Materials

Four fractions are required to be analyzed using the Canada-Wide Standard for Petroleum Hydrocarbons to decide if a site meets acceptable criteria for various land uses. The four fractions are defined as follows;

- F1- nC6 to nC10 (hexane to decane range)
- F2- nC10 to nC16 (decane to hexadecane range)
- F3- nC16 to nC34 (hexadecane to tetratriacontane range)
- F4- nC34 to nC50 (tetratriacontane to pentacontane range)

The F1 fraction is determined using a methanol extraction of a soil sample with subsequent analysis by purge and trap GC-FID.

The F2, F3, F4 fractions are soxhlet extracted using a hexane/ acetone mixture and then analyzed using GC-FID. There is an optional gravimetric method for the F4 fraction but this portion of the CWS was not being evaluated in this study.

2.1 Soils

The primary concern in selection of the materials to be spiked was that they have a low background for the F1, F2, F3, and F4 fractions so that there were minimal interferences with the spike material.

A number of materials were considered for use in this study. They ranged from highly contaminated soils and sediments through to clean artificial materials. It was decided to spike clean materials with the appropriate hydrocarbons rather than to attempt to blend contaminated materials. This was done to avoid possible homogeneity problems associated with bulk spiking of soils and their subsequent sub-sampling.

All laboratories were to be provided samples of a uniform weight such that the entire samples was used for analysis. This was done in an attempt to minimize the effect sampling might have on the application of the CWS.

Two soils were obtained from the Ontario Ministry of the Environment (OMOE). Three clays, normally used in the production of pottery, were purchased from a pottery supply store.

The five selected materials chosen were a sandy loam, a clay loam, Red Art clay, Ball clay and Kaolin clay. The two loams were dried for three days at 60°C and then crushed and sieved to <710µm. Prior to any spiking all materials were analysed by WTC to ensure a reasonably hydrocarbon free background. All solid materials were gamma irradiated at >25kGy (Isomedix Corporation, Oshawa) to ensure sterility. This was done to suppress any bacterial activity that might degrade the spiked hydrocarbon samples while in storage. There was also a possibility that some of the round robin participants might originate from outside Canada. Customs requires proof that samples be pathogen free.

2.2 Spiking Materials

In order to fully cover the four analytical fractions of the CWS F1 (nC6-nC10), F2 (nC10-nC16), F3 (nC16-nC34) and F4 (nC34-nC50) a variety of hydrocarbon products were selected as potential spiking materials.

The spiking materials selected for this study were gasoline, diesel fuel, a 5W30 oil, a 10W30 oil, a 2-stroke lawnmower oil, a 10W30 4-stroke lawnmower oil and an 80W90 lubricating oil. The gasoline and diesel fuel were rotary evaporated until no further volume change was seen. The oils were used as purchased.

All potential spiking materials were analyzed by the reference laboratory in order to establish their chromatographic profiles.

3.0 Preparation and Analysis of Stable Soil Samples

A series of test samples were prepared to evaluate spiking methods, storage conditions and the stability of the proposed test samples.

3.1 Preparation

Four materials were spiked with three distinct hydrocarbon mixtures. Ball clay samples were spiked with a mixture of gasoline/diesel/5W30 oil. Clay loam was spiked with gasoline/2-stroke oil. Sandy loam was spiked with a mixture of gasoline/diesel/5W30 oil and Kaolin was spiked with diesel/10W30 oil/ 80W90 oil. For this study, the fifth soil, the Red Art clay was not used.

All four sets of samples were spiked at room temperature using a repeating dispensing pipette. Samples were stored at -20°C until required for analysis.

3.2 Analysis

F1 fractions were analyzed using a purge and trap system with a mass selective detector (MSD). The verification laboratory at this stage had not yet finished installing the FID detector to their purge and trap system. Since these samples were being used to monitor possible losses, the semi-quantitative nature of these initial analyses was not considered a problem. The results from samples submitted over a period of seven weeks show that no loss of F1 fraction could be seen. The F1 samples were somewhat variable in concentration over the seven week period. The percent relative standard deviations for the samples submitted ranged from 12% to 30%. The worst relative standard deviation was seen with the Kaolin sample. Appendix E details the results in chart form.

F2, F3, and F4 fractions were analyzed using the CWS as written. These samples were also analyzed over a period of approximately seven weeks. No losses of any of the F2, F3 or F4 fractions were seen. The relative standard deviations (RSD) for fraction F2 ranged from a 7% to 33%. The relative standard deviations for the F3 fraction ranged from 5% to 10%, and the relative standard deviations for the F4 fraction ranged from 5% to 38%. The worst sample again, was the Kaolin sample.

The variability of the Kaolin samples was attributed to the nature of the spiking material and not the Kaolin itself. The F1 fraction data, although quite variable were a fairly low. The F2, F3, F4 data was more troubling since it appeared that hydrocarbon profile was changing even though the total hydrocarbon levels remained constant.

No further samples F1, F2, F3 and F4 were analyzed after the initial six week period since it was apparent that the variability being seen was due to sample variability and laboratory variability, and not any loss or degradation process. Appendix F details the results for all hydrocarbon fractions in chart form.

Chart 1- Clay loam 43 day stability data

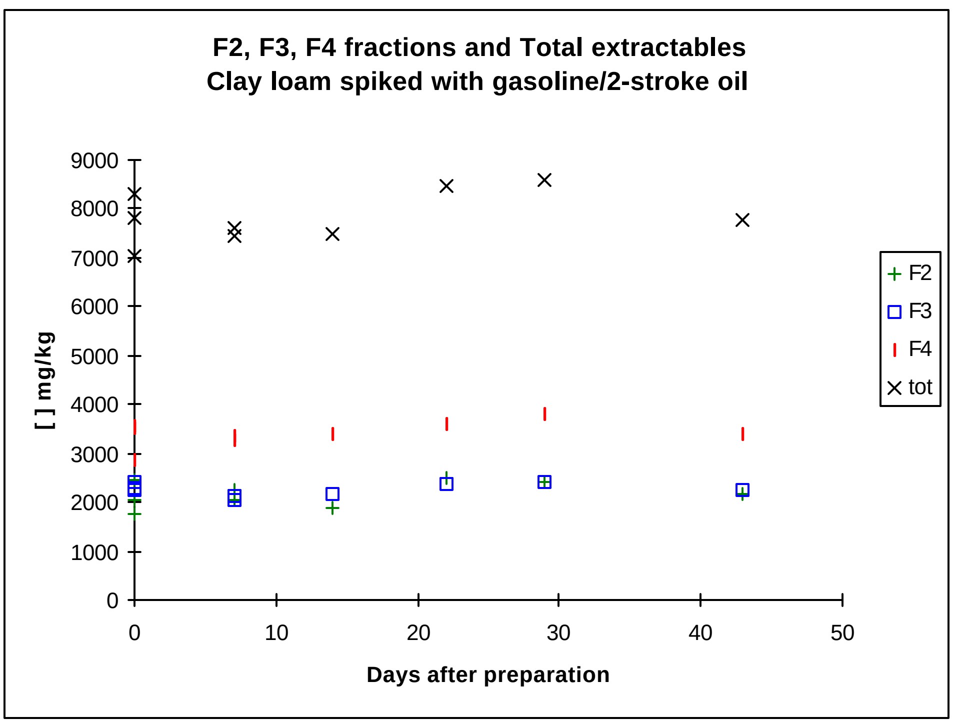


Table 1- Stability test samples data- 43 day test

Sample/ Fraction	Hydrocarbon Makeup		F1 mg/Kg	F2 mg/Kg	F3 mg/Kg	F4 mg/Kg
Ball Clay	gasoline diesel 5W30	Average	1199	1699	2760	382
		%RSD	12	7	7	7
Clay Loam	gasoline 2-stroke	Average	2788	2161	2255	3420
		%RSD	17	12	6	8
Sandy Loam	gasoline diesel 5W30	Average	1583	3641	5558	698
		%RSD	25	7	5	5
Kaolin	diesel 10W30 80W90	Average	133	5847	12654	5006
		%RSD	30	33	10	38

4.0 Interlaboratory Samples

The round robin study was designed to have two distinct types of samples. The first set of samples were test solutions designed to evaluate laboratory calibration and sample handling. These solutions were prepared and stored at -20°C in 4mL amber vials with Teflon lined solid closures. The second of samples were soils that were used to evaluate the entire analytical method.

The soils were prepared in the following manner. Clean dry material was weighed into 25mL amber jars with Teflon lined closures. All solid weights were 5 grams ±0.25 grams. The solid matrices for these samples were sandy loam, clay loam, Red Art clay, Ball clay and Kaolin clay. The entire sample was consumed by the analysis and for calculation purposes all laboratories were to use 5.00 grams as the sample weights. It was hoped this would eliminate any sampling bias that individual laboratories might introduce. All solid samples were stored at -20°C until needed.

All participating laboratories received five solution samples for F1, five solution samples for F2, F3, F4, five solid samples for F1 and five solid samples for F2, F3, F4. The solid samples were provided in duplicate for both the F1 and F2, F3, F4 fractions. All samples were shipped by courier. Samples were shipped frozen in insulated containers filled with frozen gel packs.

4.1 F1 Interlaboratory Samples

The F1 test solutions consisted of five samples (PS-1 –PS-5) that had hydrocarbons dissolved in a methanol. Sample PS-1 was a mixture of C7, C8 and C9 straight chain alkanes. Samples PS-2, PS-3, PS-4, and PS-5 were weathered gasoline in methanol. Target levels for the PS-2 – PS-4 samples were the maximum possible given the mass of gasoline used to prepare the samples. It was expected that not all of the material in the PS-2 – PS-5 samples was purgeable.

Table 2- PS test solutions- properties and concentrations

Sample	PS-1	PS-2	PS-3	PS-4	PS-5
Matrix	Methanol	Methanol	Methanol	Methanol	Methanol
Hydrocarbon Makeup	C7,C8,C9	gasoline	gasoline	gasoline	gasoline
Target Level (µg/mL)	600	4800	10000	2400	1200
Reference Level (µg/mL)	552	2887	5310	1320	728
RSD(%)	3	1	2	3	5

The F1 series of solid samples (FP-1 – FP-5) were spiked in a refrigerator at 0-4°C and all spiking weights were recorded. The relative standard deviation for the mass of spiking material applied to the F1 series of samples was FP-1, 5%, FP-2, 4%, FP-3, 8%, FP-4, 3%, FP-5, 2%.

The target levels for the FP-1 – FP-5 samples were estimated using the product hydrocarbon profiles obtained earlier in the study. The problem with the FP-3 sample may be attributed to the 2-stroke oil used. This particular product may contain stabilizers designed to make gas, oil mixtures useful over a longer storage period. The high variability of this sample is illustrated in tables and charts found elsewhere in this report. All FP samples were prepared without using a carrier solvent of any kind.

Verification samples were analyzed using the CWS. All F1 solid samples were analyzed using Purge and Trap with FID detection. The tables below summarize available data on the PT samples that were shipped to the participating laboratories.

Table 3- FP solid samples- properties and concentrations

Sample	FP-1	FP-2	FP-3	FP-4	FP-5
Matrix	Clay Loam	Kaolin Clay	Sandy Loam	Ball Clay	Red Art Clay
Hydrocarbon Makeup	gasoline, 5W30, 2-stroke, diesel (1.6:1.6:1.6:1)	gasoline, 5W30, 2-stroke, diesel (1.6:1.6:1.6:1)	gasoline, 2-stroke (1:1)	gasoline, 5W30 (1:3)	gasoline, 5W30 (1:3)
Target Level (mg/kg)	680	2730	1460	590	1180
Reference Level (mg/kg)	685	2580	271	600	920
RSD(%)	6	9	90	21	17

4.2 F2, F3, F4 Interlaboratory Samples

The F2, F3, and F4 test solution samples consisted of five samples (IJ-1 –IJ-5) that had hydrocarbons dissolved in toluene. Sample IJ-1 was a mixture of C12, C20, C30, C36, C40 and C44 straight chain alkanes. IJ-2 consisted of a mixture of gasoline, diesel and 5W30 oil. IJ-3 consisted of diesel, 10W30 and 80W90 oil. IJ-4 consisted of gasoline and 2-stroke oil and IJ-5 consisted of gasoline, diesel, 2-stroke oil and 5W30 oil.

Verification samples were analyzed using the CWS. All F2,F3 and F4 solid samples were also analyzed using an FID. The tables below summarize available data on the PT samples that were shipped to the participating laboratories.

Target levels of the IJ-1 – IJ-5 were estimated based on the chromatographic profiles obtained earlier in this study.

Table 4- IJ test solution samples - properties and concentrations

Sample	IJ-1	IJ-2	IJ-3	IJ-4	IJ-5
Matrix	Toluene	Toluene	Toluene	Toluene	Toluene
Hydrocarbon Makeup	C12, C20, C30, C36, C40, C44	gasoline, diesel, 5W30 oil.	diesel, 10W30, 80W90	Gasoline, 2-stroke	gasoline, diesel, 2-stroke, 5W30
F2 Target Level (µg/mL)	359	2040	5850	2150	3500
F3 Target Level (µg/mL)	794	3300	12650	2250	4130
F4 Target Level (µg/mL)	448	480	5000	3400	4440
F2 Reference Level (µg/mL)	550	3250	3790	3740	5870
RSD(%)	3	1	2	6	5
F3 Reference Level (µg/mL)	879	3670	12430	2860	4730
RSD(%)	2	1	1	2	5
F4 Reference Level (µg/mL)	500	564	9310	4080	5200
RSD(%)	3	5	7	6	3

The F2, F3, and F4 solid samples (FX-1 – FX-5) were spiked at room temperature and all spiking weights were recorded. The relative standard deviation for the mass of spiking material applied to the F1 series of samples was FX-1, 3%, FX-2, 6%, FXP-3, 2%, FX-4, 1%, FX-5, 2%. The F2, F3, and F4 samples were stored at -20°C until needed.

Target levels of the FX-1 – FX-5 were estimated based on the chromatographic profiles obtained earlier in this study. All FX samples were prepared without the use of a carrier solvent.

Table 5- FX solid samples - properties and concentrations

Sample	FX-1	FX-2	FX-3	FX-4	FX-5
Matrix	Kaolin clay	Sandy Loam	Red Art clay	Ball clay	Clay Loam
Hydrocarbon Makeup	gasoline, 5W30, 2-stroke, diesel (1.6:1.6:1.6:1)	2-stroke, diesel (1:1)	5W30, 2-stroke (1:1.7)	2-stroke, diesel (2.3:1)	gasoline, 2-stroke (1:1)
F2 Target Level (mg/kg)	2680	2580	9210	13000	6750
F3 Target Level (mg/kg)	2660	1020	16000	6430	3200
F4 Target Level (mg/kg)	1140	850	10200	7150	4810
F2 Reference Level (mg/kg)	1740	1500	4800	7930	6160
RSD(%)	5	10	4	6	5
F3 Reference (mg/kg)	3220	1210	20900	6910	3700
RSD(%)	1	3	2	7	5
F4 Reference Level (mg/kg)	1280	886	13100	6870	5310
RSD(%)	3	1	2	4	3

5.0 Results of the Interlaboratory Study

5.1 Data Handling

Data received from the laboratories was grouped by fraction type and sample number. The mean, standard deviation, relative standard deviation (%), and median was calculated for each sample. Data falling outside two standard deviations was removed using an iterative process. A maximum of four iterations was done on each sample data set. Most data sets required only three iterations before all outliers were removed. The mean, standard deviation, relative standard deviation (%), and median was then recalculated for each sample. Data from the laboratories presented in this report has been ordered in such a way to preserve laboratory anonymity.

An attempt was made to normalize the data using the actual spiking weights of materials for each sample. Unfortunately, an insufficient number of laboratories reported which bottles had been used to generate their data so this could not be done.

5.2 F1 Fraction

The results for the PS series of samples, which were methanol solutions that were to be purged, were encouraging. Overall relative standard deviation (RSD) was less than 25%. The FP series of solid samples were equally well done by the laboratories with overall RSD being 33%. If the FP-3 sample containing the gasoline, 2-stroke combination spike were removed the overall RSD falls to 26%. Appendix G is a summary of the PS sample results in chart form and Appendix H is a summary of the FP sample results. A summary of all laboratory data is contained in the table in Appendix I. Appendix AA contains charts showing the F1 laboratory data from each FP solid sample and the +/- 2 standard deviations after removal of the outlying data.

The similarity of the overall RSD of the PS and FP series samples seem to indicate that the proper handling of the methanol extracts prior to purging would be the key to success with the F1 fraction.

As seen in Appendix V laboratories that did not use an FID or had difficulty in achieving the required response factor criteria tended to do poorly when compared to the other laboratories.

Laboratories who's only deviation from the CWS was not using a purge and trap produced generated data that was similar to those laboratories which used a purge and trap.

Table 6- PS laboratory results summary

	PS-1	PS-2	PS-3	PS-4	PS-5
Target	600	4800	10000	2400	1200
Ref. Value	552	2887	5310	1320	728
Total Labs	36	36	36	36	36
Average	596	3094	5891	1420	754
STD DEV	378	1774	3489	761	433
RSD(%)	63	57	59	54	57
Median	577	2943	5445	1342	679.5
Non-outlier labs	29	27	28	28	26
Average	541	2892	5911	1359	661
STD DEV	163	759	1386	244	113
RSD(%)	30	26	23	18	17
Median	572	2,910	5,535	1342	661.5

.

Table 7- FP laboratory results summary

	FP-1	FP-2	FP-3	FP-4	FP-5
Target	680	2730	1460	590	1180
Ref. Value	685	2580	271	600	920
Total Labs	35	35	36	35	35
Average	911	3129	941	737	1228
STD DEV	804	3138	826	801	1116
RSD(%)	88	100	88	109	91
Median	739	2500	797.5	570	1068
Non-outlier labs	26	26	32	28	27
Average	692	2584	704	518	953
STD DEV	127	532	414	161	325
RSD(%)	18	21	59	31	34
Median	669	2,600	732.45	554.5	1000

5.3 Extractables F2,F3,F4

As seen in Appendices W - Z laboratories that did not use an FID or had difficulty in achieving the required response factor criteria tended to do poorly when compared to the other laboratories. These laboratories tended to be biased low.

There are a number of a factors at work with the F2, F3, and F4 samples extraction technique, solvent detector etc. Laboratories which did not use the required solvent or soxhlet device were more often low than high. In general, those laboratories that had difficulties with the injectable samples also had difficulties with the solid samples.

A summary of data for the sum of F2,F3 and F4 fractions and FTOT is included in Appendices S,T,U and Z. Charts plotting the laboratory data for the F2,F3 and F4 fractions and FTOT for individual samples are included in Appendices AA, BB, CC, DD and EE.

5.3.1 F2 Fraction

Good results were obtained for the IJ series of toluene solutions. The overall relative standard deviation was 13%. The FX series of solid samples were equally well done by the laboratories with overall RSD being 24%. Appendix J is a summary of the F2 IJ sample results in chart form and Appendix K is a summary of the F2 FX sample results. A summary of all laboratory data for the F2 fraction is contained in the table in Appendix L. Appendix BB contains charts showing the F2 laboratory data from each FP solid sample and the +/- 2 standard deviations after removal of the outlying data.

It was hoped that the IJ-1 sample would have better results than those obtained. This was a simple toluene solution containing only six selected n-alkane compounds.

Table 8- IJ F2 laboratory results summary

F2	IJ-1	IJ-2	IJ-3	IJ-4	IJ-5
Target	359	2040	5850	2150	3500
Ref. Value	550	3250	3790	3740	5870
Total Labs	37	37	37	37	37
Average	611	2948	3393	3450	5188
STD DEV	555	991	962	1104	1420
RSD (%)	91	34	28	32	27
Median	474	2930	3520	3390	5220
Non-outlier labs	30	31	30	28	31
Average	469	2909	3482	3506	5119
STD DEV	70	406	267	382	723
RSD(%)	15	14	8	11	14
Median	472	2930	3540	3528	5220

Table 9- FX F2 laboratory results summary

F2	FX-1	FX-2	FX-3	FX-4	FX-5
Target	2680	2580	9210	13100	6750
Ref. Value	1740	1500	4800	7930	6160
Total Labs	39	39	39	39	39
Average	1433	1344	4492	6803	4892
STD DEV	447	467	1423	2522	1549
RSD(%)	31	35	32	37	32
Median	1437	1421	4700	7006	5070
Non-outlier labs	34	36	34	32	35
Average	1419	1373	4523	7083	5061
STD DEV	337	398	873	1779	1144
RSD(%)	24	29	19	25	23
Median	1,434	1484	4,700	7031	5200

5.3.2 F3 Fraction

Very good results were obtained for the IJ series of samples. The overall relative standard deviation was less than 11%. The FX series of solid samples were equally well done by the laboratories with overall RSD being 31%. Appendix M is a summary of the F2 IJ sample results in chart form and Appendix N is a summary of the F2 FX sample results. A summary of all laboratory data for the F2 fraction is contained in the table in Appendix O. Appendix CC contains charts showing the F3 laboratory data from each FP solid sample and the +/- 2 standard deviations after removal of the outlying data.

Table 10- IJ F3 laboratory results summary

F3	IJ-1	IJ-2	IJ-3	IJ-4	IJ-5
Target	794	3300	12650	2250	4130
Ref. Value	879	3670	12430	2860	4730
Total Labs	37	37	37	37	37
Average	845	2916	10625	2717	4191
STD DEV	146	811	3529	1389	1476
RSD	17	28	33	51	35
Median	820	3110	11200	2440	4230
Non-outlier labs	27	34	30	28	27
Average	809	3104	11253	2400	4260
STD DEV	52	497	1085	282	353
RSD	6	16	10	12	8
Median	815	3,200	11,266	2430	4240

Table 11- FX F3 laboratory results summary

F3	FX-1	FX-2	FX-3	FX-4	FX-5
Target	2660	1020	16000	6430	3200
Ref. value	3220	1210	20900	6910	3700
Total Labs	39	39	39	39	39
Average	2637	915	17019	5252	3172
STD DEV	863	286	5141	1949	1283
RSD	33	31	30	37	40
Median	2730	950	16900	5474.8	3030
Non-outlier labs	32	32	29	32	31
Average	2644	876	16539	5068	3175
STD DEV	887	212	4981	1641	989
RSD	34	24	30	32	31
Median	2733	920.05	16380	5340	3070

5.3.3 F4 Fraction

The results for the IJ series of samples were good. The overall relative standard deviation was 25%. If the IJ-2 sample is dropped this relative standard deviation becomes 17%. The FX series of solid samples were equally well done by the laboratories with a relative standard deviation being 22%. Appendix P is a summary of the F4 IJ sample results in chart form. Appendix Q is a summary of the F4 FX sample results. A summary of all laboratory data for the F4 fraction is contained in the table in Appendix R. Appendix DD contains charts showing the F4 laboratory data from each FP solid sample and the +/- 2 standard deviations after removal of the outlying data.

Table 12- IJ F4 laboratory results summary

F4	IJ-1	IJ-2	IJ-3	IJ-4	IJ-5
Target	448	480	5000	3400	4440
Ref. Value	500	564	9310	4080	5200
Total Labs	37	37	37	37	37
Average	388	531	7366	3336	4133
STD DEV	135	767	2924	2063	1612
RSD(%)	35	144	40	62	39
Median	395	465	8460	3622	4652
Non-outlier labs	32	36	28	29	30
Average	395	411	8811	3680	4799
STD DEV	85	224	1068	708	725
RSD(%)	22	54	12	19	15
Median	397	458	8819	3758	4856

Table 13- FX F4 laboratory results summary

F4	FX-1	FX-2	FX-3	FX-4	FX-5
Target	1140	850	10200	7150	4810
Ref. Value	1280	886	13100	6870	5310
Total Labs	39	39	39	39	39
Average	966	677	10637	5512	4462
STD DEV	505	348	4925	2312	1896
RSD(%)	52	51	46	42	42
Median	1016	690	11290	5560	4710
Non-outlier labs	32	33	33	33	27
Average	1034	693	11325	5808	4826
STD DEV	232	192	2394	1324	600
RSD(%)	22	28	21	23	12
Median	1073	740	11604	5662	4800

6.0 Laboratory Comments

During the course of the study there was a continuous exchange of comments, questions and answers between the participating laboratories. A number of these comments also appeared with data supplied by the laboratories. These comments are summarized in Appendix FF.

Often several laboratories would make the same or similar comments as the study progressed.

Concerns over validation of the method, standards, reference materials and interpreting data were expressed in e-mails between the participants.

Technical issues were also raised concerning alternate detection systems, alternate solvents for injection of the F2,F3, F4 fractions, interpretation of the method and suitability of equipment.

Many of the issues could addressed in a workshop focusing on such details as setting the chromatographic baseline, problem samples and how to deal with them, fine tuning of the chromatographic systems and the availability of suitable standards etc.

7.0 Conclusions

It is possible to produce solid interlaboratory test samples that are sufficiently homogenous and stable to be used in interlaboratory studies.

The laboratory producing the solid samples is able to produce large quantities (>200 bottles) of a specific sample at one time and the stability of the solid samples makes them useful as long term reference materials.

