Environment Canada Environnement Canada

Design, Implementation and Results of CAEAL Interlab Study, Summer 2002

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Aussi disponible en Français

Prior Single Lab Validation

- Verified stability & linearity of calibration standards
- Verified GC conditions and response factions
- Precision estimated for each fraction
- MDL for each fraction determined
- Investigated use of 5-alpha-androstane as an internal standard - desirable
- Determined optimum method for silica gel clean–up

Reasons for the Interlab Study

- to confirm that the CWS PHC method has suitable precision and accuracy
- to confirm the data meets all CCME & potential legal requirements
- to produce proficiency testing samples with stability of a minimum of 10 weeks
- to generate an estimate of uncertainty in determination of PHC fractions that could be used for future interlab studies
- to establish study design criteria that could be used as a model for possible future proficiency testing studies
- to establish a source of suitable standards and reference materials
- to promote the use of the analytical method for the CWS.

Interlab Test samples -1

- 10 solid samples (4 natural soil, 6 clay) that were spiked with weathered hydrocarbon products,5 for volatiles, F1 and 5 for extractables F2,F3 and F4
  - Soils selected from well characterized sources
  - Samples spiked as difficulty to obtain homogeneity with real contaminated soils
  - All of the sample used to avoid sub-sampling problems

Soils used

- Clay loam & Sandy loam
  - Both dried at 60 deg for 3 days & sieved
- Red Art clay
- Ball clay
- Kaolin clay
- All irradiated to ensure stability
- Same weight in each vial – all used
- PHCs spiked into vials

Interlab Test samples - 2

- 10 ampouled standards to verify calibration and gas chromatography
  - 5 for volatiles and
  - 5 for extractables

Sample composition

F1 samples

	FP-1	FP-2	FP-3	FP-4	FP-5
Gas (weathered)	X	X	X	X	X
5W30 oil	X	X		X	X
2-stroke oil					
diesel					
approx. ratio	1:1	1:1		1:3	1:3

F2,F3,F4

	FX-1	FX-2	FX-3	FX-4	FX-5
Gas (weathered)	X				X
5W30 oil	X		X		
2-stroke oil		X	X	X	X
diesel		X		X	
approx. ratio	1:1	1:1	1:2	2.3:1	1.4:1