The interlaboratory data shows that method is inherently sound and can used with sufficient precision.

It is possible for quality data to be generated from 75% of the participating laboratories using the CWS.

8.0 Recommendations

A number of recommendations can be made upon reviewing the data and comments from this interlaboratory study.

There is a need to develop a larger stockpile of reference materials for use with the CWS. These materials could be used by laboratories for method validation purposes and on going QC purposes. They might also be useful to consultants as a source of blind audit QC samples.

There is a need to investigate the use of a standard soil for reference material production. This standard soil could also be used as a spiking medium to aid laboratories during the validation step of CWS and subsequent MDL determinations.

Another study should be run using CAEAL PT study guidelines in order to build up the information base prior to adoption as a regular CAEAL PT test group. This study should be funded with adequate resources such that any interested laboratories are allowed to participate. Once the magnitude of laboratory competence is defined, samples evaluating laboratory performance should be should be put into place as part of the regular CAEAL PT program.

9.0 Acknowledgments

The sandy loam and clay loam soils were provided by Marius Marsh of the Ontario Ministry of the Environment.

A special thanks to Enzo Barressi, and Lewnia Svoboda of Environment Canada's Wastewater Technology Centre for their analysis and interpretation of the PHC samples.

Thanks go to Richard Turle (as scientific authority) and Keijo Aspila and Mohammad Foroutan for their review comments.

List of Appendices

Appendix A List of Participating Laboratories

Laboratory	Location
Access Analytical Laboratories Inc.	AB
AGAT Laboratories (Calgary)	AB
AGAT Laboratories (Mississauga)	ON
ALS Environmental Calgary	AB
ALS Environmental Vancouver	BC
AMEC Earth & Environmental Limited (Edmonton)	AB
AMEC Earth & Environmental Limited (Mississauga)	ON
Analytical Services Laboratory	NB
Caduceon Enterprises Inc. Environmental Laboratories (Holly Lane)	ON
Cavendish Analytical Lab Ltd.	BC
Entech	ON
Environmental Technology Centre (ETC)	ON
Environmental Technology Research Labs Inc.	ON
Enviro-Test Laboratories - Sentinel Division	ON
Enviro-Test Laboratories (Edmonton)	AB
Enviro-Test Laboratories Manitoba Technology Centre Ltd.	MB
Enviro-Test Labs (Calgary)	AB
Enviro-Test Labs (Saskatoon)	SK
EP Laboratories (Prairie & Northern Region)	AB
Freshwater Institute	MB
Hemmera Envirochem Inc.	BC
Laboratory Services Branch (MOEE)	ON
Lakefield Research Limited, Analytical & Mineralogical Services	ON
Lambton Scientific	ON
Manitoba Hydro, Selkirk Chemical Laboratory	MB
Maxxam Analytics Inc. (Calgary)	AB
Norwest Labs (Calgary)	AB
Paracel Laboratories Ltd.	ON
PETROLEO BRASILEIRO S/A - PETROBRAS/CENPES/QUIMICA	Brazil
Philip Analytical Services Inc., Mississauga	ON
PSC Analytical Services Inc., Bedford (Halifax)	NS
PSC Analytical Services Inc., Burnaby	BC
PSC Analytical Services Inc., Edmonton	AB
PSC Analytical Services, Burlington	ON
Queen's Analytical Services Unit	ON
Research and Productivity Council, Chemical and Biotechnical Services	NB
Seatech Investigation Services Ltd.	NS
SRC Analytical Laboratory	SK
SRC Petroleum Analysis Lab	SK
Taiga Environmental Laboratory	NT
Wastewater Technology Centre Analytical Laboratory	ON

Appendix B **General Instructions**

CCME Petroleum Hydrocarbons in Soil

Pilot Study, May 2002

GENERAL INSTRUCTIONS

1. Ensure that you have received a diskette containing the following files (where *=lab code);
   Addendum.doc(addendum)
   *data.xls (data report form)
   General Instructions.doc
   *detailed.doc(detailed instructions , questionnaire, deviation and comment sheets)

2. Make a copy of the reporting diskette.
3. Read and understand the detailed instructions (A) provided. If there are any questions contact the party listed in the instructions by e-mail.
4. Make sure that the attached Addendum has been read and understood.
5. Process the samples according to the CCME CWS. If you receive multiple sample sets ensure that the sets are kept separate.
6. Report results using the report form files provided.
7. Complete the questionnaire (B) and report any deviations from the CWS (C) and add comments (D). Note that all comments will appear in the final report, but that the laboratory making the comments will not be identified.
8. Copy all the completed files to your backup copy.
9. E-mail results.

Appendix C **Addendum**

Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method

DRAFT ONLY

Addendum 1 issued April 29th, 2002. Note that this addendum has to be confirmed as to accuracy by the CCME. It is being distributed to the CAEAL multi-lab validation participants to assist them in this study. This addendum will be posted, once confirmed in both official languages on the CCME web site.

These addendums will be issued as errors in the text are brought to our attention. They can be emailed to richard.turle@ec.gc.ca

Changes have been made in several paragraphs to clarify the text. Please ensure analysts are using the revised version.

Please revise Section 2 third bullet to read as follows:

- F4 result, C34 to C50 hydrocarbons, are determined by integration of all area counts from the apex of the nC34 peak to the apex of the nC50 peak. The average response factor for nC10, nC16 and nC34 hydrocarbons is used for primary calibration. The GC response factor of the nC50 must be no less than 70% of the average response for the three compounds nC10, nC16 and nC34 hydrocarbons. This result gives fraction F4 **provided** that the chromatogram descends to baseline by the retention time of nC50. **Note** that only half of the nC10 and half of the nC50 peaks are included in these analyses. Similarly, the nC16 and nC34 peaks are each split between two fractions.

Please revise Section 4 last paragraph in to read as follows:

To avoid losses in the C6 to C10 fraction, carry out the methanol extraction of the samples within 48 hours of sample receipt and analyse as soon as possible but within 40 days. Samples must be kept cold (approximately 4 degrees) and must be sealed. For the C10 to C50 fractions, again holding times should be minimized but they should be extracted no later than 14 days of sample receipt and analyse as soon as possible but within 40 days. Again, samples must be kept cold (approximately 4 degrees) and must be sealed (e.g., in a screw topped vial sealed with a Teflon liner.)

Footnote: If possible, establish maximum holding times and/or use a surrogate to establish stability. nC11 has been suggested as a surrogate for Fraction F1. Methyl nonane has been suggested as a possible surrogate for Fraction F2 and 5-á-androstane for Fractions, F2, F3 and F4.

Please revise Section 5 last paragraph to read as follows:

Collect soil samples in a manner that minimizes sample handling and agitation. If possible, do not collect samples from soil exposed to direct sunlight. This may mean removing some surface soil to obtain a fresh sample. The use of specially designed airtight collection samplers is recommended. All soil must be removed from the threads of jars and vials to ensure an adequate seal. Samples must be placed on ice immediately after collection and shipped as soon as possible. Until analyzed, they must be kept at approximately 4°C or below. Freezing may cause glass sample bottles to break, thus rendering the samples useless. Ship samples to the laboratory as fast as possible. Several references are recommended for developing suitable standard operating procedures for collecting samples [5-8].

Please revise Section 8 last paragraph in to read as follows:

The following quality control criteria are mandatory and must be demonstrated before and during analysis:

Method Detection Limits (MDLs) must be met as follows:

Laboratories must achieve either an MDL that is 20% of the applicable soil type as described in the CWS PHC or the following *whichever is higher*.

- F1, C6 to C10 hydrocarbons **12 mg/kg**
- F2, C10 to C16 hydrocarbons **3.9 mg/kg**
- F3, C16 to C34 hydrocarbons **9.0 mg/kg**
- F4, C34 to C50 hydrocarbons **8 mg/kg**
- F4G (gravimetric) based on motor oil **290 mg/kg**

The average or mean for F2, F3 and F4 from these results is 7 mg/kg

Please revise Section 11.1 third bullet to read as follows:

- Mandatory instrument performance criteria for C10 to C50 are that nC50 response factor must be no less than 70% of the average of nC10, nC16 and nC34 response factors and the nC10, nC16 and nC34 response factors must be within 10% of the average response for the three compounds. This performance criterion must be met by any injection system used for hydrocarbon analysis and confirmed on a daily basis.

Please revise Appendix 3, third paragraph, second bullet to read as follows:

- For the F2 C10 to C16 and F3 C16 to C34 fractions, the MDL determination is done using soil contaminated or spiked with weathered diesel fuel at a concentration of 20 to 100 mg/kg. For the F4 C34 to C50fraction the determination must be done using SAE 30 weight motor oil. The results for the three fractions are summed and that result is applied to each of the three fractions. This approach is practical, although not accurate for each fraction. The same MDLs shall be applied to the$F2_{-PAH}$ and $F3_{-PAH}$ fraction.

Please replace Appendix 5 with the attached version.

This change reflect the change in the MDL for F1 and some other typographical errors

APPENDIX 5 – SINGLE LABORATORY METHOD VALIDATION

A validation of the method was conducted in the Emergency Science Division laboratory of the Environmental Technology Centre, during the fall and winter of 2000/01*. The purpose of this study was to estimate precision of several aspects of the method, determine method detection limits, and verify that

* Lab Validation Study Results for the "Reference method for the Canada Wide Standard for Petroleum Hydrocarbons in Soil-Tier 1 Method", Zhendi Wang and Ken Li, Environmental Science and Technology Division , Environmental Technology Centre, Environment Canada, Ottawa K1A 0H3, March 2001, revised April 2002.

standards were stable over a reasonable length of time. This information is provided to assist individual laboratories as they implement the CWS PHC method.

The main findings from this study are summarized as follows:

1. Linearity Study

Excellent linear relationship between the concentrations and GC responses are clearly demonstrated for the target compounds of Fractions 1 (C6-C10), 2 (C10-C16), 3 (C16-C34), and 4 (C34-C50) in the studied concentration range.

2. Precision Estimation Study

(1) Precision Estimation for Standards: for Fraction F1, the target compounds (benzene and toluene) demonstrated reasonable reproducibilities with the relative standard deviation (RSD) being around 12% at 0.05 ppm and 7.5% at 0.2 ppm, respectively.

The RSDs obtained from 8 determination of the C8-C30 standard were under 4%. The RSD for C50 (n = 8) was determined to be 7.3% at 25 ppm.

(2) Precision Estimation for Complete Method (gasoline spiked soil): The average recoveries were determined to be 82% at 50 ppm and 88% at 400 ppm of gasoline, respectively. The method precision from 8 measurements was determined to be 7.5% (RSD) at 50 ppm and 8.4% (RSD) at 400 ppm of gasoline, respectively.

(3) Precision Estimation for Complete Method (diesel and motor oil spiked soil): The relative standard deviations were determined to be 5.0% for F2, 3.4% for F3, and 3.5% for F4 of diesel and motor oil spiked soil samples, respectively.

3. Method Detection Limit (MDL) for F1 Using Gasoline-spiked Soil

The MDL determination was done using a spiked soil at a concentration of 50 mg/kg soil. The SD and RSD from 8 replicate analyses were determined to be 3.4% and 8.6%, respectively. Therefore, the MDL for whole gasoline is determined to be 3.7x3.14 (the appropriate one-sided 99% t-statistic) = 12 ìg/g soil or 12 mg/kg., based on a 5g sample

4. Method Detection Limit (MDL) for F2, F3, and F4 Using Diesel-spiked Soil

The MDL were determined to be 3.9, 9.0, and 8 mg/kg soil for F2, F3, and F4 (10.0 g of soil was spiked with 0.5 mg of diesel), respectively, again based on a 5g sample.

5. Determination of Method Detection Limit (MDL) for F4G (Motor Oil-spiked Soil) Using Gravimetric Method

The MDL (MDL = $t_{(n-1, \acute{a}=0.99)}$ s) by gravimetric method was determined to be 0.29 mg/g soil or 290 mg/kg soil (5.0 mg of motor oil was added to 5.0 g of soil, equivalent to 1000 mg/kg of soil).

6. Stability Study

Around 100% and 85% of recoveries for all target compounds in the C6-C10 range were demonstrated at 7 days and at 38 days, respectively.

Excellent stabilities were demonstrated for the standard C10-C50 in 62 days period with the RSDs (4 measurements at 4 different dates) being under 4%.

Appendix D **Detailed Instructions**

CCME Petroleum Hydrocarbons in Soil

Pilot Study, May 2002

A. DETAILED INSTRUCTIONS

1. Ensure that all samples identified on the enclosed sample list are accounted for. Verify that all solid samples were supplied in duplicate. In order to complete the round robin portion each laboratory should receive the following samples;

2 each of the following solid samples:
For F1 - FP-1, FP-2, FP-3, FP-4, FP-5
For F2, F3, F4 - FX-1, FX-2, FX-3, FX-4, FX-5
1 each of the following injectable/purgeable mixtures:
For F1 - PS-1, PS-2, PS-3, PS-4, PS-5
For F2, F3, F4 - IJ-1, IJ-2, IJ-3, IJ-4, IJ-5

2. Ensure that you have read and understood the CCME Method for Petroleum Hydrocarbons in soil.

3. All solid samples must be stored in a freezer until used for analysis.

4. Injectable and purgeable samples may be stored at 0 - 4 °C

5. Purgeable samples (PS-1, PS-2, PS-3, PS-4, PS-5) are ready for injection after warming to room temperature but may require dilution into methanol depending on the calibration range of your instrument.

6. Purgeable samples (PS-1, PS-2, PS-3, PS-4, PS-5) are hydrocarbons in methanol at concentrations between 100µg/mL and 15000µg/mL. A suitable aliquot should be added to water in a purge and trap vessel for analysis of the F1 fraction (C_6-C_{10} hydrocarbons).

7. Injectable samples (IJ-1, IJ-2, IJ-3, IJ-4, IJ-5) are ready for injection after warming to room temperature but may require dilution depending on the calibration range of your instrument. It will be necessary to warm the closed vials under warm water for a few minutes if samples are cloudy to ensure that all material is still in solution.

8. Injectable samples (IJ-1, IJ-2, IJ-3, IJ-4, IJ-5) are hydrocarbons in toluene at concentrations between 250µg/mL and 25000µg/mL. A suitable aliquot should be injected and analysed for the F2(C_{10}-C_{16} hydrocarbons), F3(C_{16}-C_{34} hydrocarbons), F4(C_{34}-C_{50} hydrocarbons) fractions.

9. Solid samples are to be analysed using the complete the CCME Method for Petroleum Hydrocarbons in soil. **NB: No Gravimetric Heavy Hydrocarbon Analysis is required on these samples.**

10. Assume all solid samples are 5.00g in mass and that percent moisture is negligible.

11. Samples for the F1(C_6-C_{10} hydrocarbons) are provided in a range from approximately 100 - 5000mg/kg. solid samples for analysis of the F1 fraction are labeled FP-1, FP-2, FP-3, FP-4, and FP-5. It is suggested that between 10mL and 15mL of methanol be used for the initial extraction of these samples. Given the volume of the sample container it is unlikely that 20mL of methanol can be used.

12. Samples for the F2(C_{10}-C_{16} hydrocarbons) are provided in a range from approximately 150 - 6500mg/kg. Samples for the F3(C_{16}-C_{34} hydrocarbons) are provided in a range from approximately 250 - 12500mg/kg.. Samples for the F4(C_{34}-C_{50} hydrocarbons) are provided in a range from approximately 1000 - 12500mg/kg. The solid samples for analysis of the F2,F3 and F4 fractions are labeled FX-1, FX-2, FX-3, FX-4, and FX-5.

13. Ensure that the sample numbers used for reporting data for the solid FP and FX data are noted on the data sheets in the appropriate areas.

14. A complete set of data report forms, information and comment files **must** be returned with **each** et of reported data. Facsimiles will **not** be accepted. The closing date for reporting on this study is **June 19, 2002**. These files are to be be e-mailed to Harold Malle at, **Harold.Malle@ec.gc.ca**

15. Questions or concerns regarding the samples and/or reporting may be directed to H. Malle via e-mail at the following address; **Harold.Malle@ec.gc.ca**

B. Analytical Method Summary Form

Laboratory Information

Laboratory Name:
CAEAL Registration Number:
Address:

Contact Name:
Contact Telephone Number: (
Contact e-mail:

Sample set: **1 of 1**

Summary of Method Components

F1-C_6-C_{10} Hydrocarbons

Solvent used for extraction (if no solvent used state method of extraction):

Method of sample introduction (Purge & Trap etc.):

Manufacturer:____________________
Model # (list all components):_______
____

Component Separation and Analysis:

Gas Chromatograph Manufacturer:___________________________
Model #:_________________________
Column Manufacturer:
Model #:_________________________
Length:________________________________
Diameter:_______________________
Phase Thickness:________________

Type of Detector (FID etc):

Relative C_6 and C_{10} response to toluene: C_6:____________________________
C_{10}:____________________________

F2, F3,F4-C_{10}-C_{50} Hydrocarbons

Solvent used for extraction :

Method of Extraction (Soxhlet etc.)

Method of sample introduction (auto-sampler, SPME etc.):

Manufacturer:___________________

Model # (list all components):_______

____

____

Component Separation and Analysis (include data integration system):

Gas Chromatograph Manufacturer: ________________________

Model #:________________________

____

____

Gas Chromatograph Inlet system (Split/Splitless etc.):

Column Manufacturer:____

Model #:________________________

Length:______________________________

Diameter:______________________

Phase Thickness:_______________

Type of Detector (FID etc):

Relative C_{10}, C_{16}, and C_{34} response to C_{16}: C_{10}:___________________________

C_{16}:___1.00___________________

C_{34}:___________________________

C_{50}:___NOT REQUIRED__________

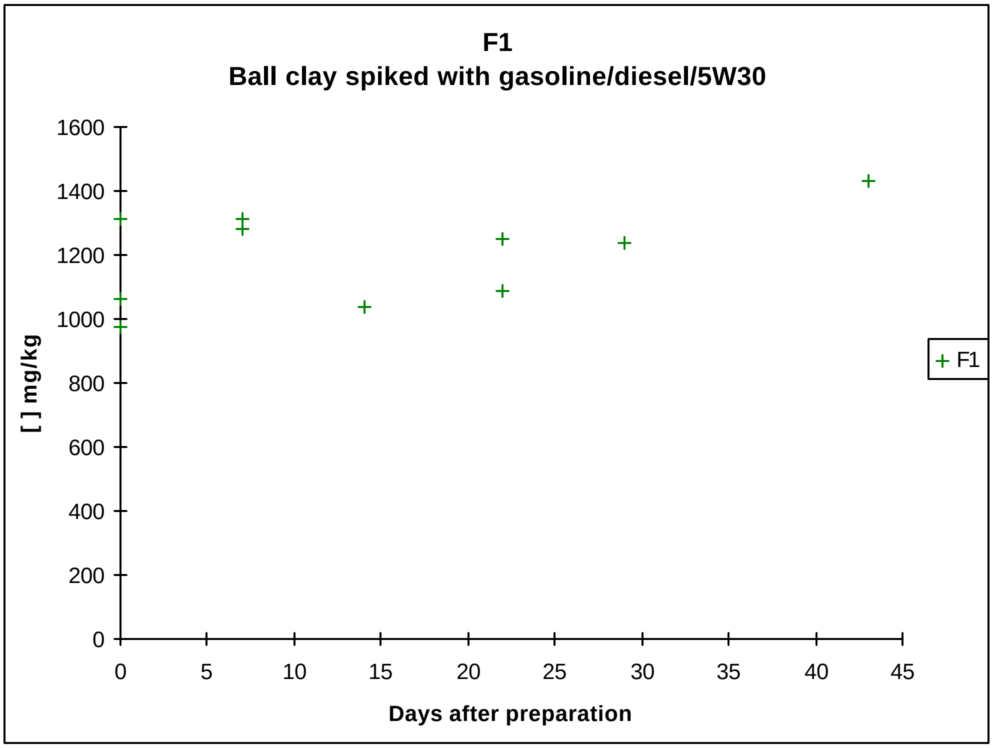
C. LIST OF DEVIATIONS

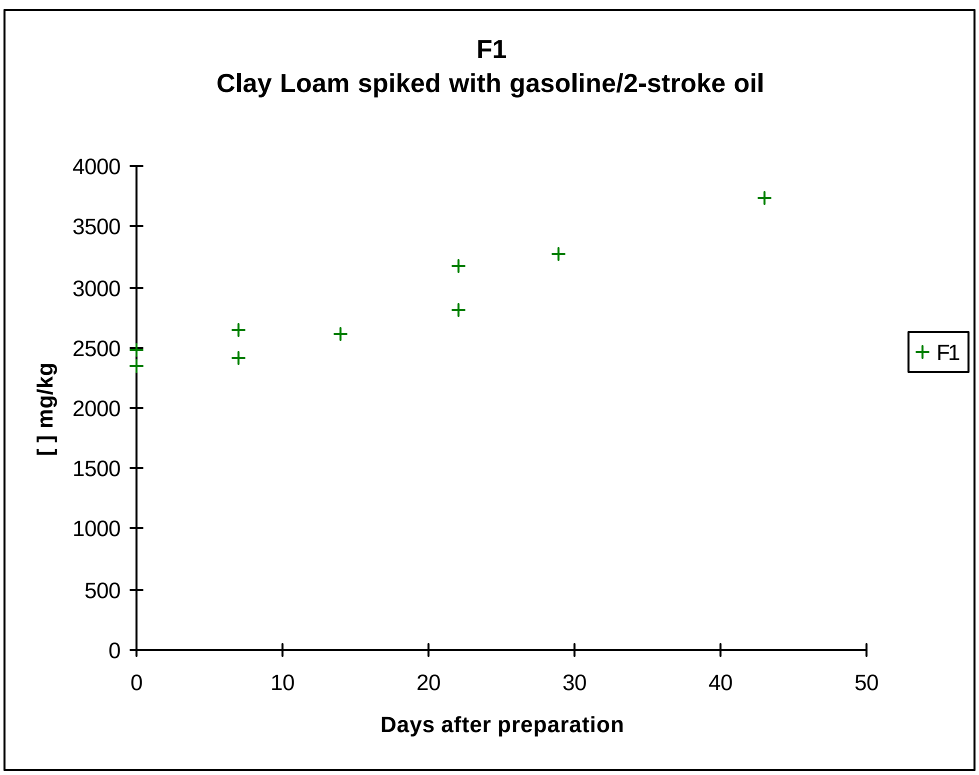
On the page below please list all deviations from the prescribed method as applied to the test samples. Please cross reference to the appropriate section contained in the CCME Method for Petroleum Hydrocarbons in soil.

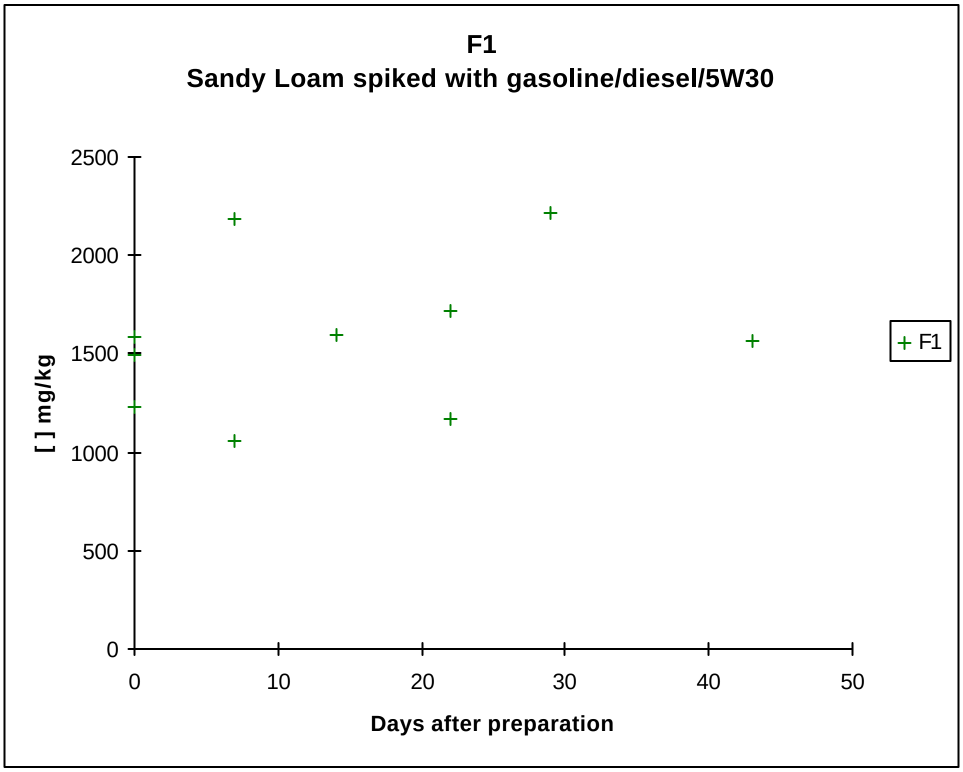
1.