Pre-shipment Testing of Samples

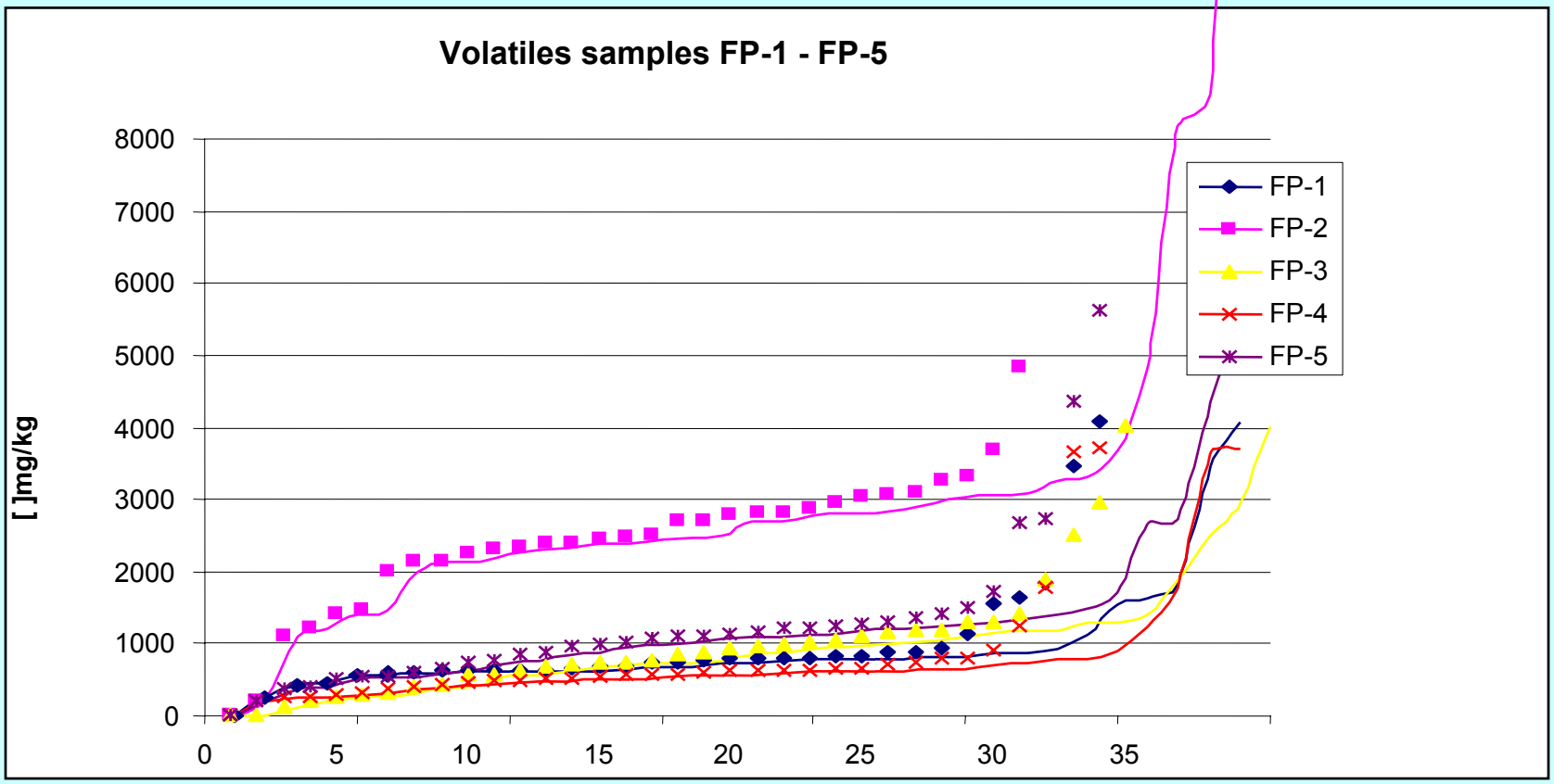
- F1 analysed by P&T with GC-MSD
  - (FID not available)
- Variable losses
  - Worst with kaolin
  - Ranges from 12 to 30%
- F2 to F4 –analysed as written
  - no losses, RSD from 7 to 33%

Participants

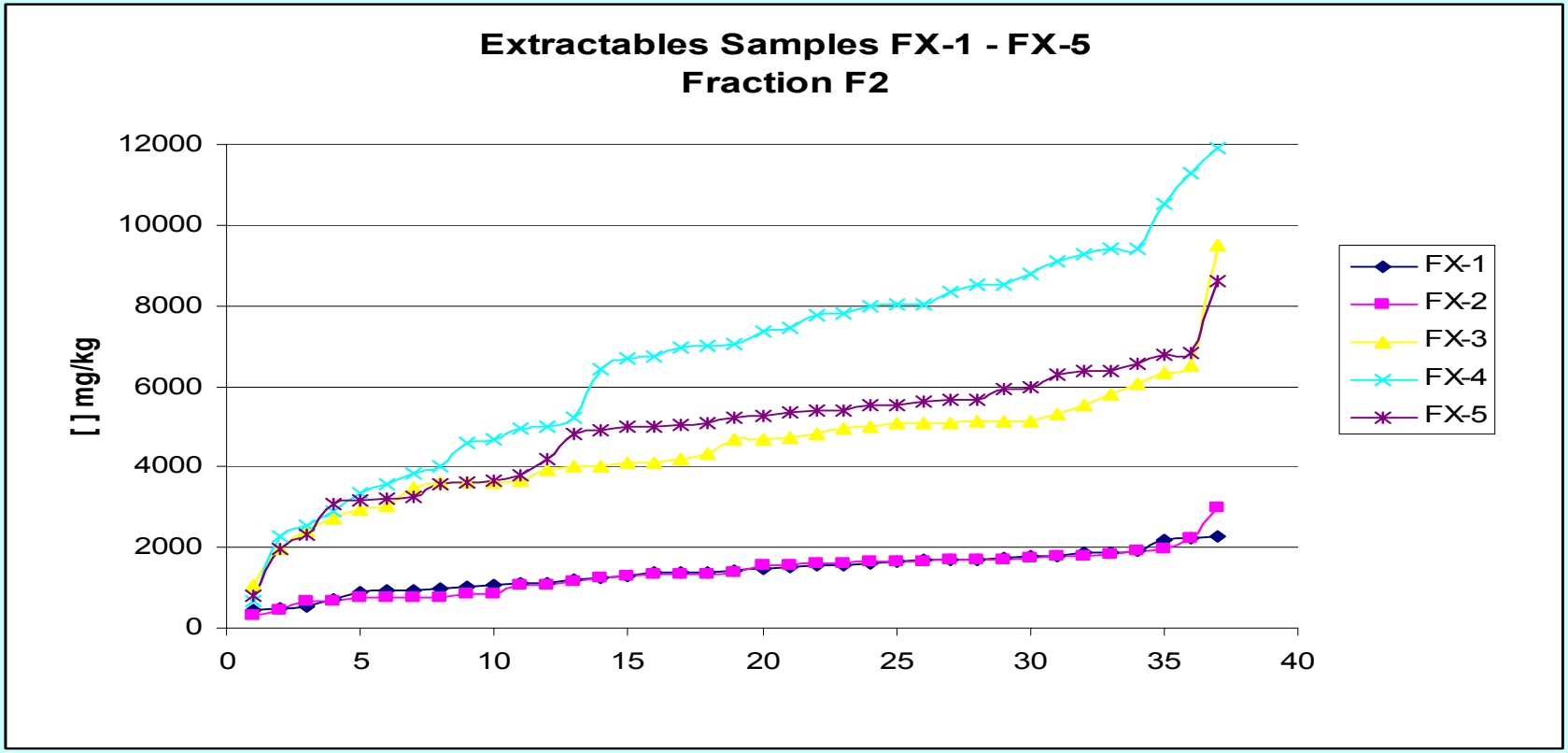
- Contacted by CAEAL
- 61 sets sent out to 41 labs
- 39 data sets returned (some incomplete) – 1 from Brazil
  - Impossible to track which vials from duplicates were used as data not returned.
- Some labs had difficulty meeting deadline