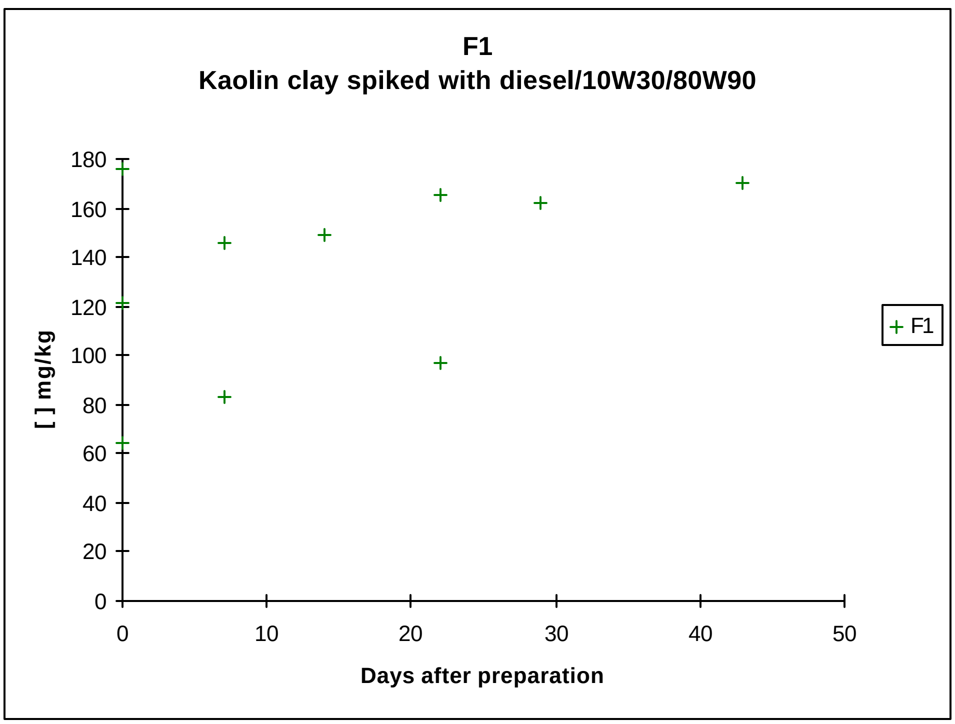
D. COMMENTS

Appendix E Stability sample Results F1 Fraction

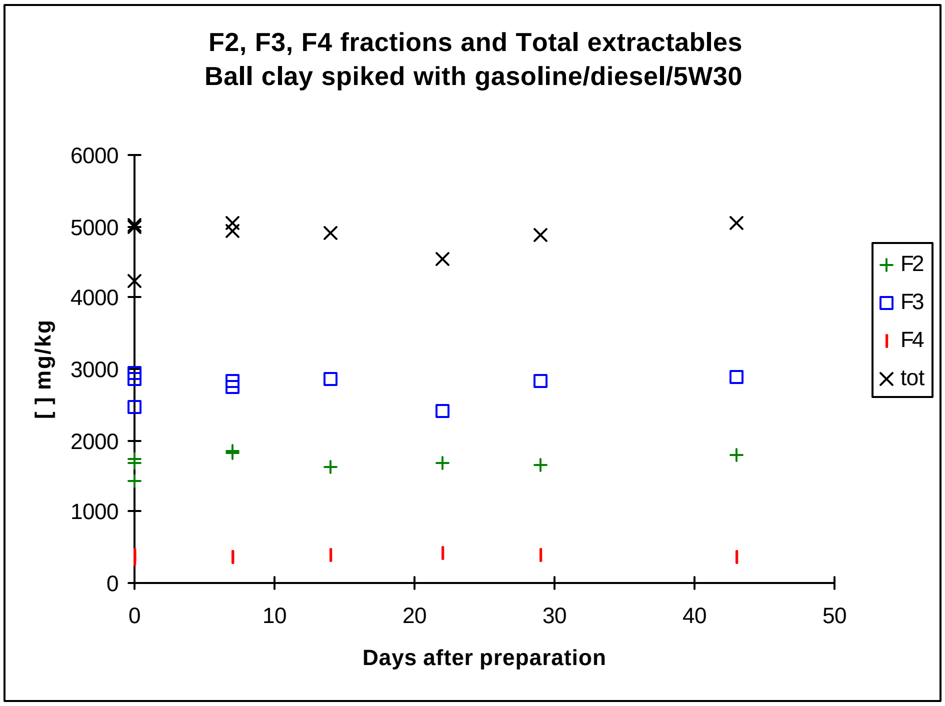


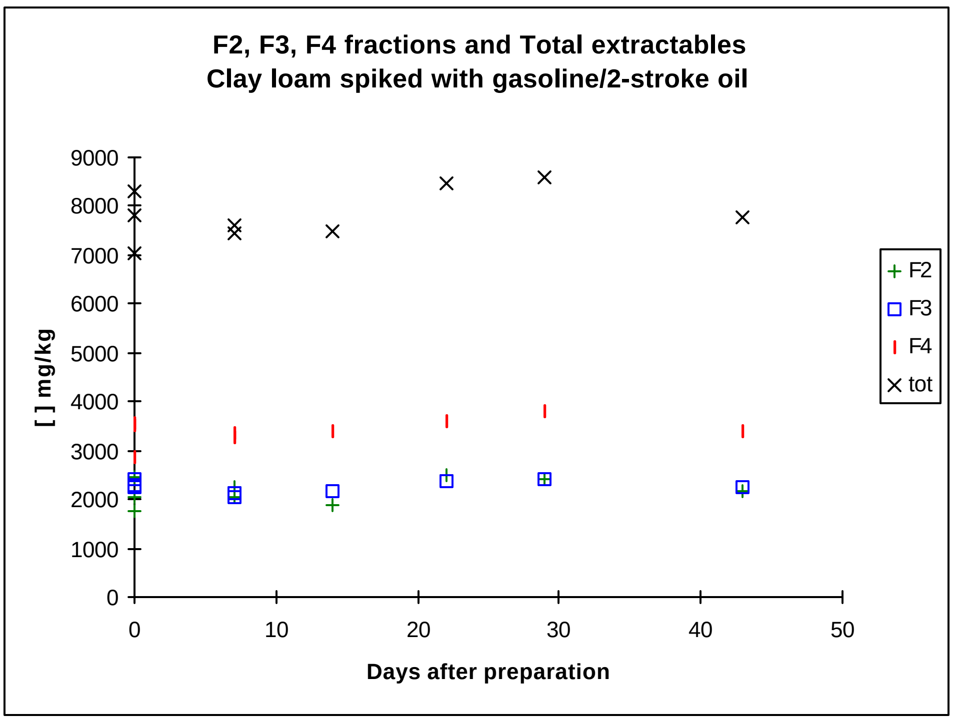


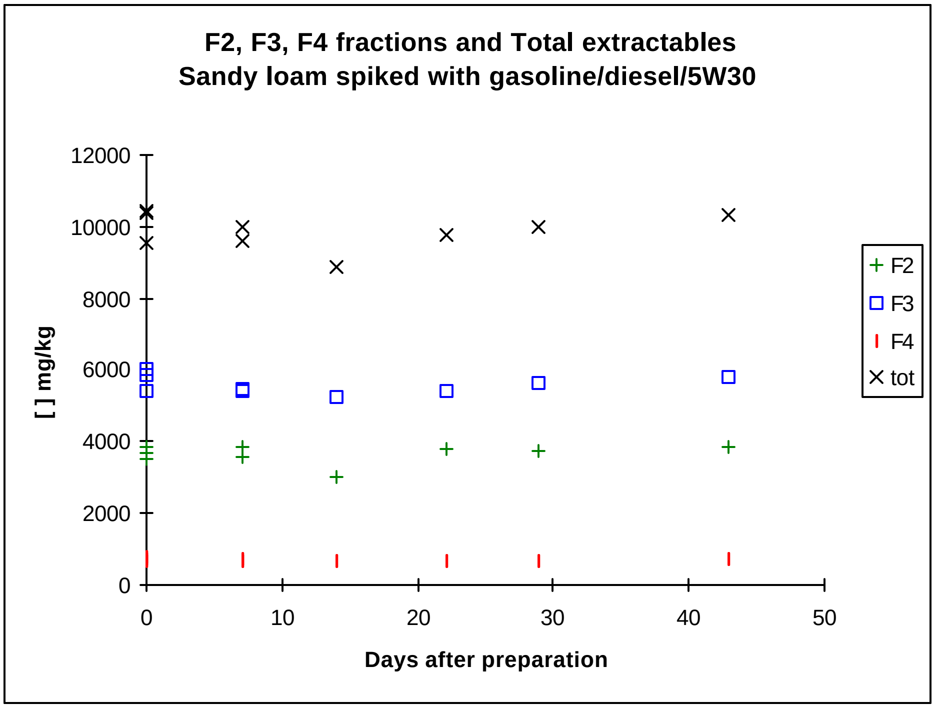

F1
Sandy Loam spiked with gasoline/diesel/5W30
2500
2000
1500
1000
500
0
[ ] mg/kg
0
10
20
30
40
50
Days after preparation
F1

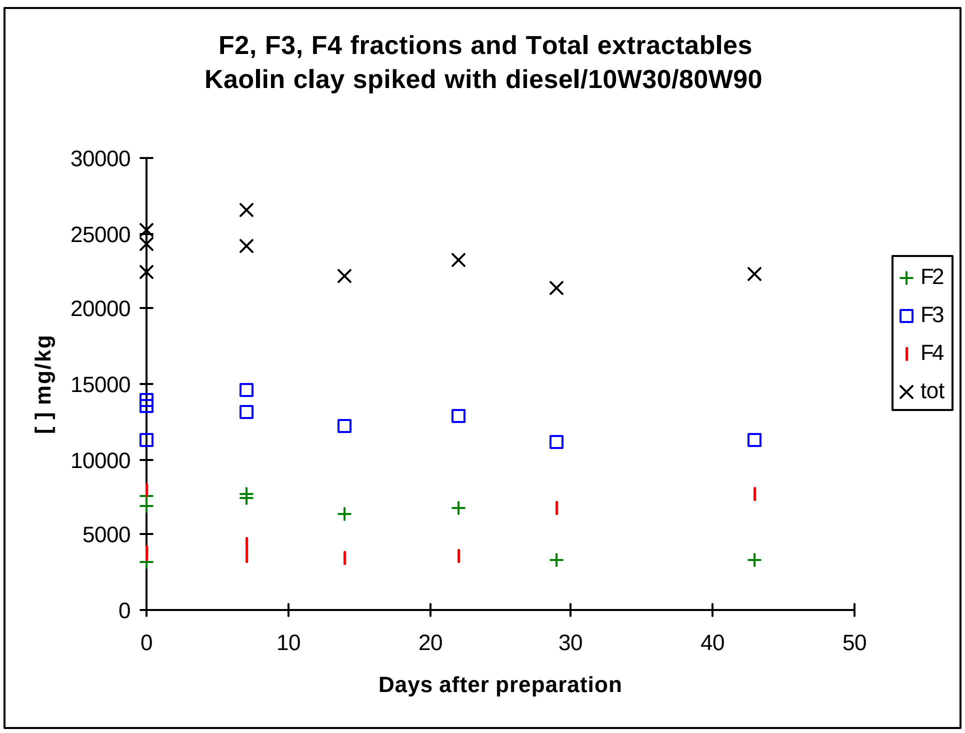

F1
Kaolin clay spiked with diesel/10W30/80W90
180
160
140
120
100
80
60
40
20
0
[ ] mg/kg
0
10
20
30
40
50
Days after preparation
F1

Appendix F **Stability-sample Results F2,F3,F4 Fractions**

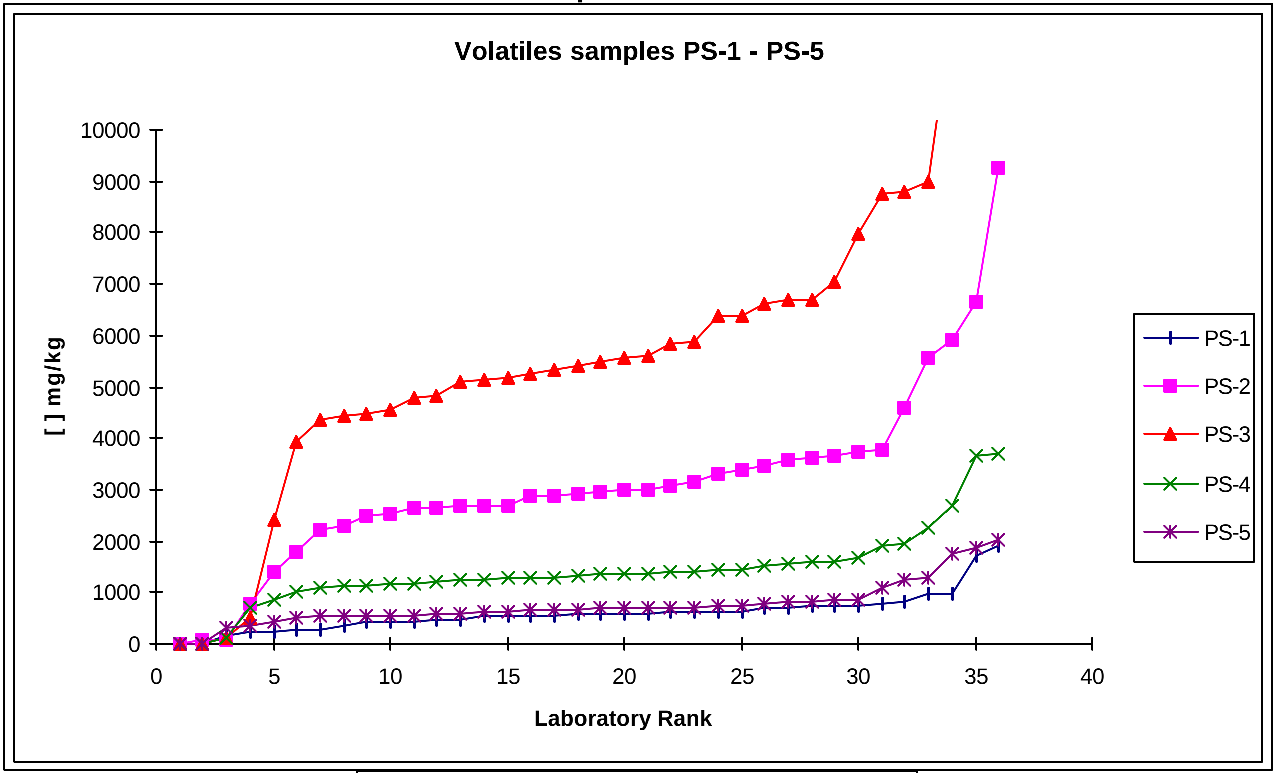





F2, F3, F4 fractions and Total extractables
Sandy loam spiked with gasoline/diesel/5W30
[ ] mg/kg
12000
10000
8000
6000
4000
2000
0
0
10
20
30
40
50
Days after preparation
F2
F3
F4
tot

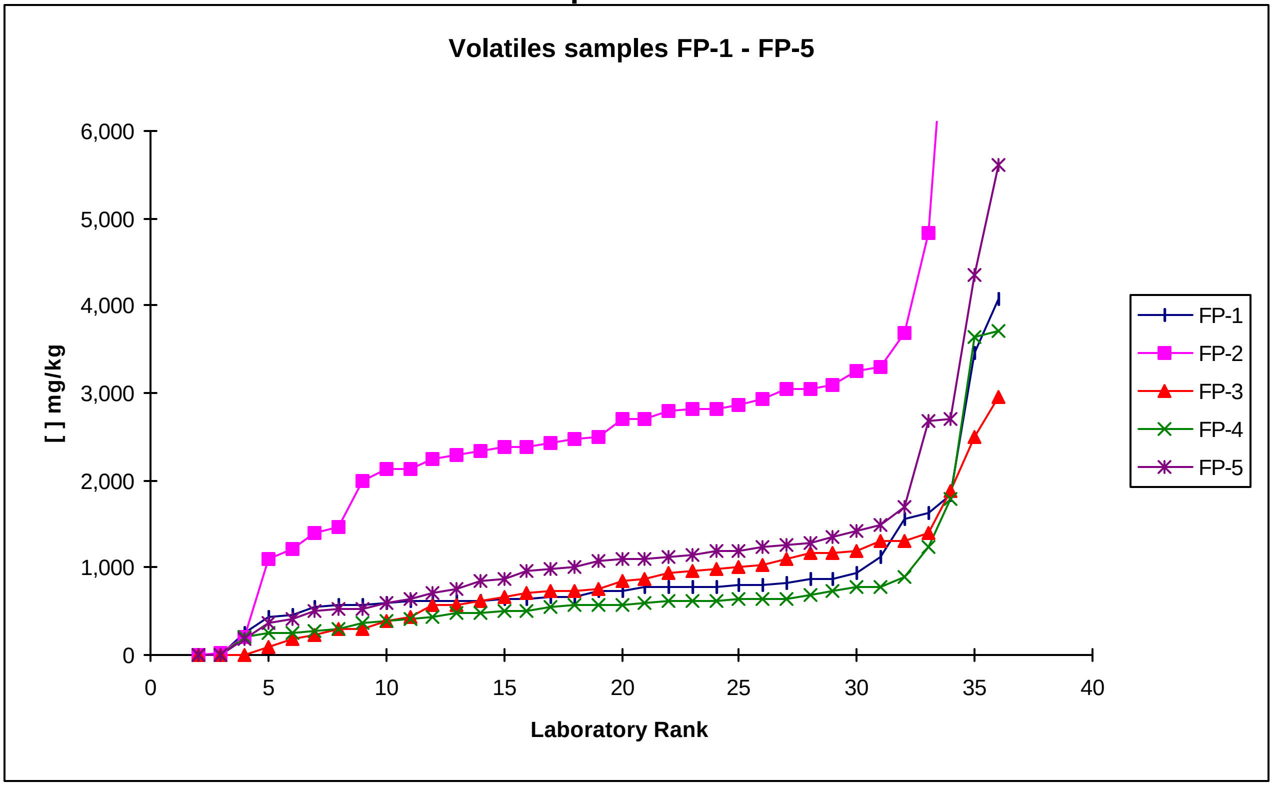

F2, F3, F4 fractions and Total extractables
Kaolin clay spiked with diesel/10W30/80W90
[ ] mg/kg
30000
25000
20000
15000
10000
5000
0
0
10
20
30
40
50
Days after preparation
F2
F3
F4
tot

Appendix G PS-1 – PS-5 Samples Data Chart



	PS-1	PS-2	PS-3	PS-4	PS-5
Target	600	4800	10000	2400	1200
Ref. Value	552	2887	5310	1320	728
Total Labs	36	36	36	36	36
Average	596	3094	5891	1420	754
STD DEV	378	1774	3489	761	433
RSD(%)	63	57	59	54	57
Median	577	2943	5445	1342	679.5
Non-outlier labs	29	27	28	28	26
Average	541	2892	5911	1359	661
STD DEV	163	759	1386	244	113
RSD(%)	30	26	23	18	17
Median	572	2,910	5,535	1342	661.5

Appendix H **FP-1 – FP-5 Samples** **Data Chart**



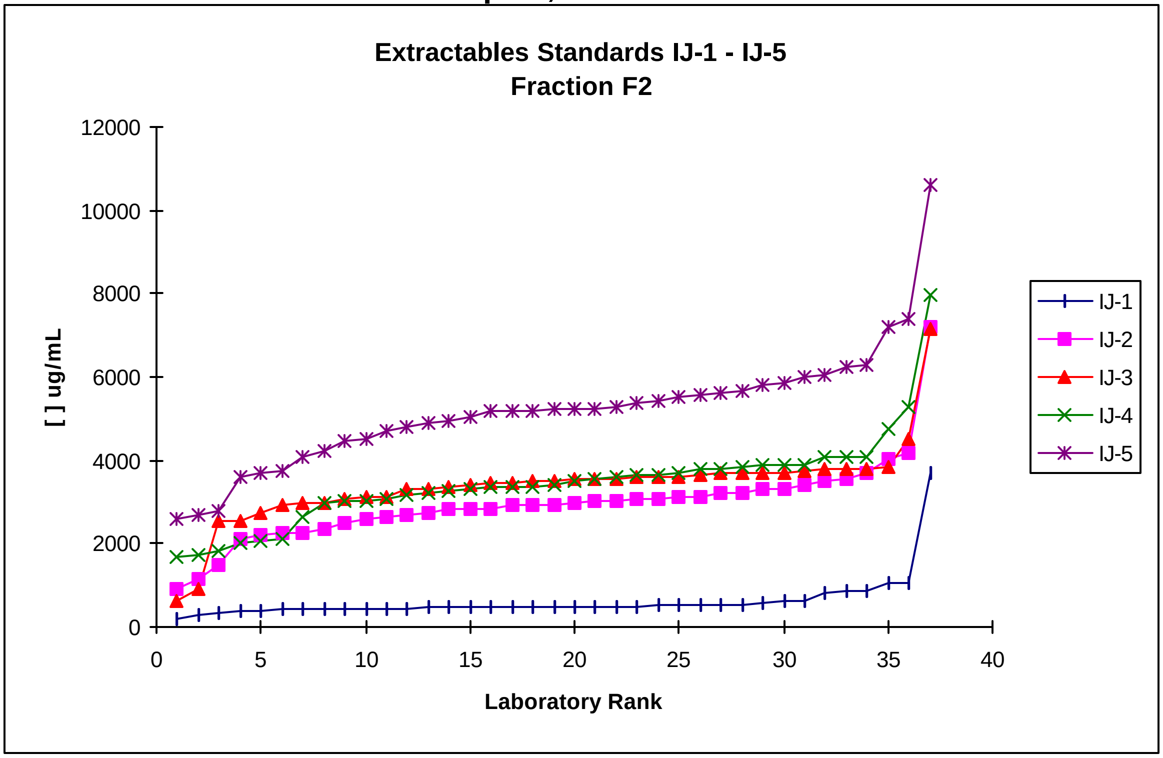
	FP-1	FP-2	FP-3	FP-4	FP-5
Target	680	2730	1460	590	1180
Ref. Value	685	2580	271	600	920
Total Labs	35	35	36	35	35
Average	911	3129	941	737	1228
STD DEV	804	3138	826	801	1116
RSD(%)	88	100	88	109	91
Median	739	2500	797.5	570	1068
Non-outlier labs	26	26	32	28	27
Average	692	2584	704	518	953
STD DEV	127	532	414	161	325
RSD(%)	18	21	59	31	34
Median	669	2,600	732.45	554.5	1000