Data processing

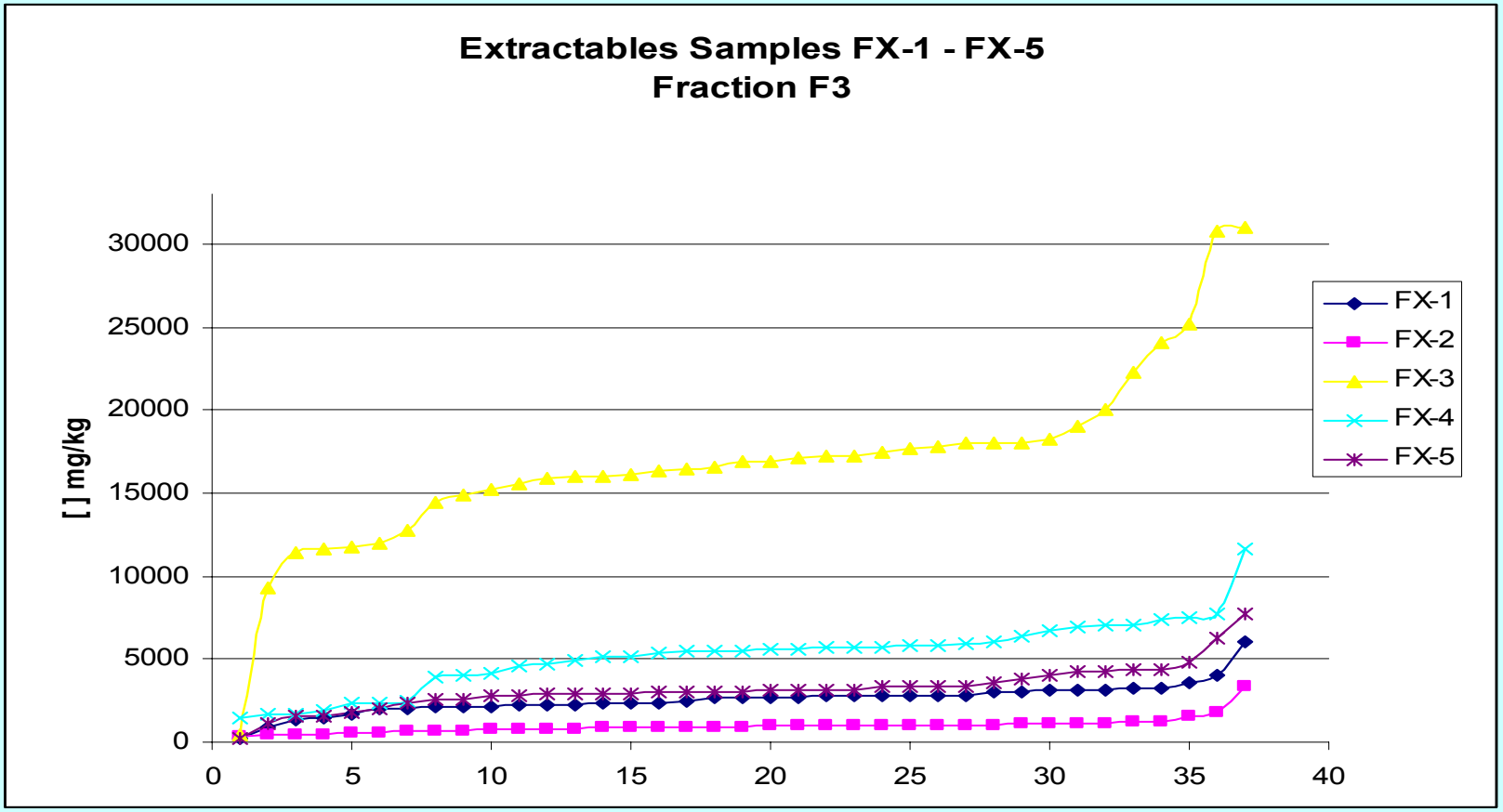
- Samples were ordered by results for each standard and soil, and fraction
- Eliminated outliers (> 2SD)
  - Visually confirmed
- Mean, medians, SD, & RSD calculated for each standard and each soil sample
- Plotted for visual expression
- Only H.Malle knows identity of participating lab