Appendix I

PS-1 – PS-5, FP-1 – FP-5 Samples
Results Summary for F_1 by Laboratory

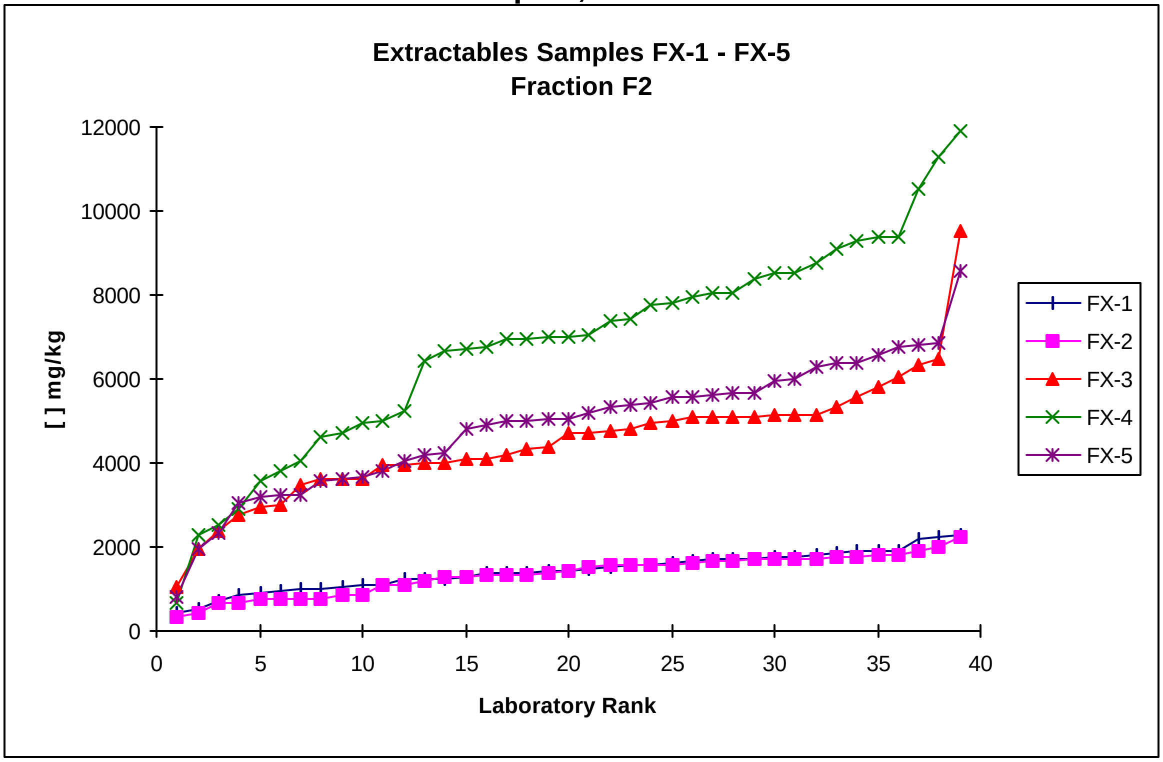
Lab #	Parameter	PS-1	PS-2	PS-3	PS-4	PS-5		Parameter	FP-1	FP-2	FP-3	FP-4	FP-5
1	F1(µg/mL)	745	1793	3930	1560	323		F1(mg/kg)	4074	18143	2488	3712	5609
2	F1(µg/mL)	763	4610	9000	1940	849		F1(mg/kg)	937	3260	1170	775	966
3	F1(µg/mL)	360	3000	5400	1400	750		F1(mg/kg)	810	2700	1300	500	1200
4	F1(µg/mL)	470	2510	5190	1150	660		F1(mg/kg)	670	2470	930	690	990
5	F1(µg/mL)	1710	9280	15200	3680	2020		F1(mg/kg)	595	2330	425	486	756
6	F1(µg/mL)	623	2880	5490	1380	701		F1(mg/kg)	626	2810	1190	633	1280
7	F1(µg/mL)	230	1400	2400	710	340		F1(mg/kg)	780	2700	1000	650	1100
8	F1(µg/mL)	683	5550	8740	1430	705		F1(mg/kg)	814	2940	1030	627	1100
9	F1(µg/mL)	620	3720	6620	1905	1080		F1(mg/kg)	1121	2125	1874	890	1500
10	F1(µg/mL)	224.6	2308	4468	1133	540.3		F1(mg/kg)	631.1	1206	723.9	253.8	1068
11	F1(µg/mL)	482	2910	5130	1180	618		F1(mg/kg)	430	2240	306	503	843
12	F1(µg/mL)	700	3300	6700	1600	780		F1(mg/kg)	650	2000	750	370	520
13	F1(µg/mL)	980	3780	8800	2240	1260		F1(mg/kg)	1830	4840	1100	1240	2680
14	F1(µg/mL)	600	3071	5865	1245	537		F1(mg/kg)	618	3046	996	415	1246
15	F1(µg/mL)	558	2700	5105	1113	531		F1(mg/kg)	570	2300	573	782	1360
16	F1(µg/mL)	620	3600	6400	1500	800		F1(mg/kg)	800	2500	390	440	600
17	F1(µg/mL)	440	61	120	1100	540		F1(mg/kg)	260	1100	290	200	370
18	F1(µg/mL)	530	3,150	5,580	1,300	646		F1(mg/kg)	880	2,860	958	741	1,410
19	F1(µg/mL)	170.5	6659.7	12326.7	3643.4	1882.9		F1(mg/kg)	1621.9	8620.4	2956.7	1782	2709.9
20	F1(µg/mL)	414	3010	5592	1392	748		F1(mg/kg)	668	2431	98.7	488	186
21	F1(µg/mL)	990	3400	6700	1600	830		F1(mg/kg)	860	3100	1300	630	1200
22	F1(µg/mL)	1910	3580	5250	2690	1740		F1(mg/kg)	3450	3690	4010	3647	4350
23	F1(µg/mL)	735	3650	7060	1670	863		F1(mg/kg)	4.19	11.5	7.12	6.53	5.09
24	F1(µg/mL)	415	2692	4424	1216	595		F1(mg/kg)	773	2789	618	573	863
25	F1(µg/mL)	810	5900	16000	1260	1300		F1(mg/kg)	1550	8190	240	280	1700
26	F1(µg/mL)	585	2890	5340	1350	603		F1(mg/kg)	770	2380	860	570	1130
27	F1(µg/mL)							F1(mg/kg)					
28	F1(µg/mL)	4.52	62.6	3.95	0.32	0.55		F1(mg/kg)	790	3040	6	259	721
29	F1(µg/mL)	537	2208	4547	1018	492		F1(mg/kg)	607	1404	699	308	533
30	F1(µg/mL)	572	2505	4368	848	441		F1(mg/kg)	461	1457	194	387	406
31	F1(µg/mL)	267	3456	7989	1334	696		F1(mg/kg)	559	2378	845	598	1148
32	F1(µg/mL)	530	2700	4800	1300	560		F1(mg/kg)	580	3300	1400	570	1000
33	F1(µg/mL)	608	764	500	122	629		F1(mg/kg)	743	205	566	612	509
34	F1(µg/mL)	582	2640	5820	1440	699		F1(mg/kg)	739	2130	741	539	1270
35	F1(µg/mL)							F1(mg/kg)					
36	F1(µg/mL)	721	2976	4806	1373	663		F1(mg/kg)	622	2809	665	620	642
37	F1(µg/mL)	0.345	1.58	3.044	0.856	0.605		F1(mg/kg)	0.257	0.818	0.222	0.178	0.344
38	F1(µg/mL)							F1(mg/kg)					
39	F1(µg/mL)	259	2656	6394	1303	706		F1(mg/kg)			1158		
	Total Labs	36	36	36	36	36		Total Labs	35	35	36	35	35
	Average	596	3094	5891	1420	754		Average	911	3129	941	737	1228
	STD DEV	378	1774	3489	761	433		STD DEV	804	3138	826	801	1116
	RSD(%)	63	57	59	54	57		RSD(%)	88	100	88	109	91
	Median	577	2943	5445	1342	679.5		Median	739	2500	797.5	570	1068
	Non-outlier labs	29	27	28	28	26		Non-outlier labs	26	26	32	28	27
	Average	541	2892	5911	1359	661		Average	692	2584	704	518	953
	STD DEV	163	759	1386	244	113		STD DEV	127	532	414	161	325
	RSD(%)	30	26	23	18	17		RSD(%)	18	21	59	31	34
	Median	572	2,910	5,535	1342	661.5		Median	669	2,600	732.45	554.5	1000

Appendix J **IJ-1 – IJ-5 Samples, F2 Fraction Data Chart**



F2	IJ-1	IJ-2	IJ-3	IJ-4	IJ-5
Target	359	2040	5850	2150	3500
Ref. Value	550	3250	3790	3740	5870
Total Labs	37	37	37	37	37
Average	611	2948	3393	3450	5188
STD DEV	555	991	962	1104	1420
RSD (%)	91	34	28	32	27
Median	474	2930	3520	3390	5220
Non-outlier labs	30	31	30	28	31
Average	469	2909	3482	3506	5119
STD DEV	70	406	267	382	723
RSD(%)	15	14	8	11	14
Median	472	2930	3540	3528	5220

Appendix K FX-1 – FX-5 Samples, F2 Fraction Data Chart



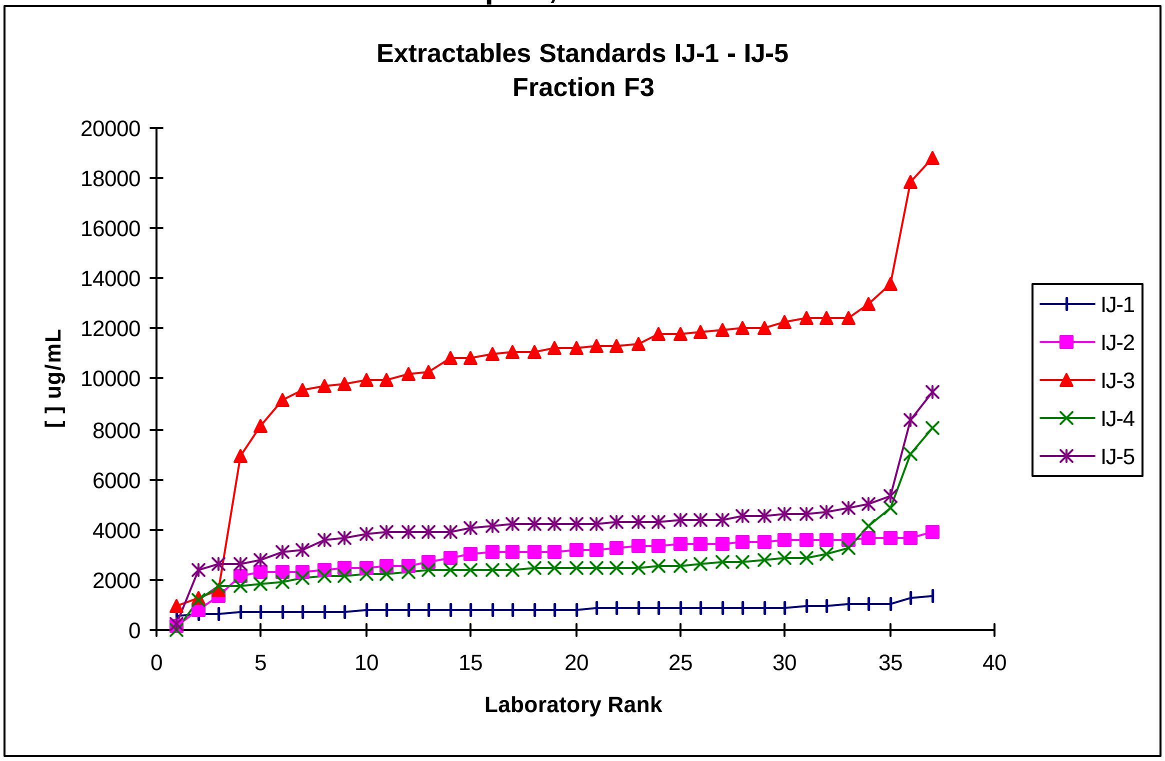
F2	FX-1	FX-2	FX-3	FX-4	FX-5
Target	2680	2580	9210	13100	6750
Ref. Value	1740	1500	4800	7930	6160
Total Labs	39	39	39	39	39
Average	1433	1344	4492	6803	4892
STD DEV	447	467	1423	2522	1549
RSD(%)	31	35	32	37	32
Median	1437	1421	4700	7006	5070
Non-outlier labs	34	36	34	32	35
Average	1419	1373	4523	7083	5061
STD DEV	337	398	873	1779	1144
RSD(%)	24	29	19	25	23
Median	1,434	1484	4,700	7031	5200

Appendix L

IJ-1 – IJ-5, FX-1 – FX-5 Samples
Results Summary for F_2 by Laboratory

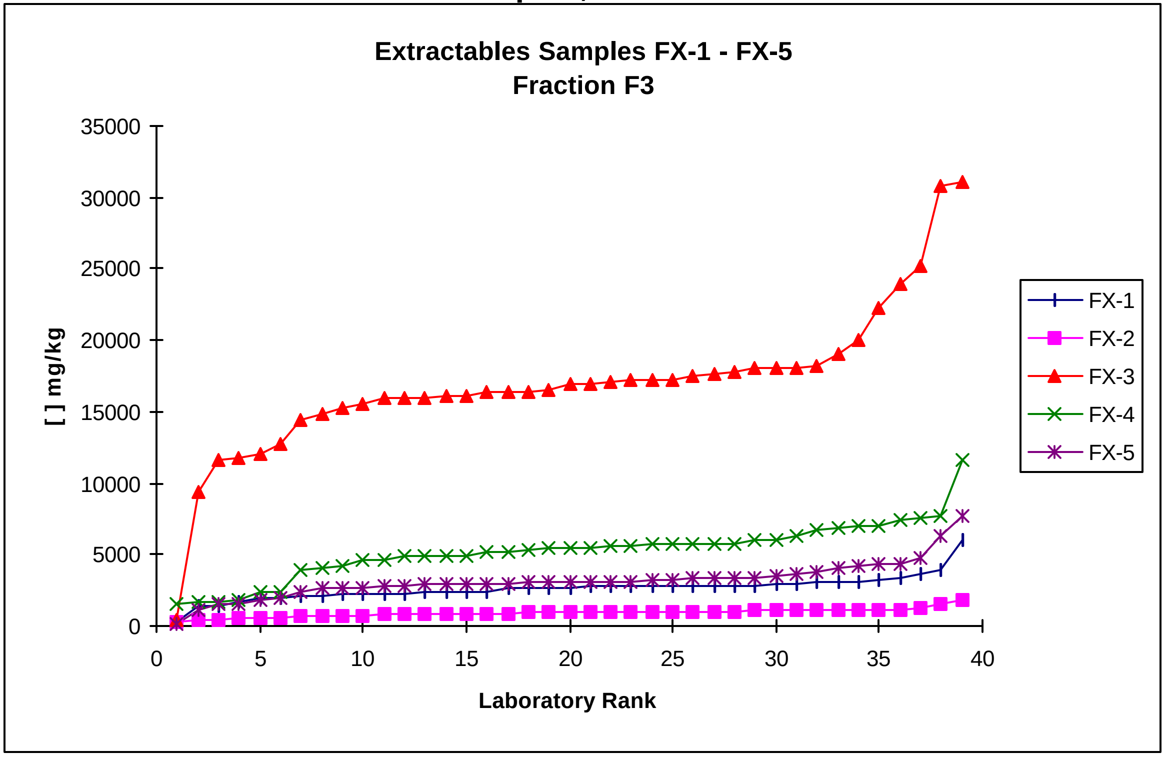
Lab #	Parameter	PS-1	PS-2	PS-3	PS-4	PS-5		Parameter	FP-1	FP-2	FP-3	FP-4	FP-5
1	F2(µg/mL)	835	3196	3483	3871	6028		F2(mg/kg)	1371	1572	5004	7970	5385
2	F2(µg/mL)	494	3140	3860	3780	5430		F2(mg/kg)	2230	1830	6050	8540	5640
3	F2(µg/mL)	480	3,300	3,000	3,900	6,000		F2(mg/kg)	1,800	1,900	4,700	4,700	3,800
4	F2(µg/mL)	580	2830	3530	3260	5050		F2(mg/kg)	1880	1670	6320	10510	6840
5	F2(µg/mL)	530	2370	2990	3700	5500		F2(mg/kg)	917	838	4188	6690	3180
6	F2(µg/mL)	526	3553	3474	4094	6238		F2(mg/kg)	1403	1357	3605	6725	5646
7	F2(µg/mL)	430	3700	3700	3600	5300		F2(mg/kg)	2200	1700	5800	9300	6000
8	F2(µg/mL)	875	3390	3670	3890	4780		F2(mg/kg)	2280	2240	9510	11900	8590
9	F2(µg/mL)	3710	7200	7170	7980	10600		F2(mg/kg)	1628	1636	5090	11280	5200
10	F2(µg/mL)	406.2	2198	3756	2128	4226		F2(mg/kg)	1404	1774	4090	8766	4814
11	F2(µg/mL)	535	3200	3700	3860	5810		F2(mg/kg)	1580	1980	5110	8360	5670
12	F2(µg/mL)	490	3500	3800	4100	6300		F2(mg/kg)	1900	1800	6500	9400	6400
13	F2(µg/mL)	470	2700	3380	3150	4900		F2(mg/kg)	1570	1740	5090	8530	5550
14	F2(µg/mL)	1053	4176	4493	4765	7372		F2(mg/kg)	1111	1091	4816	7433	5063
15	F2(µg/mL)	472	3055	3455	4095	5860		F2(mg/kg)	1750	1350	4930	7360	6550
16	F2(µg/mL)	460	2600	3100	3000	4500		F2(mg/kg)	1300	1400	4700	7000	5000
17	F2(µg/mL)	850	2500	3300	1700	3600		F2(mg/kg)	930	750	2400	4600	3600
18	F2(µg/mL)	469	3,010	3,520	3,020	4,950		F2(mg/kg)	1,780	1,550	5,320	8,040	5,940
19	F2(µg/mL)	174	1135	929	1831	2614		F2(mg/kg)	1054	740	1951	2530	3233
20	F2(µg/mL)	452	2275	2948	3058	4461		F2(mg/kg)	501	655	2931	5002	3257
21	F2(µg/mL)	480	3100	3800	3300	5400		F2(mg/kg)	1700	1700	5550	9100	6400
22	F2(µg/mL)	380	2120	2567	2630	3710		F2(mg/kg)	1005	1075	3630	650	3670
23	F2(µg/mL)	283	908	634	2003	2700		F2(mg/kg)	426	313	3020	2290	1970
24	F2(µg/mL)	518	3303	3693	3777	5568		F2(mg/kg)	1216	1650	4321	5238	4898
25	F2(µg/mL)	1052	4010	3616	5260	7200		F2(mg/kg)	1710	662	4010	4968	6787
26	F2(µg/mL)	474	2910	3590	3370	5220		F2(mg/kg)	1430	1270	4010	7800	5010
27	F2(µg/mL)	601	2270	2720	3490	4720		F2(mg/kg)	995	1170	3600	3830	3060
28	F2(µg/mL)	422	2821	3417	3566	5167		F2(mg/kg)	1531	1288	4103	8049	5332
29	F2(µg/mL)	438	3082	3141	3656	5640		F2(mg/kg)	1117	748	3947	6951	4198
30	F2(µg/mL)	435	3045	3310	3666	5655		F2(mg/kg)	1697	1343	5120	7760	5548
31	F2(µg/mL)							F2(mg/kg)	1887	1711	5146	7031	6305
32	F2(µg/mL)	412	2815	3551	3221	5180		F2(mg/kg)	730	858	2741	4025	2319
33	F2(µg/mL)	449	1470	2560	2080	3740		F2(mg/kg)	870	770	3500	3550	3570
34	F2(µg/mL)	467	2930	3560	3370	5240		F2(mg/kg)	1660	1590	5100	9400	5420
35	F2(µg/mL)	472	2930	3600	3390	5200		F2(mg/kg)	1490	1590	4740	6420	5070
36	F2(µg/mL)	604	2623	3798	1739	2778		F2(mg/kg)	1249	434	1071	2897	789
37	F2(µg/mL)	325	2,732	3,055	3,003	4,078		F2(mg/kg)	1240	1547	4378	7006	4068
38								F2(mg/kg)	1,437	1,421	3,959	6,741	4,249
39	F2(µg/mL)	518	2984	3676	3364	5243		F2(mg/kg)	1909	1712	5147	6960	6783
	Total Labs	37	37	37	37	37		Total Labs	39	39	39	39	39
	Average	611	2948	3393	3450	5188		Average	1433	1344	4492	6803	4892
	STD DEV	555	991	962	1104	1420		STD DEV	447	467	1423	2522	1549
	RSD (%)	91	34	28	32	27		RSD(%)	31	35	32	37	32
	Median	474	2930	3520	3390	5220		Median	1437	1421	4700	7006	5070
	Non-outlier labs	30	31	30	28	31		Non-outlier labs	34	36	34	32	35
	Average	469	2909	3482	3506	5119		Average	1419	1373	4523	7083	5061
	STD DEV	70	406	267	382	723		STD DEV	337	398	873	1779	1144
	RSD(%)	15	14	8	11	14		RSD(%)	24	29	19	25	23
	Median	472	2930	3540	3528	5220		Median	1,434	1484	4,700	7031	5200

Appendix M **IJ-1 – IJ-5 Samples, F3 Fraction Data Chart**



F3	IJ-1	IJ-2	IJ-3	IJ-4	IJ-5
Target	794	3300	12650	2250	4130
Ref. Value	879	3670	12430	2860	4730
Total Labs	37	37	37	37	37
Average	845	2916	10625	2717	4191
STD DEV	146	811	3529	1389	1476
RSD	17	28	33	51	35
Median	820	3110	11200	2440	4230
Non-outlier labs	27	34	30	28	27
Average	809	3104	11253	2400	4260
STD DEV	52	497	1085	282	353
RSD	6	16	10	12	8
Median	815	3,200	11,266	2430	4240

Appendix N FX-1 – FX-5 Samples, F3 Fraction Data Chart



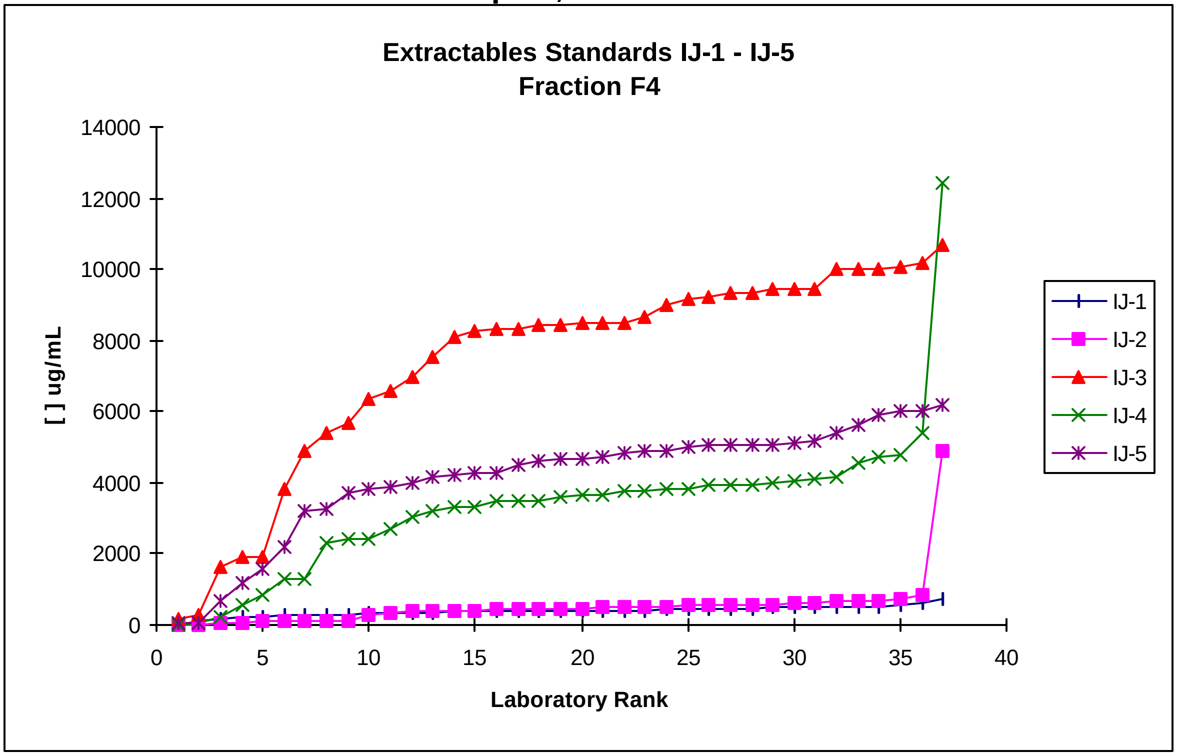
F3	FX-1	FX-2	FX-3	FX-4	FX-5
Target	2660	1020	16000	6430	3200
Ref. value	3220	1210	20900	6910	3700
Total Labs	39	39	39	39	39
Average	2637	915	17019	5252	3172
STD DEV	863	286	5141	1949	1283
RSD	33	31	30	37	40
Median	2730	950	16900	5474.8	3030
Non-outlier labs	32	32	29	32	31
Average	2644	876	16539	5068	3175
STD DEV	887	212	4981	1641	989
RSD	34	24	30	32	31
Median	2733	920.05	16380	5340	3070

Appendix O

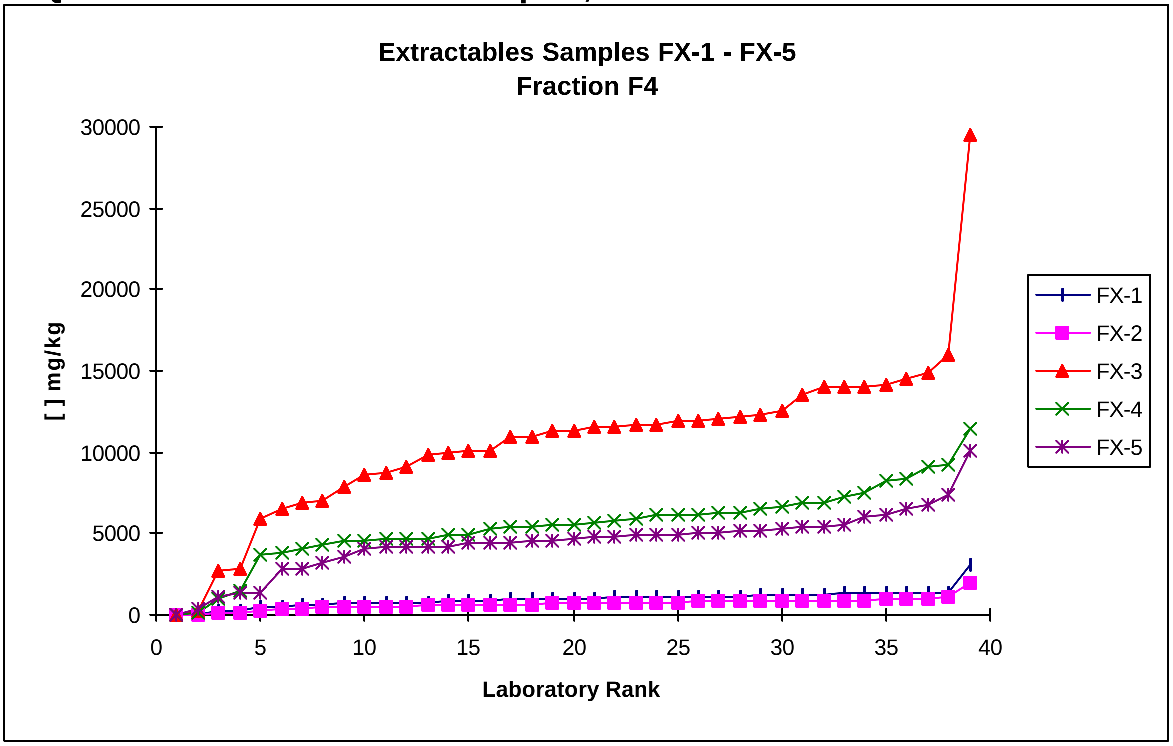
IJ-1 – IJ-5, FX-1 – FX-5 Samples
Results Summary for F_3 by Laboratory

Lab #	Parameter	PS-1	PS-2	PS-3	PS-4	PS-5		Parameter	FP-1	FP-2	FP-3	FP-4	FP-5
1	F3(µg/mL)	739	2894	9924	2082	3698		F3(mg/kg)	2022	824	14396	4965	2604
2	F3(µg/mL)	758	2480	9840	2360	3070		F3(mg/kg)	2830	839	17500	5720	2760
3	F3(µg/mL)	860	3,600	10,000	2,400	4,200		F3(mg/kg)	3,300	1,200	18,000	3,900	2,900
4	F3(µg/mL)	730	2430	8140	1860	3180		F3(mg/kg)	2390	770	15910	5340	2610
5	F3(µg/mL)	1030	2500	11100	2550	4150		F3(mg/kg)	2780	1020	16900	5140	6320
6	F3(µg/mL)	793	3199	11756	2748	4225		F3(mg/kg)	2336	916	15563	5641	3626
7	F3(µg/mL)	820	3600	12000	2500	4400		F3(mg/kg)	3000	1100	20000	5800	3400
8	F3(µg/mL)	654	2730	6930	1730	3870		F3(mg/kg)	2290	863	18000	5470	3020
9	F3(µg/mL)	884	3520	12400	2790	4870		F3(mg/kg)	2780	995	17220	7730	3130
10	F3(µg/mL)	1044	2568	13760	4155	5340		F3(mg/kg)	2635	924.1	25160	7051	4783
11	F3(µg/mL)	886	3600	12400	2840	4580		F3(mg/kg)	3620	1530	22300	7360	4350
12	F3(µg/mL)	800	3200	11000	2600	4400		F3(mg/kg)	3100	1100	24000	6900	4300
13	F3(µg/mL)	820	3110	11100	2350	3880		F3(mg/kg)	2110	1060	17200	5970	2970
14	F3(µg/mL)	855	3561	12282	3275	4588		F3(mg/kg)	2778	1058	18220	6330	3153
15	F3(µg/mL)	844	3705	11950	2710	4565		F3(mg/kg)	2670	910	17100	5530	2850
16	F3(µg/mL)	940	3500	12000	2900	4300		F3(mg/kg)	2100	1000	16000	7500	3100
17	F3(µg/mL)	850	2300	9600	1200	2600		F3(mg/kg)	2000	660	16000	4600	2900
18	F3(µg/mL)	1,320	3,890	18,800	4,880	8,390		F3(mg/kg)	3,980	1,810	30,800	11,600	7,760
19	F3(µg/mL)	992	2302	17860	6991	9477		F3(mg/kg)	3248	580	31012	2389	1112
20	F3(µg/mL)	1003	2559	12440	3050	4716		F3(mg/kg)	1414	641	18990	5716	4248
21	F3(µg/mL)	860	3700	13000	2500	5000		F3(mg/kg)	3100	950	18000	7000	4000
22	F3(µg/mL)	720	2280	9200	1780	2765		F3(mg/kg)	2390	555	15240	4150	2390
23	F3(µg/mL)	635	834	939	4	247		F3(mg/kg)	217	416	454	1490	185
24	F3(µg/mL)	847	3372	11231	2457	4043		F3(mg/kg)	2275	1037	17780	4044	3784
25	F3(µg/mL)	780	3640	10810	2220	4397		F3(mg/kg)	2240	497	12000	1876	1838
26	F3(µg/mL)	815	3400	11200	2440	4230		F3(mg/kg)	3100	1040	16100	5810	3040
27	F3(µg/mL)	879	2180	10200	2170	3560		F3(mg/kg)	1720	484	11700	1720	1570
28	F3(µg/mL)	822	3293	11753	2378	3876		F3(mg/kg)	2730	1033	17640	6705	3397
29	F3(µg/mL)	733	3022	10800	2142	3818		F3(mg/kg)	2428	823	16561	6086	3024
30	F3(µg/mL)	743	3075	10240	2267	3943		F3(mg/kg)	2799	782	16380	5688	2892
31	F3(µg/mL)							F3(mg/kg)	2846	1086	16906	5114	3343
32	F3(µg/mL)	800	3085	11845	2552	4616		F3(mg/kg)	2999	703	9335	5475	3380
33	F3(ug/mL)	592	1330	1280	8050	2380		F3(mg/kg)	1380	295	12800	1680	1590
34	F3(µg/mL)	803	3390	11300	2420	4240		F3(mg/kg)	2180	1080	16400	5580	2940
35	F3(µg/mL)	814	3410	11300	2440	4240		F3(mg/kg)	2680	1050	14900	4690	3170
36	F3(µg/mL)	1242	182	1564	2391	4275		F3(mg/kg)	6041	1181	11603	2328	1980
37	F3(µg/mL)	722	3,085	9,745	1,889	2,606		F3(mg/kg)	2740	955	16349	4935	3030
38								F3(mg/kg)	2,848	827	16,129	4,856	2,698
39	F3(µg/mL)	854	3352	11425	2476	4329		F3(mg/kg)	2736	1080	17210	4935	3552
	Total Labs	37	37	37	37	37		Total Labs	39	39	39	39	39
	Average	845	2916	10625	2717	4191		Average	2637	915	17019	5252	3172
	STD DEV	146	811	3529	1389	1476		STD DEV	863	286	5141	1949	1283
	RSD	17	28	33	51	35		RSD	33	31	30	37	40
	Median	820	3110	11200	2440	4230		Median	2730	950	16900	5474.8	3030
	Non-outlier labs	27	34	30	28	27		Non-outlier labs	32	32	29	32	31
	Average	809	3104	11253	2400	4260		Average	2644	876	16539	5068	3175
	STD DEV	52	497	1085	282	353		STD DEV	887	212	4981	1641	989
	RSD	6	16	10	12	8		RSD	34	24	30	32	31
	Median	815	3,200	11,266	2430	4240		Median	2733	920.05	16380	5340	3070

Appendix P IJ-1 – IJ-5 Samples, F4 Fraction Data Chart



F4	IJ-1	IJ-2	IJ-3	IJ-4	IJ-5
Target	448	480	5000	3400	4440
Ref. Value	500	564	9310	4080	5200
Total Labs	37	37	37	37	37
Average	388	531	7366	3336	4133
STD DEV	135	767	2924	2063	1612
RSD(%)	35	144	40	62	39
Median	395	465	8460	3622	4652
Non-outlier labs	32	36	28	29	30
Average	395	411	8811	3680	4799
STD DEV	85	224	1068	708	725
RSD(%)	22	54	12	19	15
Median	397	458	8819	3758	4856



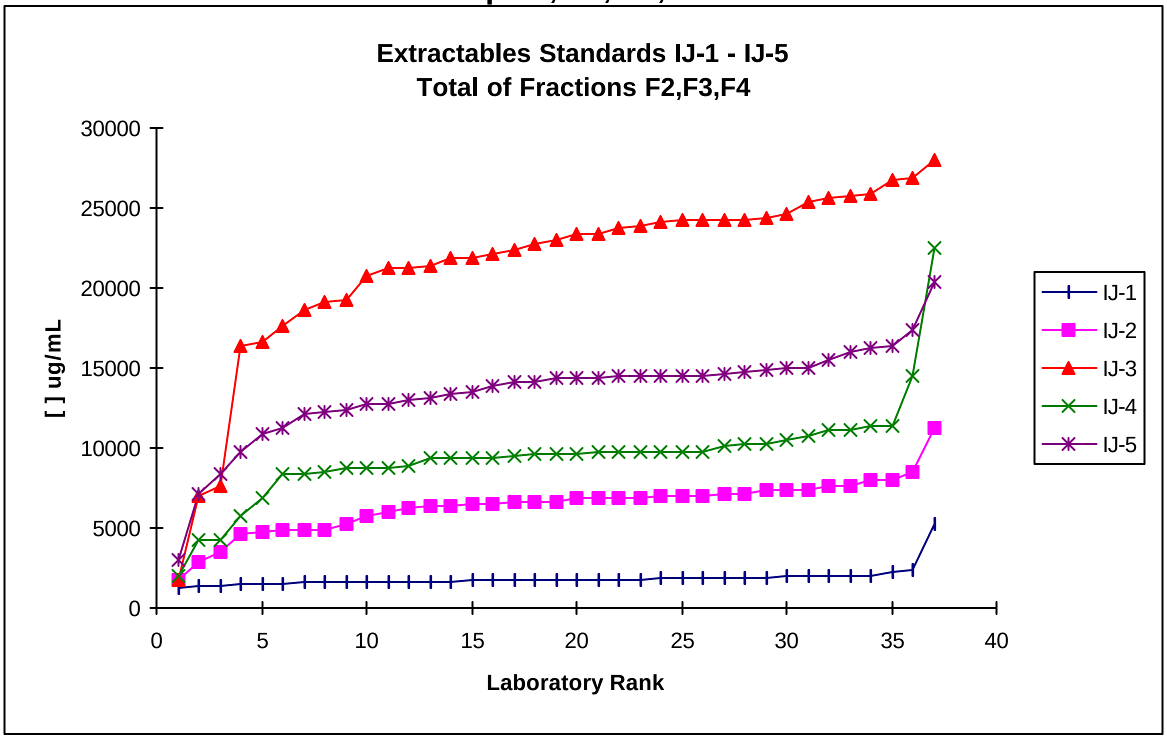
F4	FX-1	FX-2	FX-3	FX-4	FX-5
Target	1140	850	10200	7150	4810
Ref. Value	1280	886	13100	6870	5310
Total Labs	39	39	39	39	39
Average	966	677	10637	5512	4462
STD DEV	505	348	4925	2312	1896
RSD(%)	52	51	46	42	42
Median	1016	690	11290	5560	4710
Non-outlier labs	32	33	33	33	27
Average	1034	693	11325	5808	4826
STD DEV	232	192	2394	1324	600
RSD(%)	22	28	21	23	12
Median	1073	740	11604	5662	4800

Appendix R

IJ-1 – IJ-5, FX-1 – FX-5 Samples
Results Summary for F_4 by Laboratory

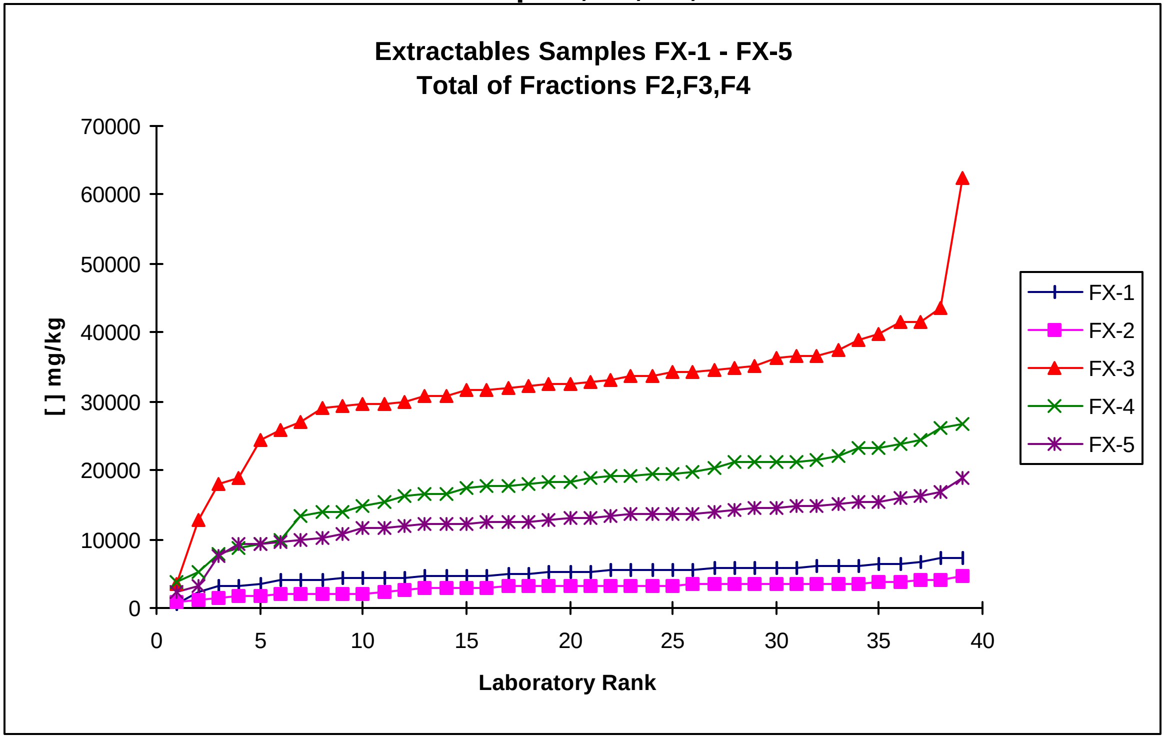
Lab #	Parameter	PS-1	PS-2	PS-3	PS-4	PS-5		Parameter	FP-1	FP-2	FP-3	FP-4	FP-5
1	F4(µg/mL)	394	465	8506	3641	4682		F4(mg/kg)	815	645	10067	5830	4418
2	F4(µg/mL)	383	115	8470	3290	4260		F4(mg/kg)	1100	681	11700	6900	5080
3	F4(µg/mL)	340	680	10,000	4,800	6,200		F4(mg/kg)	1,300	1,000	14,000	4,900	4,800
4	F4(µg/mL)	290	690	7520	3320	4010		F4(mg/kg)	1030	650	10960	6130	4230
5	F4(µg/mL)	480	400	8650	3500	4250		F4(mg/kg)	630	320	8630	4670	2800
6	F4(µg/mL)	373	395	8099	3468	4507		F4(mg/kg)	935	845	9882	5546	4744
7	F4(µg/mL)	410	640	10000	4100	5200		F4(mg/kg)	1300	910	14000	8200	5200
8	F4(µg/mL)	756	823	7000	4140	6010		F4(mg/kg)	1320	997	16000	9240	7360
9	F4(µg/mL)	598	519	8460	3770	4900		F4(mg/kg)	978	657	10050	7250	4085
10	F4(µg/mL)	368.6	113.4	6366	2408	3857		F4(mg/kg)	678.4	527.7	7004	5385	4190
11	F4(µg/mL)	510	558	9320	4040	5120		F4(mg/kg)	1400	1160	14200	7560	6110
12	F4(µg/mL)	240	300	6600	2700	3700		F4(mg/kg)	730	490	11000	4900	4600
13	F4(µg/mL)	450	390	9220	200	4180		F4(mg/kg)	780	740	11500	6920	4400
14	F4(µg/mL)	410	726	10063	3026	5395		F4(mg/kg)	1046	784	6480	4660	4125
15	F4(µg/mL)	514	668	10160	4540	5610		F4(mg/kg)	1150	690	12500	6140	4710
16	F4(µg/mL)	340	430	8300	3800	4700		F4(mg/kg)	650	820	10000	5300	1100
17	F4(µg/mL)	230	40	5700	1300	2200		F4(mg/kg)	690	490	8700	4700	3600
18	F4(µg/mL)	8.51	127	1,910	858	1,200		F4(mg/kg)	263	157	2,800	1,530	1,300
19	F4(µg/mL)	401	19	295	562	649		F4(mg/kg)	3100	2012	29480	11410	10080
20	F4(µg/mL)	268	95.9	5424	2310	3201		F4(mg/kg)	284	249	7880	4022	4209
21	F4(µg/mL)	540	600	10000	4700	5900		F4(mg/kg)	1400	760	14000	8300	6500
22	F4(µg/mL)	276	356	4910	2410	3280		F4(mg/kg)	730	440	6930	3810	3200
23	F4(µg/mL)	287	0.5	192	8	59		F4(mg/kg)	10	10	36	30	50
24	F4(µg/mL)	445	504	9315	3951	4906		F4(mg/kg)	907	871	12108	4567	6074
25	F4(µg/mL)	190	390	1920	1300	1590		F4(mg/kg)	446	144	2728	1036	1329
26	F4(µg/mL)	481	539	9430	3960	5040		F4(mg/kg)	1330	773	12300	6670	4940
27	F4(µg/mL)	522	139	8270	3210	3800		F4(mg/kg)	460	317	9090	3640	2790
28	F4(µg/mL)	320	451	10661	5407	6016		F4(mg/kg)	1231	930	14852	9102	6805
29	F4(µg/mL)	386	490	8446	3622	4652		F4(mg/kg)	1016	634	11290	6560	4922
30	F4(µg/mL)	395	469	8294	3627	4589		F4(mg/kg)	1164	588	11284	6120	4596
31	F4(µg/mL)							F4(mg/kg)	1169	836	11733	5662	5204
32	F4(µg/mL)	447	435	9175	3831	5015		F4(mg/kg)	1200	537	5863	5886	5063
33	F4(µg/mL)	347	49	3830	12400	5070		F4(mg/kg)	883	616	14500	4550	4420
34	F4(µg/mL)	463	542	9440	3950	5050		F4(mg/kg)	930	855	13500	4250	5350
35	F4(µg/mL)	460	548	9450	3970	5050		F4(mg/kg)	1160	847	12200	5560	5290
36	F4(µg/mL)	136	4878	1653	83	59		F4(mg/kg)	18	52	211	82	416
37	F4(µg/mL)	398	546	8,506	3,466	4,201		F4(mg/kg)	1115	807	11900	6270	5451
38								F4(mg/kg)	1,215	740	11,604	6,259	4,959
39	F4(µg/mL)	486	529	8987	3758	4811		F4(mg/kg)	1110	818	11876	5430	5535
	Total Labs	37	37	37	37	37		Total Labs	39	39	39	39	39
	Average	388	531	7366	3336	4133		Average	966	677	10637	5512	4462
	STD DEV	135	767	2924	2063	1612		STD DEV	505	348	4925	2312	1896
	RSD(%)	35	144	40	62	39		RSD(%)	52	51	46	42	42
	Median	395	465	8460	3622	4652		Median	1016	690	11290	5560	4710
	Non-outlier labs	32	36	28	29	30		Non-outlier labs	32	33	33	33	27
	Average	395	411	8811	3680	4799		Average	1034	693	11325	5808	4826
	STD DEV	85	224	1068	708	725		STD DEV	232	192	2394	1324	600
	RSD(%)	22	54	12	19	15		RSD(%)	22	28	21	23	12
	Median	397	458	8819	3758	4856		Median	1073	740	11604	5662	4800

Appendix S **IJ-1 – IJ-5 Samples, F2, F3,F4 Total Fraction Data Chart**



	IJ-1	IJ-2	IJ-3	IJ-4	IJ-5
Total Labs	37	37	37	37	37
Average	1845	6395	21384	9504	13512
STD DEV	612	1665	5578	3123	2965
RSD	33	26	26	33	22
Median	1740	6594	23000	9598	14383
Final labs	33	33	29	30	29
Average	1735	6586	23362	9721	14202
STD DEV	180	1004	2012	845	1149
RSD	10	15	9	9	8
Median	1740	6849	23700	9651.605	14408

Appendix T FX-1 – FX-5 Samples, F2, F3,F4 Total Data Chart



	FX-1	FX-2	FX-3	FX-4	FX-5
Total Labs	39	39	39	39	39
Average	5036	2936	32149	17566	12527
STD DEV	1322	852	9166	5449	3268
RSD	26	29	29	31	26
Median	5300	3220	32627	18423	12990
Final labs	32	33	30	32	35
Average	5278	3118	32909	18956	13050
STD DEV	749	583	3312	2982	1991
RSD	14	19	10	16	15
Median	5358	3251	32705.5	19030	13036

Appendix U IJ-1 – IJ-5, FX-1 – FX-5 Samples

Results Summary for F_{TOT} by Laboratory

Lab #	Parameter	PS-1	PS-2	PS-3	PS-4	PS-5		Parameter	FP-1	FP-2	FP-3	FP-4	FP-5
1	Ftot(µg/mL)	1968	6555	21913	9594	14408		Ftot(mg/kg)	4208	3041	29467	18765	12407
2	Ftot(µg/mL)	1635	5735	22170	9430	12760		Ftot(mg/kg)	6160	3350	35250	21160	13480
3	Ftot(µg/mL)	1680	7580	23000	11100	16400		Ftot(mg/kg)	6400	4100	36700	13500	11500
4	Ftot(µg/mL)	1600	5950	19190	8440	12240		Ftot(mg/kg)	5300	3090	33190	21980	13680
5	Ftot(µg/mL)	2040	5270	22740	9750	13900		Ftot(mg/kg)	4327	2178	29718	16500	12300
6	Ftot(µg/mL)	1692	7147	23329	10310	14970		Ftot(mg/kg)	4674	3118	29050	17912	14016
7	Ftot(µg/mL)	1660	7940	25700	10200	14900		Ftot(mg/kg)	6500	3710	39800	23300	14600
8	Ftot(µg/mL)	2285	6943	17600	9760	14660		Ftot(mg/kg)	5890	4100	43510	26610	18970
9	Ftot(µg/mL)	5192	11239	28030	14540	20370		Ftot(mg/kg)	5386	3288	32360	26260	12415
10	Ftot(µg/mL)	1818.8	4879.4	23882	8691	13423		Ftot(mg/kg)	4717.4	3225.8	36254	21202	13787
11	Ftot(µg/mL)	1931	7358	25420	10740	15510		Ftot(mg/kg)	6600	4670	41610	23280	16130
12	Ftot(µg/mL)	1530	7000	21400	9400	14400		Ftot(mg/kg)	5730	3390	41500	21200	15300
13	Ftot(µg/mL)	1740	6200	23700	5700	12960		Ftot(mg/kg)	4460	3540	33790	21420	12920
14	Ftot(µg/mL)	2318	8463	26838	11066	17355		Ftot(mg/kg)	4935	2933	29516	18423	12341
15	Ftot(µg/mL)	1830	7428	25565	11345	16035		Ftot(mg/kg)	5570	2950	34530	19030	14110
16	Ftot(µg/mL)	1740	6530	23400	9700	13500		Ftot(mg/kg)	4050	3220	30700	19800	9200
17	Ftot(µg/mL)	1930	4840	18600	4200	8400		Ftot(mg/kg)	3620	1900	27100	13900	10100
18	Ftot(µg/mL)	1797.51	7027	24230	8758	14540		Ftot(mg/kg)	6023	3517	38920	21170	15000
19	Ftot(µg/mL)	1567	3456	19084	9384	12740		Ftot(mg/kg)	7402	3332	62443	16329	14425
20	Ftot(µg/mL)	1723	4929.9	20812	8418	12378		Ftot(mg/kg)	2199	1545	29801	14740	11714
21	Ftot(µg/mL)	1880	7400	26800	10500	16300		Ftot(mg/kg)	6200	3410	37550	24400	16900
22	Ftot(µg/mL)	1376	4756	16677	6820	9755		Ftot(mg/kg)	4125	2070	25800	8610	9260
23	Ftot(µg/mL)	1205	1742.5	1765	2015	3006		Ftot(mg/kg)	653	739	3510	3810	2205
24	Ftot(µg/mL)	1810	7179	24239	10185	14517		Ftot(mg/kg)	4398	3558	34209	13849	14756
25	Ftot(µg/mL)	2022	8040	16346	8780	13187		Ftot(mg/kg)	4396	1303	18738	7880	9954
26	Ftot(µg/mL)	1770	6849	24220	9770	14490		Ftot(mg/kg)	5860	3083	32410	20280	12990
27	Ftot(µg/mL)	2002	4589	21190	8870	12080		Ftot(mg/kg)	3175	1971	24390	9190	7420
28	Ftot(µg/mL)	1564	6565	25831	11351	15059		Ftot(mg/kg)	5492	3251	36595	23856	15534
29	Ftot(µg/mL)	1557	6594	22387	9420	14110		Ftot(mg/kg)	4561	2205	31798	19597	12144
30	Ftot(µg/mL)	1573	6589	21844	9560	14187		Ftot(mg/kg)	5660	2713	32784	19568	13036
31	Ftot(µg/mL)							Ftot(mg/kg)	5902	3633	33785	17807	14852
32	Ftot(µg/mL)	1659.67	6334.97	24570.8	9603.21	14811.24		Ftot(mg/kg)	4928.89	2097.92	17939.37	15385.91	10762.19
33	Ftot(µg/mL)	1388	2849	7670	22530	11190		Ftot(mg/kg)	3133	1681	30800	9780	9580
34	Ftot(µg/mL)	1733	6862	24300	9740	14530		Ftot(mg/kg)	4770	3525	35000	19230	13710
35	Ftot(µg/mL)	1746	6888	24350	9800	14490		Ftot(mg/kg)	5330	3487	31840	16670	13530
36	Ftot(µg/mL)	1982	7683	7015	4213	7112		Ftot(mg/kg)	7308	1667	12885	5307	3185
37	Ftot(µg/mL)	1445	6363	21306	8358	10885		Ftot(mg/kg)	5095	3309	32627	18211	12549
38	Ftot(µg/mL)							Ftot(mg/kg)	5500	2988	31692	17856	11906
39	Ftot(µg/mL)	1858	6865	24088	9598	14383		Ftot(µg/mL)	5755	3610	34233	17325	15870
	Total Labs	37	37	37	37	37		Total Labs	39	39	39	39	39
	Average	1845	6395	21384	9504	13512		Average	5036	2936	32149	17566	12527
	STD DEV	612	1665	5578	3123	2965		STD DEV	1322	852	9166	5449	3268
	RSD	33	26	26	33	22		RSD	26	29	29	31	26
	Median	1740	6594	23000	9598	14383		Median	5300	3220	32627	18423	12990
	Non-outlier labs	33	33	29	30	29		Non-outlier labs	32	33	30	32	35
	Average	1735	6586	23362	9721	14202		Average	5278	3118	32909	18956	13050
	STD DEV	180	1004	2012	845	1149		STD DEV	749	583	3312	2982	1991
	RSD	10	15	9	9	8		RSD	14	19	10	16	15
	Median	1740	6849	23700	9651.605	14408		Median	5358	3251	32705.5	19030	13036