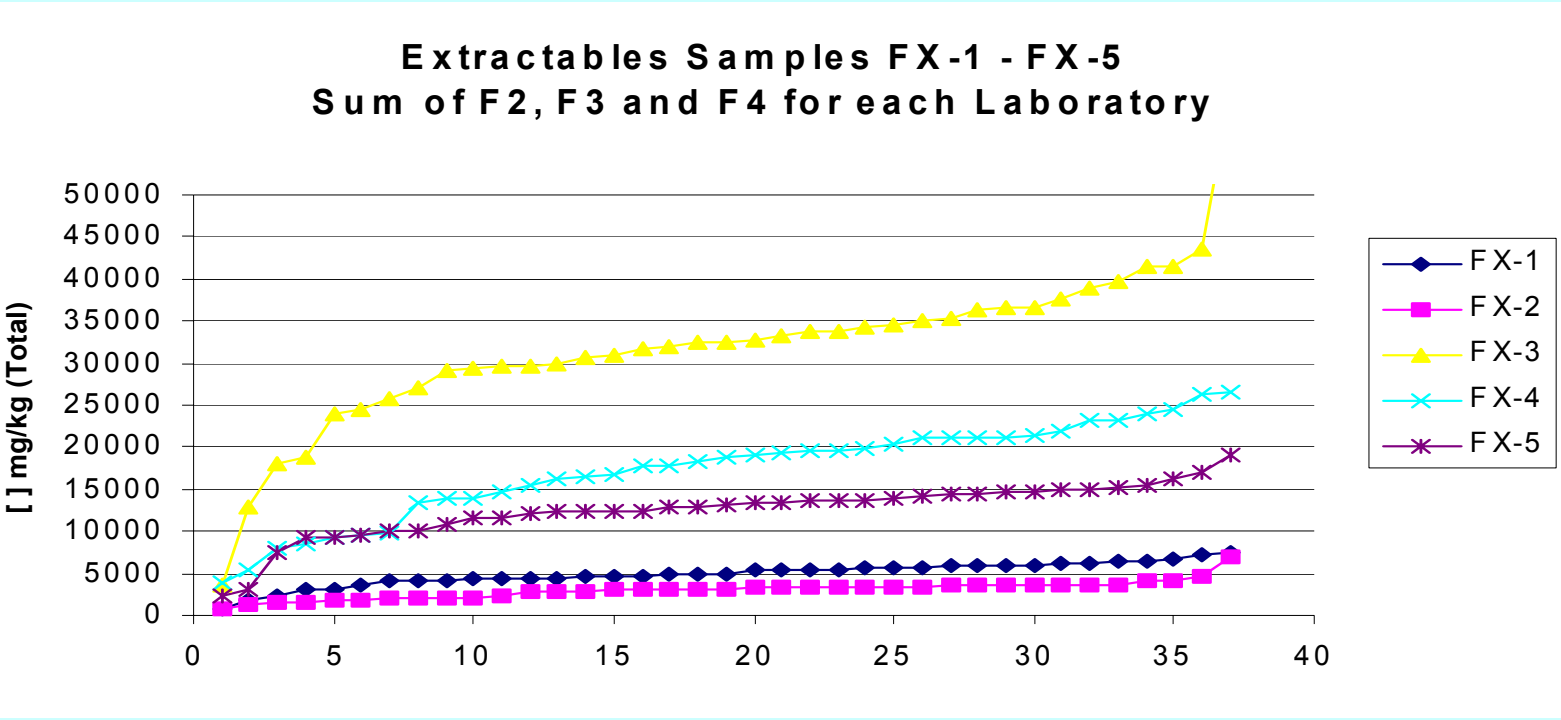
Sample	FP-1	FP-2	FP-3	FP-4	FP-5
Target values	683	2734	1456	4591	1183
All labs	34	34	35	34	34
Average	938	3221	967	758	1264
STD DEV	800	3137	822	802	1112
RSD	85	97	85	106	88
Median	741	2600	845	571.5	1084
Non-outlier labs	23	23	28	27	27
Average	702	2636	801	530	953
STD DEV	100	376	345	152	325
RSD	14	14	43	29	34
Median	670	2700	797.5	570	1000