Appendix V Deviations from CWS and Z-score Summary for F_1 by Laboratory

Lab #	Param	MeOH	P&T	FID	RF	DB-1	PS-1	PS-2	PS-3	PS-4	PS-5	FP-1	FP-2	FP-3	FP-4	FP-5
1	F1	✓	✓	✓	✓	✓	1.25	-1.45	-1.43	0.82	**-2.98**	**26.6**	**29.3**	**4.31**	**19.8**	**14.3**
2	F1	?	?	?	?	?	1.36	**2.26**	**2.23**	**2.38**	1.66	1.93	1.27	1.13	1.60	0.04
3	F1	✓	✖	✓	✓	✓	-1.11	0.14	-0.37	0.17	0.79	0.93	0.22	1.44	-0.11	0.76
4	F1	✓	✓	✓	✓	✓	-0.43	-0.50	-0.52	-0.85	-0.01	-0.17	-0.21	0.55	1.07	0.11
5	F1	✓	✓	✓	✖	✓	**7.16**	**8.41**	**6.70**	**9.51**	**11.99**	-0.76	-0.48	-0.67	-0.20	-0.61
6	F1	✓	✖	?	✓	✓	0.50	-0.02	-0.30	0.09	0.35	-0.52	0.42	1.17	0.71	1.00
7	F1	✓	✓	?	✖	✓	-1.90	-1.96	**-2.53**	**-2.66**	**-2.83**	0.70	0.22	0.71	0.82	0.45
8	F1	✓	✖	✓	✓	✖	0.87	**3.50**	**2.04**	0.29	0.39	0.96	0.67	0.79	0.68	0.45
9	F1	?	?	?	?	?	0.49	1.09	0.51	**2.24**	**3.70**	**3.38**	-0.86	**2.83**	**2.31**	1.68
10	F1	✓	✓	✓	✖	✓	-1.94	-0.77	-1.04	-0.92	-1.06	-0.48	**-2.59**	0.05	-1.64	0.35
11	F1	✓	✓	✓	✖	✓	-0.36	0.02	-0.56	-0.73	-0.38	**-2.06**	-0.65	-0.96	-0.09	-0.34
12	F1	✓	✖	?	✓	✖	0.98	0.54	0.57	0.99	1.05	-0.33	-1.10	0.11	-0.92	-1.33
13	F1	✓	✓	✖	✓	?	**2.69**	1.17	**2.08**	**3.61**	**5.28**	**8.96**	**4.24**	0.96	**4.48**	**5.31**
14	F1	?	✓	?	✓	?	0.36	0.24	-0.03	-0.47	-1.09	-0.58	0.87	0.71	-0.64	0.90
15	F1	✓	✓	✓	✖	?	0.11	-0.25	-0.58	-1.01	-1.15	-0.96	-0.53	-0.32	1.64	1.25
16	F1	✓	✓	✓	✖	✓	0.49	0.93	0.35	0.58	1.23	0.85	-0.16	-0.76	-0.48	-1.08
17	F1	✓	✓	✓	✖	✓	-0.62	**-3.73**	**-4.18**	-1.06	-1.07	**-3.40**	**-2.79**	-1.00	-1.97	-1.79
18	F1	✓	✖	✓	✓	✓	-0.07	0.34	-0.24	-0.24	-0.13	1.48	0.52	0.61	1.38	1.40
19	F1	✓	✖	✖	✖	✖	**-2.27**	**4.96**	**4.63**	**9.36**	**10.78**	**7.32**	**11.4**	**5.44**	**7.84**	**5.40**
20	F1	?	?	?	?	?	-0.78	0.16	-0.23	0.14	0.77	-0.19	-0.29	-1.46	-0.19	**-2.36**
21	F1	✓	✖	?	✓	✓	**2.75**	0.67	0.57	0.99	1.49	1.32	0.97	1.44	0.70	0.76
22	F1	✓	✓	✖	✖	✖	**8.39**	0.91	-0.48	**5.45**	**9.52**	**21.7**	**2.08**	**7.98**	**19.4**	**10.4**
23	F1	✓	✓	✓	?	✓	1.19	1.00	0.83	1.28	1.78	-5.41	-4.84	-1.68	**-3.17**	-2.91
24	F1	?	?	?	?	?	-0.77	-0.26	-1.07	-0.58	-0.58	0.64	0.39	-0.21	0.34	-0.28
25	F1	✓	✓	✖	✖	?	1.65	**3.96**	**7.28**	-0.40	**5.64**	**6.75**	**10.54**	-1.12	-1.48	**2.30**
26	F1	✓	✖	✓	✓	✓	0.27	0.00	-0.41	-0.04	-0.51	0.62	-0.38	0.38	0.32	0.54
27	F1															
28	F1	?	?	?	?	?	**-3.29**	**-3.73**	**-4.26**	**-5.56**	**-5.82**	0.77	0.86	-1.69	-1.61	-0.71
29	F1	✓	✓	?	✓	✖	-0.02	-0.90	-0.98	-1.39	-1.49	-0.67	**-2.22**	-0.01	-1.30	-1.29
30	F1	✓	✓	?	✓	✖	0.19	-0.51	-1.11	-2.09	-1.94	-1.81	**-2.12**	-1.23	-0.81	-1.68
31	F1	?	?	?	?	?	-1.68	0.74	1.50	-0.10	0.31	-1.04	-0.39	0.34	0.50	0.60
32	F1	✓	✓	✓	✓	✓	-0.07	-0.25	-0.80	-0.24	-0.89	-0.88	1.35	1.68	0.32	0.14
33	F1	?	✓	✓	?	✖	0.41	**-2.80**	**-3.90**	**-5.06**	-0.28	0.40	**-4.48**	-0.33	0.58	-1.36
34	F1	✓	✓	✓	✓	✖	0.25	-0.33	-0.07	0.33	0.34	0.37	-0.85	0.09	0.13	0.97
35	F1															
36	F1	✓	✓	?	✓	✖	1.10	0.11	-0.80	0.06	0.02	-0.55	0.42	-0.09	0.63	-0.96
37	F1	✓	✓	✓	✖	?	**-3.31**	**-3.81**	**-4.26**	**-5.56**	**-5.82**	**-5.44**	**-4.86**	-1.70	**-3.21**	**-2.93**
38	F1															
39	F1	?	?	?	?	?	-1.73	-0.31	0.35	-0.23	0.40			1.10		

Legend

- MeOH Methanol used?
- P&T Purge and Trap used?
- FID FID used?
- RF RF criteria met?
- DB-1 DB-1 column or equivalent used?
- ✓ Yes
- ✖ No
- ? Insufficient information

Appendix W Deviations from CWS and Z-score Summary for F_2 by Laboratory

Lab #	Param	Hex/Ace	Sox	FID	RF	DB-1	IJ-1	IJ-2	IJ-3	IJ-4	IJ-5	FX-1	FX-2	FX-3	FX-4	FX-5
1	F2	✓	✓	✓	✓	✓	**5.22**	0.71	0.00	0.95	1.26	-0.14	0.50	0.55	0.50	0.28
2	F2	?	?	?	?	?	0.36	0.57	1.41	0.72	0.43	**2.40**	1.15	1.75	0.82	0.51
3	F2	✓	✖	✓	✓	✓	0.16	0.96	-1.80	1.03	1.22	1.13	1.32	0.20	-1.34	-1.10
4	F2	✖	✖	✓	✓	✓	1.58	-0.19	0.18	-0.64	-0.10	1.37	0.74	**2.06**	1.93	1.56
5	F2	✓	✓	✓	✖	✓	0.87	-1.33	-1.84	0.51	0.53	-1.49	-1.34	-0.38	-0.22	-1.64
6	F2	✓	✓	?	✓	✓	0.81	1.59	-0.03	1.54	1.55	-0.05	-0.04	-1.05	-0.20	0.51
7	F2	✓	✓	?	✓	✓	-0.56	1.95	0.81	0.24	0.25	**2.32**	0.82	1.46	1.25	0.82
8	F2	✖	✖	✓	✓	✓	**5.79**	1.18	0.70	1.00	-0.47	**2.55**	**2.18**	**5.71**	**2.71**	**3.09**
9	F2	?	?	?	?	?	**46.24**	**10.57**	**13.79**	**11.70**	**7.58**	0.62	0.66	0.65	**2.36**	0.12
10	F2	✓	✓	✓	✓	✓	-0.90	-1.75	1.02	**-3.60**	-1.24	-0.04	1.01	-0.50	0.95	-0.22
11	F2	✓	✓	✓	✓	✓	0.94	0.72	0.81	0.92	0.96	0.48	1.52	0.67	0.72	0.53
12	F2	✓	✓	✓	✓	✓	0.30	1.46	1.19	1.55	1.63	1.43	1.07	**2.27**	1.30	1.17
13	F2	✓	✓	✓	✓	✓	0.01	-0.52	-0.38	-0.93	-0.30	0.45	0.92	0.65	0.81	0.43
14	F2	?	?	✓	✓	✖	**8.33**	**3.12**	**3.78**	**3.29**	**3.12**	-0.91	-0.71	0.34	0.20	0.00
15	F2	✖	✖	✓	✓	?	0.04	0.36	-0.10	1.54	1.02	0.98	-0.06	0.47	0.16	1.30
16	F2	✓	✓	✓	✓	✖	-0.13	-0.76	-1.43	-1.32	-0.86	-0.35	0.07	0.20	-0.05	-0.05
17	F2	✓	✓	?	✖	✖	**5.43**	-1.01	-0.68	**-4.72**	**-2.10**	-1.45	-1.56	**-2.43**	-1.40	-1.28
18	F2	✓	✓	✓	✖	✓	0.00	0.25	0.14	-1.27	-0.23	1.07	0.44	0.91	0.54	0.77
19	F2	✖	✖	✖	✖	✖	**-4.21**	**-4.37**	**-9.55**	**-4.38**	**-3.46**	-1.08	-1.59	**-2.95**	**-2.56**	-1.60
20	F2	?	?	?	?	?	-0.24	-1.56	**-2.00**	-1.17	-0.91	**-2.72**	-1.80	-1.82	-1.17	-1.58
21	F2	✓	✖	?	✖	✓	0.16	0.47	1.19	-0.54	0.39	0.83	0.82	1.18	1.13	1.17
22	F2	✓	✖	✓	✓	✓	-1.27	-1.94	**-3.42**	**-2.29**	-1.95	-1.23	-0.75	-1.02	**-3.62**	-1.22
23	F2	✓	✓	✓	✖	?	**-2.65**	**-4.93**	**-10.65**	**-3.93**	**-3.35**	**-2.94**	**-2.66**	-1.72	**-2.69**	**-2.70**
24	F2	?	?	?	?	?	0.70	0.97	0.79	0.71	0.62	-0.60	0.69	-0.23	-1.04	-0.14
25	F2	✓	✖	✓	✓	✓	**8.32**	**2.71**	0.50	**4.59**	**2.88**	0.86	-1.79	-0.59	-1.19	1.51
26	F2	✓	✓	✓	✓	✓	0.07	0.00	0.40	-0.36	0.14	0.03	-0.26	-0.59	0.40	-0.04
27	F2	✖	✖	✓	✓	✖	1.88	-1.57	**-2.85**	-0.04	-0.55	-1.26	-0.51	-1.06	-1.83	-1.75
28	F2	?	?	?	?	?	-0.67	-0.22	-0.24	0.16	0.07	0.33	-0.21	-0.48	0.54	0.24
29	F2	✓	✓	?	✓	✖	-0.44	0.43	-1.28	0.39	0.72	-0.90	-1.57	-0.66	-0.07	-0.75
30	F2	✓	✖	✓	✓	✖	-0.49	0.33	-0.64	0.42	0.74	0.82	-0.08	0.68	0.38	0.43
31	F2	?	?	?	?	?						1.39	0.85	0.71	-0.03	1.09
32	F2	✓	✓	✓	✓	✓	-0.81	-0.23	0.25	-0.75	0.08	**-2.04**	-1.29	**-2.04**	-1.72	**-2.40**
33	F2	?	✖	✓	?	✓	-0.29	**-3.55**	**-3.45**	**-3.73**	-1.91	-1.63	-1.51	-1.17	-1.99	-1.30
34	F2	✓	✖	✓	✓	✓	-0.03	0.05	0.29	-0.36	0.17	0.71	0.54	0.66	1.30	0.31
35	F2	✓	✖	✓	✓	✓	0.04	0.05	0.44	-0.30	0.11	0.21	0.54	0.25	-0.37	0.01
36	F2	✖	✓	?	✓	✓	1.92	-0.70	1.18	**-4.62**	**-3.24**	-0.50	**-2.36**	**-3.95**	**-2.35**	**-3.74**
37	F2	✓	✓	✓	✓	✓	**-2.06**	-0.44	-1.60	-1.32	-1.44	-0.53	0.44	-0.17	-0.04	-0.87
38	F2	✓	✓	✓	✓	✓						0.05	0.12	-0.65	-0.19	-0.71
39	F2	?	?	?	?	?	0.70	0.18	0.72	-0.37	0.17	1.45	0.85	0.72	-0.07	1.51

Legend
- Hex/Ace — Hexane / acetone used?
- Sox — Soxhlet used?
- FID — FID used?
- RF — RF criteria met?
- DB-1 — DB-1 column or equivalent used?
- ✓ — Yes
- ✖ — No
- ? — Insufficient information

Appendix X Deviations from CWS and Z-score Summary for F_3 by Laboratory

Lab #	Param	Hex/Ace	Sox	FID	RF	DB-1	IJ-1	IJ-2	IJ-3	IJ-4	IJ-5	FX-1	FX-2	FX-3	FX-4	FX-5
1	F3	✔	✔	✔	✔	✔	-1.33	-0.42	-1.23	-1.13	-1.59	-0.70	-0.25	-0.43	-0.06	-0.58
2	F3	?	?	?	?	?	-0.97	-1.25	-1.30	-0.14	**-3.37**	0.21	-0.17	0.19	0.40	-0.42
3	F3	✔	✖	✔	✔	✔	0.98	1.00	-1.16	0.00	-0.17	0.74	1.53	0.29	-0.71	-0.28
4	F3	✖	✖	✔	✔	✔	-1.50	-1.36	**-2.87**	-1.92	**-3.06**	-0.29	-0.50	-0.13	0.17	-0.57
5	F3	✔	✔	✔	✖	✔	**4.23**	-1.21	-0.14	0.53	-0.31	0.15	0.68	0.07	0.04	**3.18**
6	F3	✔	✔	?	✔	✔	-0.30	0.19	0.46	1.23	-0.10	-0.35	0.19	-0.20	0.35	0.46
7	F3	✔	✔	?	✔	✔	0.22	1.00	0.69	0.35	0.40	0.40	1.06	0.69	0.45	0.23
8	F3	✖	✖	✔	✔	✔	**-2.95**	-0.75	**-3.99**	**-2.38**	-1.10	-0.40	-0.06	0.29	0.24	-0.16
9	F3	?	?	?	?	?	1.44	0.84	1.06	1.38	1.73	0.15	0.56	0.14	1.62	-0.05
10	F3	✔	✔	✔	✔	✔	**4.50**	-1.08	**2.31**	**6.23**	**3.06**	-0.01	0.23	1.73	1.21	1.63
11	F3	✔	✔	✔	✔	✔	1.48	1.00	1.06	1.56	0.91	1.10	3.09	1.16	1.40	1.19
12	F3	✔	✔	✔	✔	✔	-0.16	0.19	-0.23	0.71	0.40	0.51	1.06	1.50	1.12	1.14
13	F3	✔	✔	✔	✔	✔	0.22	0.01	-0.14	-0.18	-1.08	-0.60	0.87	0.13	0.55	-0.21
14	F3	?	?	✔	✔	✖	0.89	0.92	0.95	3.10	0.93	0.15	0.86	0.34	0.77	-0.02
15	F3	✖	✖	✔	✔	?	0.68	1.21	0.64	1.10	0.87	0.03	0.16	0.11	0.28	-0.33
16	F3	✔	✔	✔	✔	✖	**2.51**	0.80	0.69	1.77	0.11	-0.61	0.59	-0.11	1.48	-0.08
17	F3	✔	✔	?	✖	✖	0.79	-1.62	-1.52	-4.26	-4.71	-0.73	-1.02	-0.11	-0.29	-0.28
18	F3	✔	✔	✔	✖	✔	**9.77**	**1.58**	**6.96**	**8.80**	**11.71**	1.51	**4.41**	**2.86**	**3.98**	**4.64**
19	F3	✖	✖	✖	✖	✖	**3.50**	-1.61	**6.09**	**16.3**	**14.80**	0.68	-1.40	**2.91**	-1.63	**-2.09**
20	F3	?	?	?	?	?	**3.71**	-1.10	1.09	**2.31**	1.29	-1.39	-1.11	0.49	0.39	1.09
21	F3	✔	✖	?	✖	✔	0.98	1.20	1.61	0.35	**2.10**	0.51	0.35	0.29	1.18	0.83
22	F3	✔	✖	✔	✔	✔	-1.69	-1.66	-1.89	**-2.20**	**-4.24**	-0.29	-1.51	-0.26	-0.56	-0.79
23	F3	✔	✔	✔	✖	?	**-3.32**	**-4.57**	**-9.51**	**-8.51**	**-11.4**	**-2.74**	**-2.17**	**-3.23**	**-2.18**	**-3.02**
24	F3	?	?	?	?	?	0.73	0.54	-0.02	0.20	-0.61	-0.42	0.76	0.25	-0.62	0.62
25	F3	✔	✖	✔	✔	✔	-0.55	1.08	-0.41	-0.64	0.39	-0.46	-1.79	-0.91	-1.95	-1.35
26	F3	✔	✔	✔	✔	✔	0.12	0.60	-0.05	0.14	-0.08	0.51	0.77	-0.09	0.45	-0.14
27	F3	✖	✖	✔	✔	✖	1.35	-1.86	-0.97	-0.82	-1.98	-1.04	-1.85	-0.97	**-2.04**	-1.62
28	F3	?	?	?	?	?	0.26	0.38	0.46	-0.08	-1.09	0.10	0.74	0.22	1.00	0.22
29	F3	✔	✔	?	✔	✖	-1.44	-0.16	-0.42	-0.92	-1.25	-0.24	-0.25	0.00	0.62	-0.15
30	F3	✔	✖	✔	✔	✖	-1.25	-0.06	-0.93	-0.47	-0.90	0.18	-0.44	-0.03	0.38	-0.29
31	F3	?	?	?	?	?						0.23	0.99	0.07	0.03	0.17
32	F3	✔	✔	✔	✔	✔	-0.16	-0.04	0.55	0.54	1.01	0.40	-0.81	-1.45	0.25	0.21
33	F3	?	✖	✔	?	✔	**-4.14**	**-3.57**	**-9.19**	**20.1**	**-5.33**	-1.42	**-2.74**	-0.75	**-2.07**	-1.60
34	F3	✔	✖	✔	✔	✔	-0.11	0.58	0.04	0.07	-0.06	-0.52	0.96	-0.03	0.31	-0.24
35	F3	✔	✖	✔	✔	✔	0.10	0.62	0.04	0.14	-0.06	0.04	0.82	-0.33	-0.23	0.00
36	F3	✖	✔	?	✔	✔	**8.28**	**-5.88**	**-8.93**	-0.03	0.04	**3.83**	1.44	-0.99	-1.67	-1.21
37	F3	✔	✔	✔	✔	✔	-1.65	-0.04	-1.39	-1.82	-4.69	0.11	0.37	-0.04	-0.08	-0.15
38	F3	✔	✔	✔	✔	✔						0.23	-0.23	-0.08	-0.13	-0.48
39	F3	?	?	?	?	?	0.87	0.50	0.16	0.27	0.20	0.10	0.96	0.13	-0.08	0.38

Legend
- Hex/Ace — Hexane / acetone used?
- Sox — Soxhlet used?
- FID — FID used?
- RF — RF criteria met?
- DB-1 — DB-1 column or equivalent used?
- ✔ — Yes
- ✖ — No
- ? — Insufficient information

Appendix Y Deviations from CWS and Z-score Summary for F_4 by Laboratory

Lab #	Param	Hex/Ace	Sox	FID	RF	DB-1	IJ-1	IJ-2	IJ-3	IJ-4	IJ-5	FX-1	FX-2	FX-3	FX-4	FX-5
1	F4	✓	✓	✓	✓	✓	-0.02	0.24	-0.29	-0.05	-0.16	-0.94	-0.25	-0.53	0.02	-0.68
2	F4	?	?	?	?	?	-0.15	-1.32	-0.32	-0.55	-0.74	0.28	-0.06	0.16	0.83	0.42
3	F4	✓	✖	✓	✓	✓	-0.65	1.20	1.11	1.58	1.93	1.14	1.60	1.12	-0.69	-0.04
4	F4	✖	✖	✓	✓	✓	-1.24	1.25	-1.21	-0.51	-1.09	-0.02	-0.22	-0.15	0.24	-0.99
5	F4	✓	✓	✓	✖	✓	0.99	-0.05	-0.15	-0.25	-0.76	-1.74	-1.94	-1.13	-0.86	**-3.38**
6	F4	✓	✓	?	✓	✓	-0.26	-0.07	-0.67	-0.30	-0.40	-0.43	0.79	-0.60	-0.20	-0.14
7	F4	✓	✓	?	✓	✓	0.17	1.03	1.11	0.59	0.55	1.14	1.13	1.12	1.81	0.62
8	F4	✖	✖	✓	✓	✓	**4.24**	1.84	-1.70	0.65	1.67	1.23	1.58	1.95	**2.59**	**4.22**
9	F4	?	?	?	?	?	**2.38**	0.48	-0.33	0.13	0.14	-0.24	-0.19	-0.53	1.09	-1.24
10	F4	✓	✓	✓	✓	✓	-0.32	-1.33	**-2.29**	-1.80	-1.30	-1.53	-0.86	-1.81	-0.32	-1.06
11	F4	✓	✓	✓	✓	✓	1.35	0.66	0.48	0.51	0.44	1.57	**2.43**	1.20	1.32	**2.14**
12	F4	✓	✓	✓	✓	✓	-1.83	-0.49	**-2.07**	-1.38	-1.51	-1.31	-1.05	-0.14	-0.69	-0.38
13	F4	✓	✓	✓	✓	✓	0.64	-0.09	0.38	**-4.92**	-0.85	-1.09	0.24	0.07	0.84	-0.71
14	F4	?	?	✓	✓	✖	0.17	1.41	1.17	-0.92	0.82	0.05	0.47	**-2.02**	-0.87	-1.17
15	F4	✖	✖	✓	✓	?	1.39	1.15	1.26	1.22	1.12	0.50	-0.01	0.49	0.25	-0.19
16	F4	✓	✓	✓	✓	✖	-0.65	0.09	-0.48	0.17	-0.14	-1.65	0.66	-0.55	-0.38	**-6.21**
17	F4	✓	✓	?	✖	✖	-1.94	-1.66	**-2.91**	**-3.36**	**-3.58**	-1.48	-1.05	-1.10	-0.84	**-2.04**
18	F4	✓	✓	✓	✖	✓	**-4.55**	-1.27	**-6.46**	**-3.99**	**-4.96**	**-3.32**	**-2.78**	**-3.56**	**-3.23**	**-5.88**
19	F4	✖	✖	✖	✖	✖	0.07	-1.75	**-7.97**	**-4.41**	**-5.72**	**8.89**	**6.85**	**7.58**	**4.23**	**8.76**
20	F4	?	?	?	?	?	-1.50	-1.41	**-3.17**	-1.94	**-2.20**	**-3.23**	**-2.31**	-1.44	-1.35	-1.03
21	F4	✓	✖	?	✖	✓	1.70	0.85	1.11	1.44	1.52	1.57	0.35	1.12	1.88	**2.79**
22	F4	✓	✖	✓	✓	✓	-1.40	-0.24	-3.65	-1.79	**-2.09**	-1.31	-1.31	-1.84	-1.51	**-2.71**
23	F4	✓	✓	✓	✖	?	-1.27	-1.83	**-8.07**	**-5.19**	**-6.53**	**-4.41**	**-3.55**	**-4.72**	**-4.37**	**-7.96**
24	F4	?	?	?	?	?	0.58	0.42	0.47	0.38	0.15	-0.55	0.93	0.33	-0.94	2.08
25	F4	✓	✖	✓	✓	✓	**-2.41**	-0.09	**-6.45**	**-3.36**	**-4.42**	**-2.53**	**-2.85**	**-3.59**	**-3.61**	**-5.83**
26	F4	✓	✓	✓	✓	✓	1.00	0.57	0.58	0.40	0.33	1.27	0.42	0.41	0.65	0.19
27	F4	✖	✖	✓	✓	✖	1.49	-1.21	-0.51	-0.66	-1.38	**-2.47**	-1.95	-0.93	-1.64	**-3.39**
28	F4	?	?	?	?	?	-0.89	0.18	1.73	**2.44**	1.68	0.85	1.23	1.47	**2.49**	**3.30**
29	F4	✓	✓	?	✓	✖	-0.11	0.35	-0.34	-0.08	-0.20	-0.08	-0.31	-0.01	0.57	0.16
30	F4	✓	✖	✓	✓	✖	-0.01	0.26	-0.48	-0.07	-0.29	0.56	-0.54	-0.02	0.24	-0.38
31	F4	?	?	?	?	?						0.58	0.74	0.17	-0.11	0.63
32	F4	✓	✓	✓	✓	✓	0.60	0.11	0.34	0.21	0.30	0.72	-0.81	-2.28	0.06	0.40
33	F4	?	✖	✓	?	✓	-0.57	-1.62	**-4.66**	**12.32**	0.37	-0.65	-0.40	1.33	-0.95	-0.68
34	F4	✓	✖	✓	✓	✓	0.79	0.59	0.59	0.38	0.35	-0.45	0.84	0.91	-1.18	0.87
35	F4	✓	✖	✓	✓	✓	0.76	0.61	0.60	0.41	0.35	0.54	0.80	0.37	-0.19	0.77
36	F4	✖	✓	?	✓	✓	**-3.05**	**19.97**	**-6.70**	**-5.08**	**-6.53**	**-4.37**	**-3.33**	**-4.64**	**-4.33**	**-7.35**
37	F4	✓	✓	✓	✓	✓	0.03	0.61	-0.29	-0.30	-0.82	0.35	0.59	0.24	0.35	1.04
38	F4	✓	✓	✓	✓	✓						0.78	0.24	0.12	0.34	0.22
39	F4	?	?	?	?	?	1.06	0.53	0.16	0.11	0.02	0.33	0.65	0.23	-0.29	1.18

Legend
- Hex/Ace — Hexane / acetone used?
- Sox — Soxhlet used?
- FID — FID used?
- RF — RF criteria met?
- DB-1 — DB-1 column or equivalent used?
- ✓ — Yes
- ✖ — No
- ? — Insufficient information

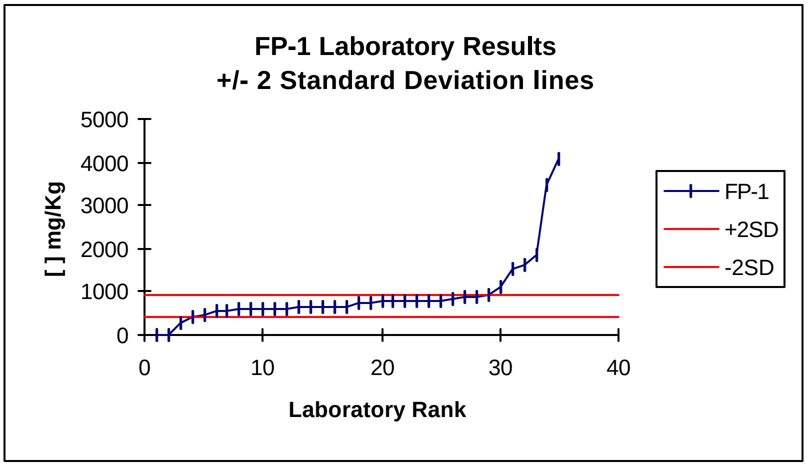
Appendix Z Deviations from CWS and Z-score Summary for F_{TOT} by Laboratory

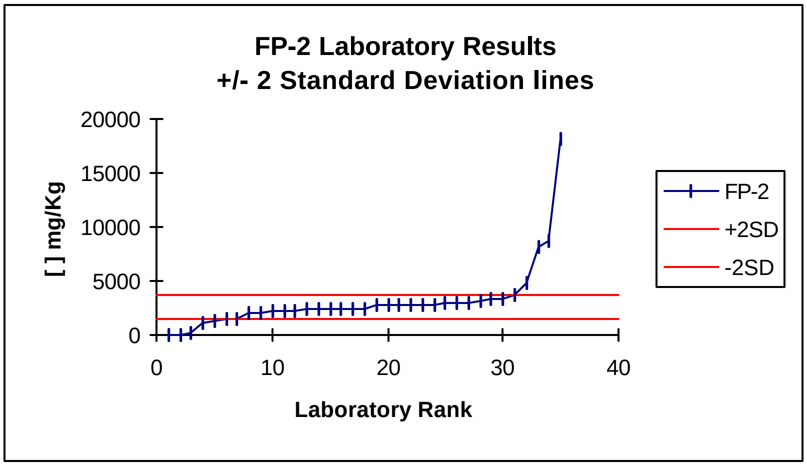
Lab #	Param	Hex/Ace	Sox	FID	RF	DB-1	IJ-1	IJ-2	IJ-3	IJ-4	IJ-5	FX-1	FX-2	FX-3	FX-4	FX-5
1	FTOT	✓	✓	✓	✓	✓	1.30	-0.03	-0.72	-0.15	0.18	-1.43	-0.13	-1.04	-0.06	-0.32
2	FTOT	?	?	?	?	?	-0.55	-0.85	-0.59	-0.34	-1.26	1.18	0.40	0.71	0.74	0.22
3	FTOT	✓	✖	✓	✓	✓	-0.30	0.99	-0.18	1.63	1.91	1.50	1.68	1.14	-1.83	-0.78
4	FTOT	✖	✖	✓	✓	✓	-0.75	-0.63	**-2.07**	-1.52	-1.71	0.03	-0.05	0.08	1.01	0.32
5	FTOT	✓	✓	✓	✖	✓	1.70	-1.31	-0.31	0.03	-0.26	-1.27	-1.61	-0.96	-0.82	-0.38
6	FTOT	✓	✓	?	✓	✓	-0.24	0.56	-0.02	0.70	0.67	-0.81	0.00	-1.17	-0.35	0.49
7	FTOT	✓	✓	?	✓	✓	-0.42	1.35	1.16	0.57	0.61	1.63	1.01	**2.08**	1.46	0.78
8	FTOT	✖	✖	✓	✓	✓	**3.06**	0.36	**-2.86**	0.05	0.40	0.82	1.68	**3.20**	**2.57**	**2.97**
9	FTOT	?	?	?	?	?	**19.21**	**4.63**	**2.32**	**5.70**	**5.37**	0.14	0.29	-0.17	**2.45**	-0.32
10	FTOT	✓	✓	✓	✓	✓	0.47	-1.70	0.26	-1.22	-0.68	-0.75	0.18	1.01	0.75	0.37
11	FTOT	✓	✓	✓	✓	✓	1.09	0.77	1.02	1.21	1.14	1.76	**2.66**	**2.63**	1.45	1.55
12	FTOT	✓	✓	✓	✓	✓	-1.14	0.41	-0.98	-0.38	0.17	0.60	0.47	**2.59**	0.75	1.13
13	FTOT	✓	✓	✓	✓	✓	0.03	-0.38	0.17	-4.76	-1.08	-1.09	0.72	0.27	0.83	-0.07
14	FTOT	?	?	✓	✓	✖	**3.24**	1.87	1.73	1.59	**2.74**	-0.46	-0.32	-1.02	-0.18	-0.36
15	FTOT	✖	✖	✓	✓	?	0.53	0.84	1.09	1.92	1.59	0.39	-0.29	0.49	0.02	0.53
16	FTOT	✓	✓	✓	✓	✖	0.03	-0.06	0.02	-0.02	-0.61	-1.64	0.17	-0.67	0.28	-1.93
17	FTOT	✓	✓	?	✖	✖	1.08	-1.74	**-2.37**	**-6.53**	**-5.05**	**-2.21**	**-2.09**	-1.75	-1.70	-1.48
18	FTOT	✓	✓	✓	✖	✓	0.35	0.44	0.43	-1.14	0.29	0.99	0.68	1.82	0.74	0.98
19	FTOT	✖	✖	✖	✖	✖	-0.93	-3.12	-2.13	-0.40	-1.27	2.84	0.37	**8.92**	-0.88	0.69
20	FTOT	?	?	?	?	?	-0.07	-1.65	-1.27	-1.54	-1.59	-4.11	-2.70	-0.94	-1.41	-0.67
21	FTOT	✓	✖	?	✖	✓	0.81	0.81	1.71	0.92	1.83	1.23	0.50	1.40	1.83	1.93
22	FTOT	✓	✖	✓	✓	✓	-1.99	-1.82	**-3.32**	**-3.43**	**-3.87**	-1.54	-1.80	**-2.15**	**-3.47**	-1.90
23	FTOT	✓	✓	✓	✖	?	**-2.94**	**-4.82**	**-10.7**	**-9.12**	**-9.74**	**-6.18**	**-4.08**	**-8.88**	**-5.08**	**-5.45**
24	FTOT	?	?	?	?	?	0.42	0.59	0.44	0.55	0.27	-1.18	0.75	0.39	-1.71	0.86
25	FTOT	✓	✖	✓	✓	✓	1.60	1.45	-3.49	-1.11	-0.88	-1.18	-3.11	-4.28	-3.71	-1.55
26	FTOT	✓	✓	✓	✓	✓	0.20	0.26	0.43	0.06	0.25	0.78	-0.06	-0.15	0.44	-0.03
27	FTOT	✖	✖	✓	✓	✖	1.48	-1.99	-1.08	-1.01	-1.85	**-2.81**	-1.97	**-2.57**	**-3.27**	**-2.83**
28	FTOT	?	?	?	?	?	-0.95	-0.02	1.23	1.93	0.75	0.29	0.23	1.11	1.64	1.25
29	FTOT	✓	✓	?	✓	✖	-0.99	0.01	-0.48	-0.36	-0.08	-0.96	-1.57	-0.34	0.21	-0.46
30	FTOT	✓	✖	✓	✓	✖	-0.90	0.00	-0.75	-0.19	-0.01	0.51	-0.69	-0.04	0.21	-0.01
31	FTOT	?	?	?	?	?						0.83	0.88	0.26	-0.39	0.90
32	FTOT	✓	✓	✓	✓	✓	-0.42	-0.25	0.60	-0.14	0.53	-0.47	-1.75	**-4.52**	-1.20	-1.15
33	FTOT	?	✖	✓	?	✓	-1.93	**-3.72**	**-7.80**	**15.16**	**-2.62**	**-2.86**	**-2.46**	-0.64	**-3.08**	-1.74
34	FTOT	✓	✖	✓	✓	✓	-0.01	0.28	0.47	0.02	0.29	-0.68	0.70	0.63	0.09	0.33
35	FTOT	✓	✖	✓	✓	✓	0.06	0.30	0.49	0.09	0.25	0.07	0.63	-0.32	-0.77	0.24
36	FTOT	✖	✓	?	✓	✓	1.37	1.09	**-8.13**	**-6.52**	**-6.17**	**2.71**	**-2.49**	**-6.05**	**-4.58**	**-4.95**
37	FTOT	✓	✓	✓	✓	✓	-1.61	-0.22	-1.02	-1.61	**-2.89**	-0.24	0.33	-0.09	-0.25	-0.25
38	FTOT	✓	✓	✓	✓	✓						0.30	-0.22	-0.37	-0.37	-0.57
39	FTOT	?	?	?	?	?	0.68	0.28	0.36	-0.15	0.16	0.64	0.84	0.40	-0.55	1.42

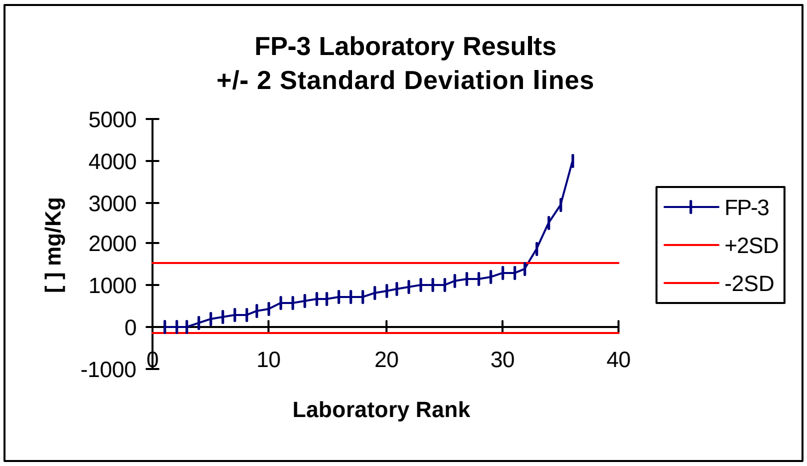
Legend

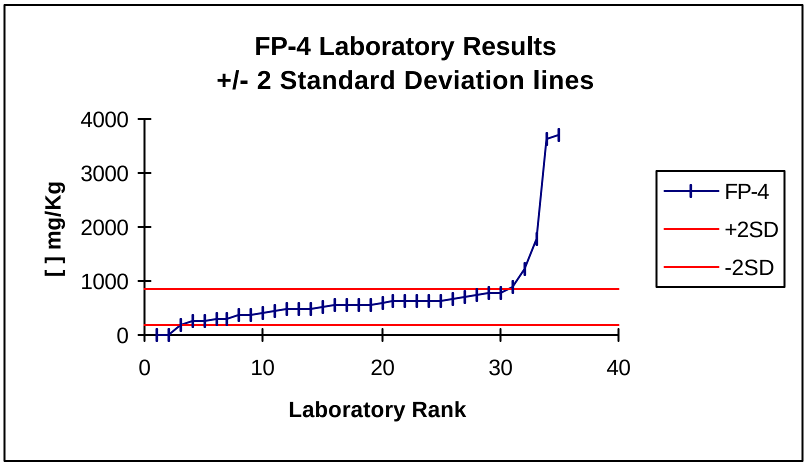
Hex/Ace	Hexane / acetone used?
Sox	Soxhlet used?
FID	FID used?
RF	RF criteria met?
DB-1	DB-1 column or equivalent used?
✓	Yes
✖	No
?	Insufficient information

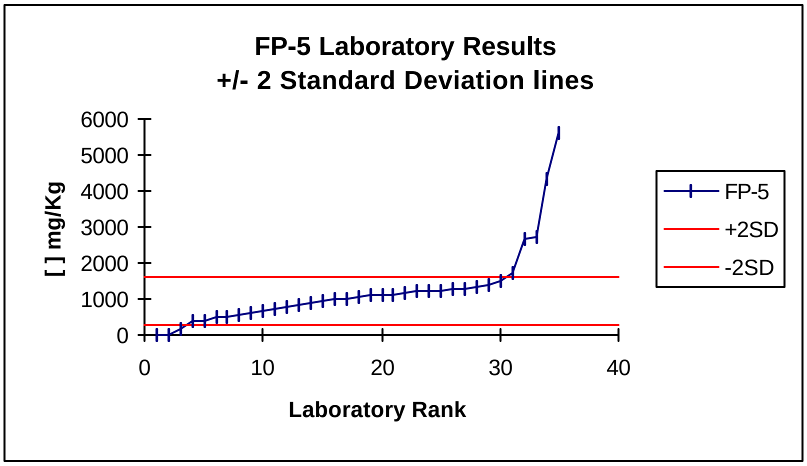
Appendix AA **FP-1 - FP-5 Sample Results Plots with +/-Standard Deviation Lines Outliers removed**



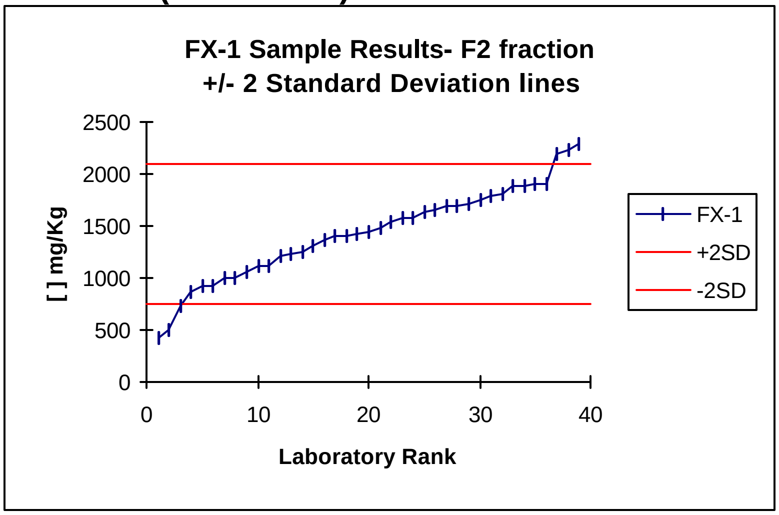


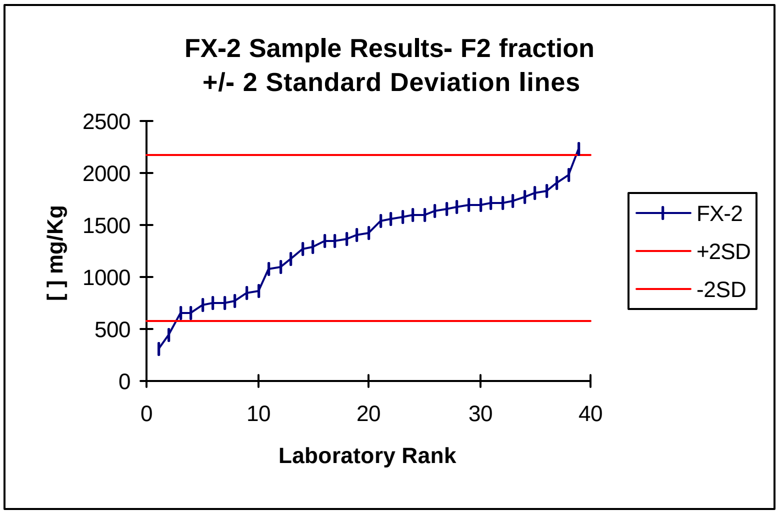


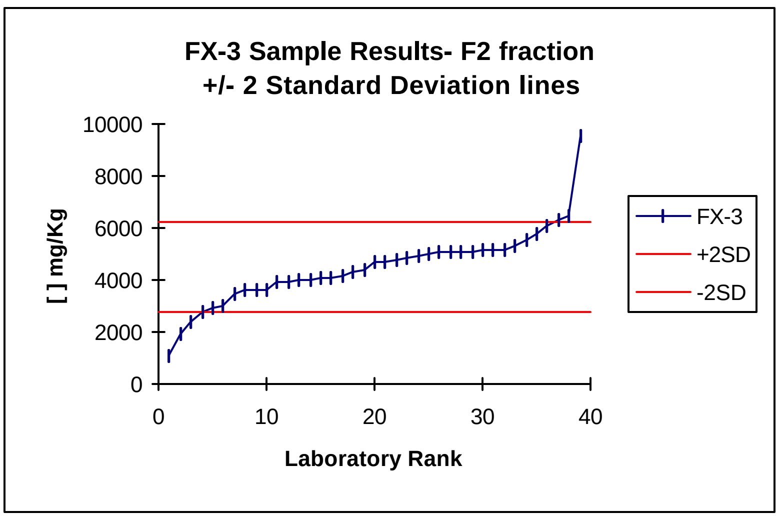

FP-4 Laboratory Results
+/- 2 Standard Deviation lines
4000
3000
2000
1000
0
[ ] mg/Kg
0
10
20
30
40
Laboratory Rank
FP-4
+2SD
-2SD

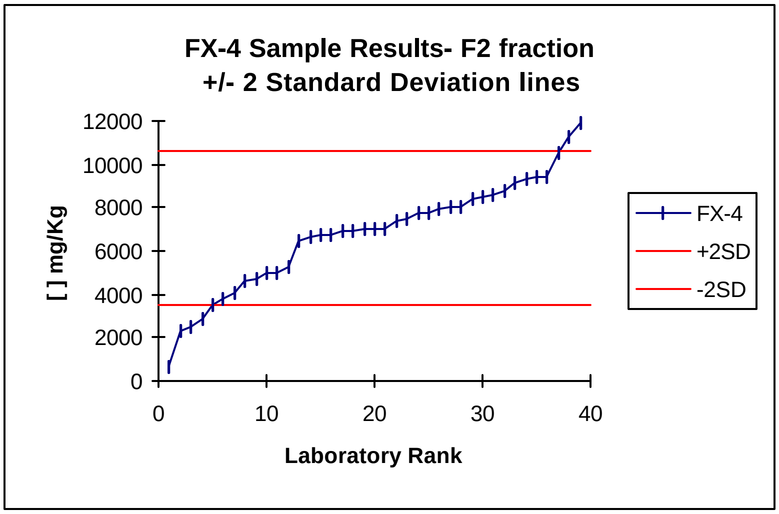

FP-5 Laboratory Results
+/- 2 Standard Deviation lines
6000
5000
4000
3000
2000
1000
0
[ ] mg/Kg
0
10
20
30
40
Laboratory Rank
FP-5
+2SD
-2SD

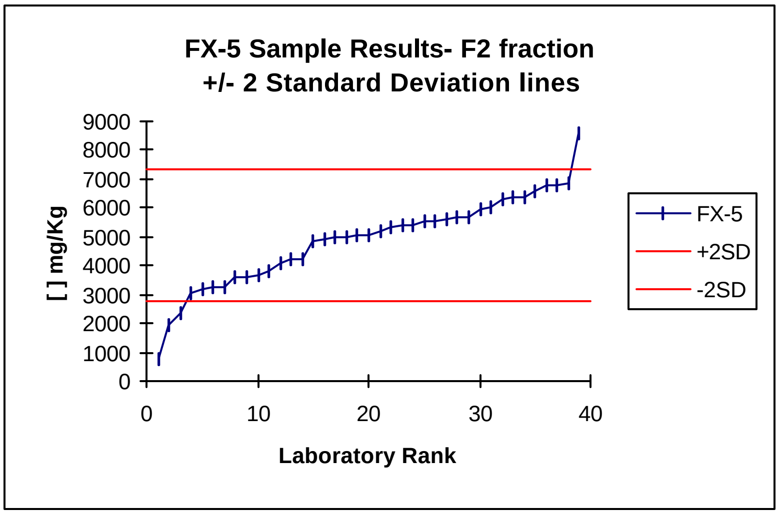
Appendix BB FX-1 - FX-5 Sample Results Plots with +/-Standard Deviation Lines (Fraction F2) Outliers removed