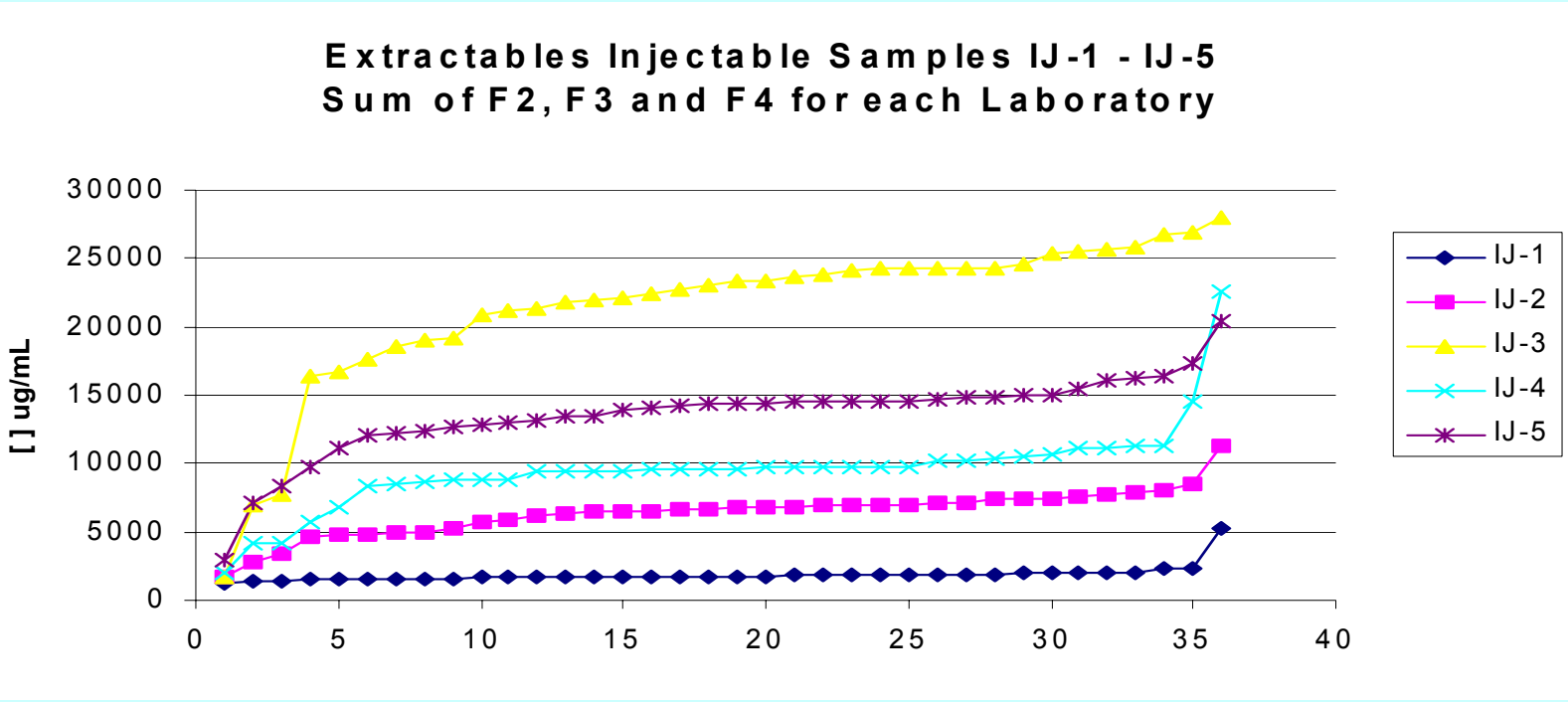
Samples	FX-1	FX-2	FX-3	FX-4	FX-5
All labs	37	37	37	37	37
average	1401	1371	4470	6702	4890
stddev	475	547	1461	2651	1551
rsd	34	40	33	40	32
median	1430	1400	4700	7031	5200
Non-outlier labs	31	33	31	32	33
average	1409	1356	4440	6853	5069
stddev	341	411	850	2054	1117
rsd	24	30	19	30	22
median	1,430	1,400	4,700	7,196	5,243



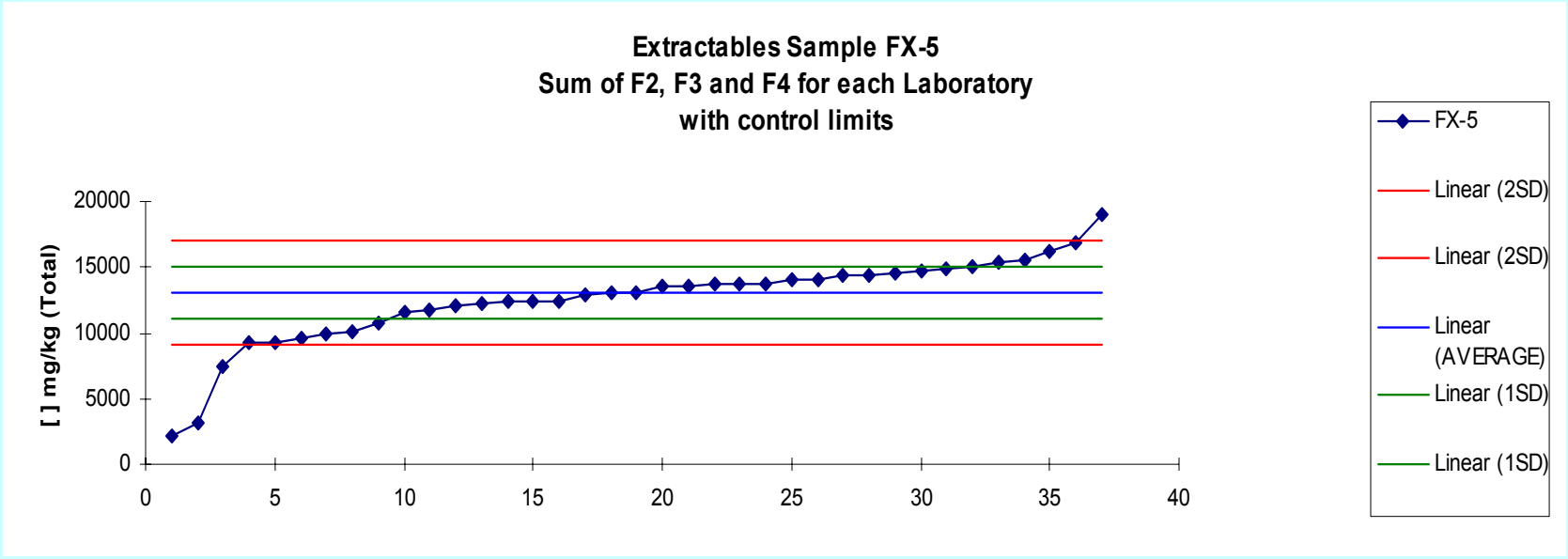
Sample	Fx-1	FX-2	FX-3	FX-4	FX-5
All labs	37	37	37	37	37
average	2577	977	16905	5204	3209
stddev	932	496	5359	2052	1328
rsd	36	51	32	39	41
median	2670	950	16900	5530	3040
Non-outlier labs	29	25	25	29	28
average	2625	986	16916	5759	3272
stddev	384	120	1290	1013	552
rsd	15	12	8	18	17
median	2680	1020	16906	5688	3115



	FX-1	FX-2	FX-3	FX-4	FX-5
Total labs	37	37	37	37	37
average	4916	3012	31874	17332	12503
Std dev	1445	1083	9501	5748	3324
rsd	29	36	30	33	27
median	4935	3220	32410	18765	13036
Non-outlier labs	30	33	31	30	33
average	5206	2966	32913	19571	13055
Std dev	824	718	4526	3538	1993
rsd	16	24	14	18	15
median	5315	3220	32784	19582.5	13480



	IJ-1	IJ-2	IJ-3	IJ-4	IJ-5
Total labs	36	36	36	36	36
average	1856	6396	21386	9536	13585
std dev	617	1689	5657	3161	2973
rsd	33	26	26	33	22
median	1743	6721.5	23164.5	9600.605	14391.5
Non-outlier labs	30	32	26	29	29
average	1744	6593	23766	9768	14202
std dev	175	1019	1663	819	1149
rsd	10	15	7	8	8
median	1740	6855.5	23985	9700	14408
Target	1600	5820	23500	7500	10200



Total labs	37
average	12503
std dev	3324
rsd	27
median	13036

Non-outlier labs	33
average	13055
std dev	1993
rsd	15
median	13480
Target	15000

Conclusion -1

- Study met aims
- Overall precision across all soil samples/ fractions was ~23 %RSD (ampouled standards were ~15%RSD)
- 75% labs proved their capability to provide good results with this method.
- Can produce Reference Materails for PT studies
- Method has been validated!!!

Conclusion - 2

- Lab that failed:
  - no obvious overall answer
  - Maybe getting the average 70% for CnC10, nC16 & nC34 is a problem?
  - The further the deviation from the method more chance of failure

Points for discussion

- Why did labs not follow method?
  - Solvent?
  - Columns?
  - Detectors?
- How to achieve the 70% RF easily?
- How can we improve the method?
- Reaction to the comments?

Acknowledgements

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