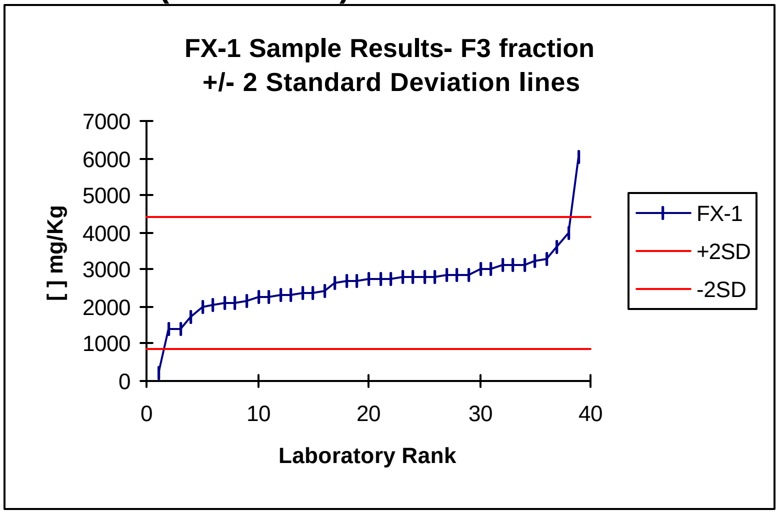


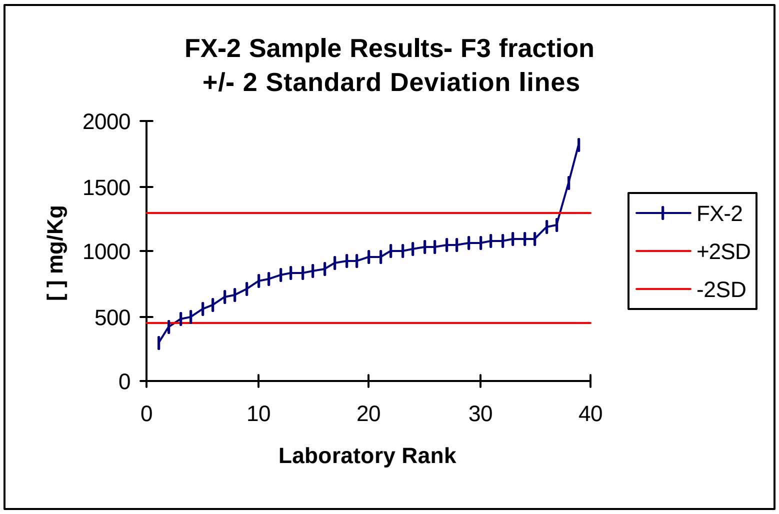


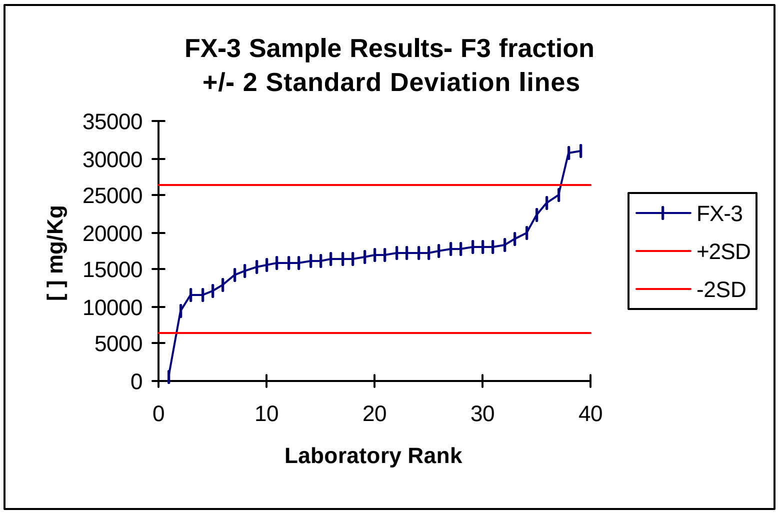

FX-4 Sample Results- F2 fraction
+/- 2 Standard Deviation lines
[ ] mg/Kg
12000
10000
8000
6000
4000
2000
0
0
10
20
30
40
Laboratory Rank
FX-4
+2SD
-2SD

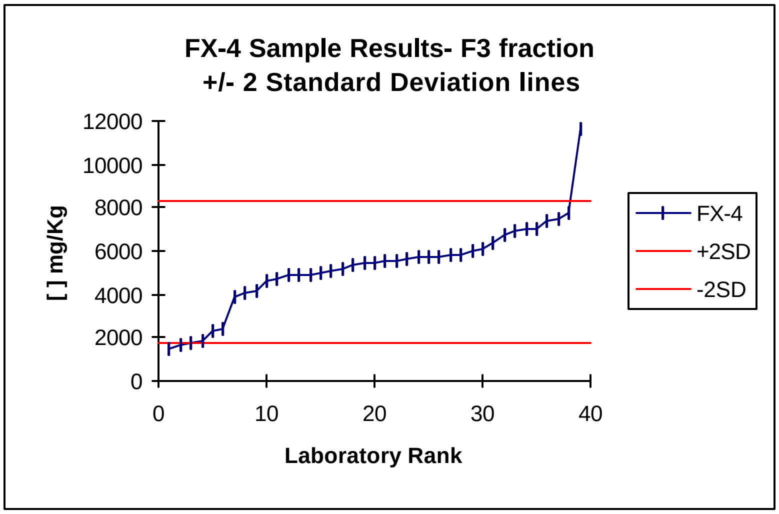

FX-5 Sample Results- F2 fraction
+/- 2 Standard Deviation lines
[ ] mg/Kg
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0
10
20
30
40
Laboratory Rank
FX-5
+2SD
-2SD

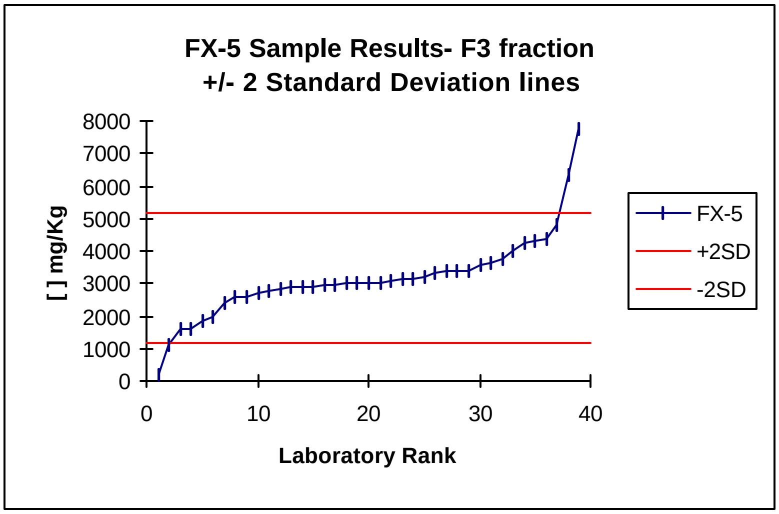
Appendix CC FX-1 - FX-5 Sample Results Plots with +/-Standard Deviation Lines (Fraction F3) Outliers removed



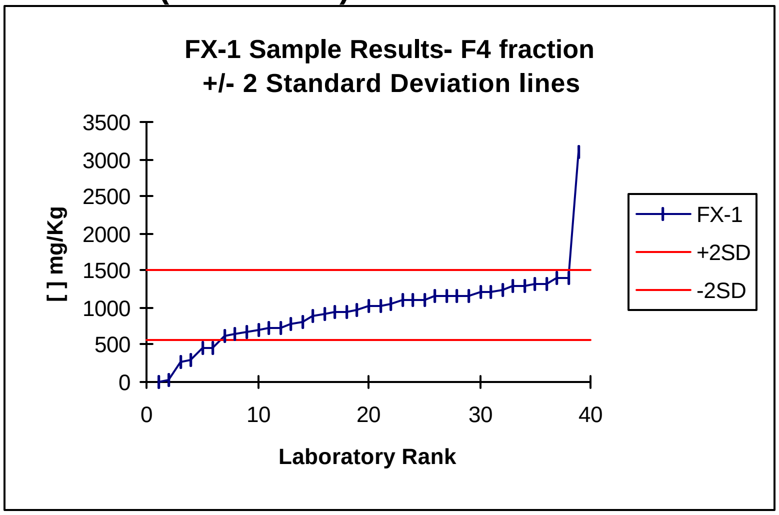


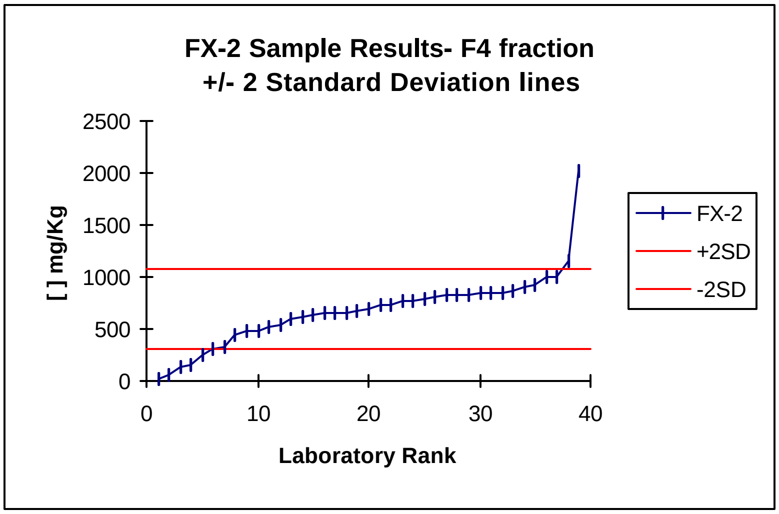


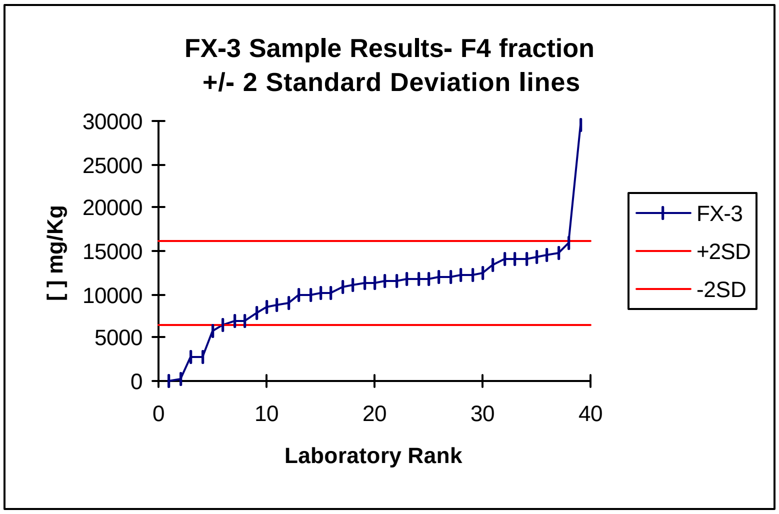

FX-4 Sample Results- F3 fraction
+/- 2 Standard Deviation lines
12000
10000
8000
6000
4000
2000
0
[ ] mg/Kg
0
10
20
30
40
Laboratory Rank
FX-4
+2SD
-2SD

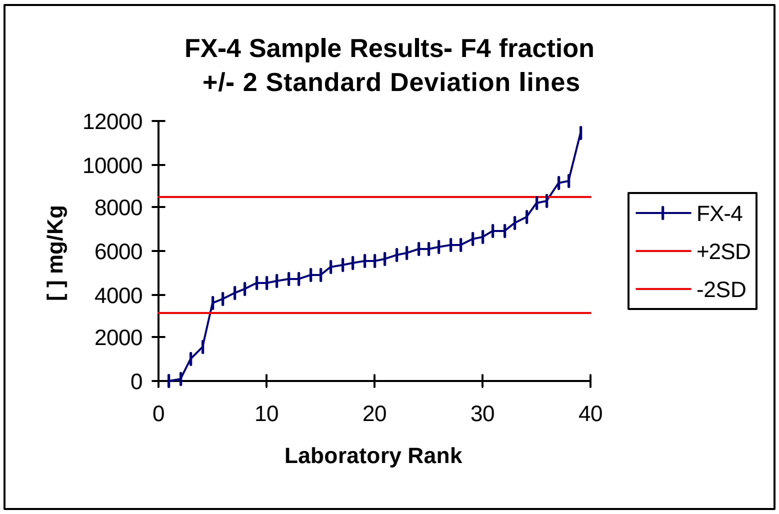

FX-5 Sample Results- F3 fraction
+/- 2 Standard Deviation lines
8000
7000
6000
5000
4000
3000
2000
1000
0
[ ] mg/Kg
0
10
20
30
40
Laboratory Rank
FX-5
+2SD
-2SD

Appendix DD FX-1 - FX-5 Sample Results Plots with +/-Standard Deviation Lines (Fraction F4) Outliers removed

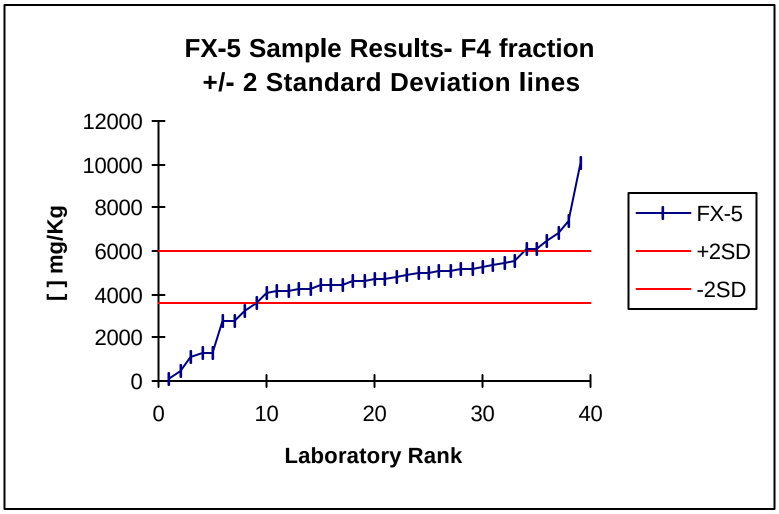






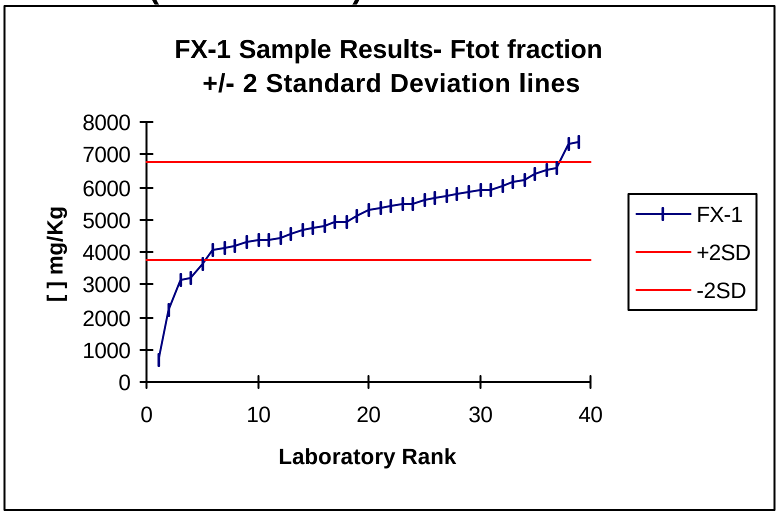


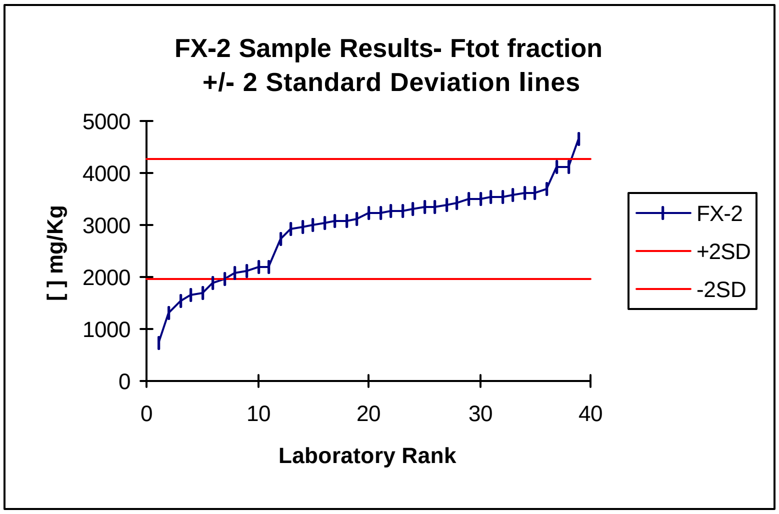
FX-4 Sample Results- F4 fraction
+/- 2 Standard Deviation lines
12000
10000
8000
6000
4000
2000
0
[ ] mg/Kg
0
10
20
30
40
Laboratory Rank
FX-4
+2SD
-2SD

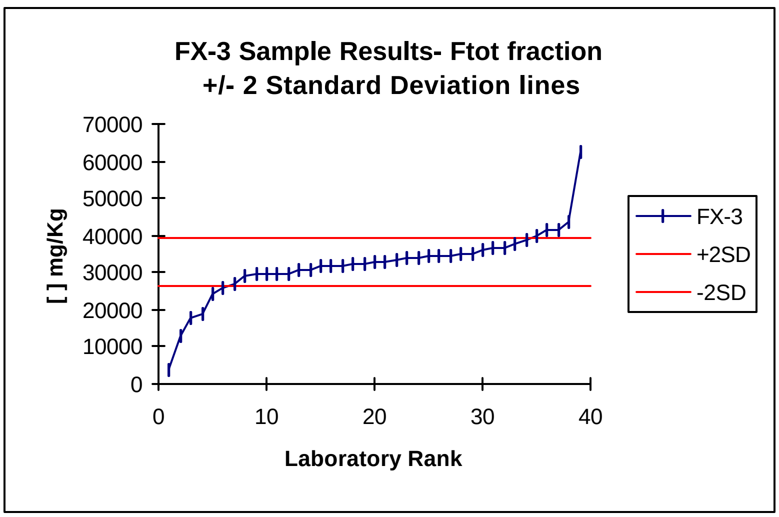


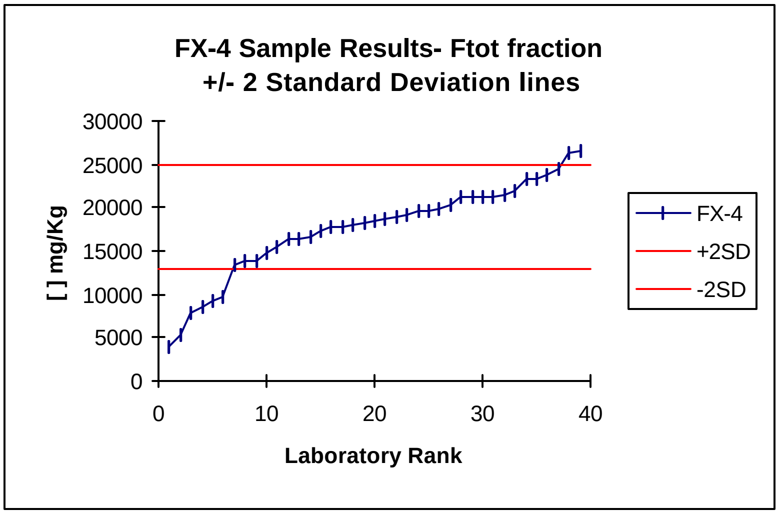
FX-5 Sample Results- F4 fraction
+/- 2 Standard Deviation lines
12000
10000
8000
6000
4000
2000
0
[ ] mg/Kg
0
10
20
30
40
Laboratory Rank
FX-5
+2SD
-2SD

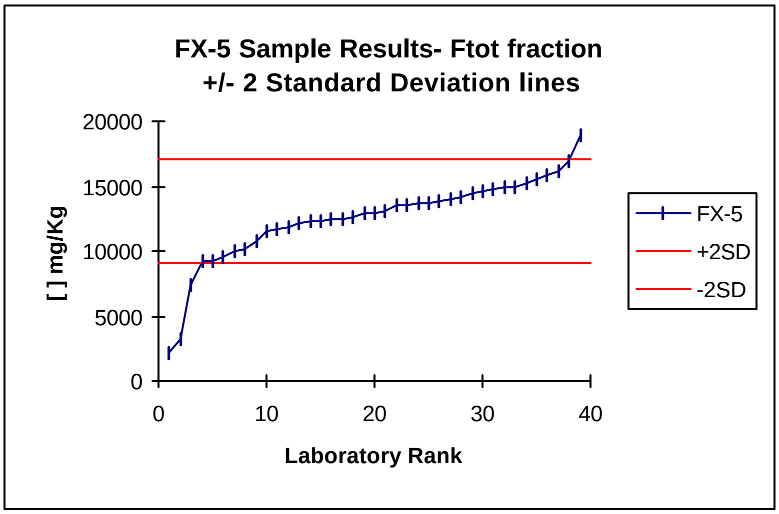
Appendix EE FX-1 - FX-5 Sample Results Plots with +/-Standard Deviation Lines (Fraction Ftot) Outliers removed








FX-4 Sample Results- Ftot fraction
+/- 2 Standard Deviation lines
[ ] mg/Kg
30000
25000
20000
15000
10000
5000
0
0
10
20
30
40
Laboratory Rank
FX-4
+2SD
-2SD


FX-5 Sample Results- Ftot fraction
+/- 2 Standard Deviation lines
[ ] mg/Kg
20000
15000
10000
5000
0
0
10
20
30
40
Laboratory Rank
FX-5
+2SD
-2SD

Appendix FF Summary of Client Comments

- When there is a need to analyze BTEX and PAH fractions as part of PHC procedure, GC/MS instrument must be used. For this reason, a development of a method, which allows to analyze F1, F2, F3, F4 fractions and BTEX, PAH individual compounds on one instrumental setup, would save a lot of time and labor for environmental laboratory. To do that, we have to come up with an appropriate standard other then Toluene or C10, C16 and C34. It could be a standardized gasoline, for volatile fraction and light oil, for heavier fractions of PHC.
- The standards used should be clearly indicated by each lab;
- GC chromatograms should be attached with the reports for reference and comparison;
- The area of the solvent blanks should be deducted, in particular for the lightly contaminated soils.
- Why is the final solvent for extractables Toluene? Toluene interferes slightly with the C10 peak. C10 falls on the tail of the toluene solvent. Can make a difference at low levels
- It is the requirement of our regulatory agency that the CCME Method for Petroleum Hydrocarbons in Soil is followed. Deviations from the method have not been permitted to date. No process is in place to verify whether or not validated deviations are acceptable.
- **Problems with 5 gram minimum weight requirement for split extracts.**

The method contains the following prescribed element: "A minimum sample size of 5 g dry weight for each analysis is required unless limited by insufficient sample."

By our interpretation of this requirement, if we are to perform an oil and grease (F4G) analysis and a GC analysis (F2-F4) from a single extract, we then need to extract a minimum of 10 grams of sample (dry weight). This requirement is excessive, and essentially eliminates the possibility of using an Accelerated Solvent Extraction device (ASE) to perform a combined extraction (using a 33mL cell size).

We do agree with and support the requirement for a minimum sample size of 5 grams, in order to achieve a representative sample.

We understand that the "5 grams for each analysis" requirement is intended to prevent requirements with sensitivity. However, the addenda that were recently distributed to labs participating in this study specify minimum requirements for sensitivity and detection limits. Provided that our total sample size is greater than 5 grams (to meet the criteria for representativeness), and provided we can also meet the detection limit requirements of the method, there should be no objection to our using than 5 grams of sample *for each test.*

We strongly suggest that the method be modified so that 5 grams is the minimum sample requirement, for purposes of obtaining a representative sample, regardless of whether the sample extract will be split. The detection limit requirements of the addenda are sufficient to dictate the sensitivity requirements of the method.

2. **In our view, the requirement that nC10, nC16, and nC34 responses be within ±10% of each other is too restrictive, and does not allow for normal analytical variability.**

It is extremely difficult to meet this requirement reliably using splitless injection. It can be met with on-column injection, but the on-column technique is very high-maintenance and unreliable (injection of high level samples, or samples containing non-volatile residues rapidly causes severe performance degradation). Use of on-column thus causes an unjustified high frequency of QC failures, leading to more re-work and significantly higher analytical costs. For the CCME method, we would support a more reasonable relative response requirement of ± 20% for C10, 16 and 34.

On-column is also required to meet the C50 relative response criteria, but some jurisdictions may substitute the F4G oil and grease determination in lieu of the C34-50 GC fraction, which is also our preferred approach to the method.

3. Clarification is required to the F2-F4 GC method in the following paragraph (found in the Calibration section):

"Linearity of the detector must be established using products such as diesel or motor oil and with the single compound calibration standards. Linearity must be within 15% in each of the calibrated ranges for products and within 10% for single compouns."

My interpretation of this is as follows:

- Linearity for diesel and motor oil must be established during method validation. [Verifying linearity with each calibration would be extremely impractical. It would involve running at least 2-3 standards of diesel and motor oil in addition to all the discreet hydrocarbon standards with each calibration, which for us is daily. This should be described under the method validation section, not under the calibration section].
- Linearity for single components must be verified daily with calibration standards.
- Linearity of products must be verified by comparison of hydrocarbon product concentration vs response.
- Linearity of single compounds must be verified by comparison of single compound concentration vs response.
- I interpret linearity "within 15%" to mean that no point within the range should deviate from the best fit line (using either an averaged fit or regression fit) by more than 15%.

4. Most liquid-transfer purge and trap autosamplers (i.e. Aquatek 70) cannot meet the 0.7 relative response requirement for decane relative to toluene (in F1) due to aliphatic discrimination problems.

This is not of particular concern to ALS, since we are not using liquid transfer autosamplers, but many labs do. If Teflon tubing is replaced with PEEK or glass tubing, the problem is improved, but still will not be resolved. Note also that aliphatics in water samples adsorb to the Teflon septum of the purge and trap vials that are used for calibration standards in this type of autosampler. This is a significant issue that needs further discussion, particularly if the method is ever to be used for water samples.

5. A detailed procedure for the determination of equivalence is needed immediately! Alberta is not accepting alternative methods until an equivalence procedure is established.

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