Test Group Summary Report
C77 Pesticides in Soil
June 2020 PT Round

Issued: October 1, 2020

PTC | Proficiency Testing Canada

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1.0 The Proficiency Testing Report

The Proficiency Testing Report consists of two parts.

- *PTC Proficiency Testing Report*: This report contains participant-specific data and other confidential information. This report is emailed to participants at the end of the PT round.
- *Test Group Summary Report*: A Test Group Summary Report is created for each quantified test group at the end of the PT round. These reports contain more detailed information on the round than are found in the participant-specific PTC Proficiency Testing Report. These reports do not contain any confidential information and are made available on the PTC web site.

2.0 Definitions

The participant-specific PTC Proficiency Testing Report contains some terms that new participants may not be familiar with.

Code:	The registration code that is unique to each analyte that a participant is registered for.
App:	If a participant is accredited by CALA, this three-digit number is the appendix number that the accredited method is assigned to.
N:	The number of participants results that were used to calculate the summary statistics. This excludes qualified data (e.g., <) and any results that were flagged as outliers.
Assigned:	The Assigned Value is the robust mean of the reported results, outliers excluded. This is often referred to as the "target" value.
$\pm u$*:*	The uncertainty of the assigned value.
Reported:	The result reported by the participant.
s:	The Standard Deviation of Proficiency Assessment. This value is used to determine the acceptance limits for the PT evaluation.
z-Score:	A value assigned to each reported result that is a measure of the degree to which it deviates from the Assigned Value.
Score:	The composite score of the four results reported for each analyte. It is normalized to a score out of 100.
Bias:	A flag assigned if bias is detected using the re-scaled *z*-score procedure.

3.0 Scoring System

Participant performance is evaluated for each proficiency testing sample by a quantitative method that is consistent with ISO/IEC 17043:2010 *Conformity assessment — General requirements for proficiency testing*, the *International Harmonized Protocol for Proficiency Testing of (Chemical) Analytical Laboratories* (2006), and ISO 13528:2015 *Statistical methods for use in proficiency testing by interlaboratory comparisons*.

The following is a brief description of the evaluation procedure used by PTC. The detailed evaluation procedure is described in PROC09 – PT Evaluation *Procedure*, which is available on the PTC website www.PTCanada.org).

3.1 HOMOGENEITY AND STABILITY ASSESSMENT

Homogeneity and stability are assessed using participant data. Regression analysis is performed on reported result against order of sample production (Homogeneity) and reported result against date of analysis (Stability). If the slope is significantly different than zero for either then the Standard Deviation of Proficiency Assessment (s) is increased to minimize the impact.

3.2 THE Z SCORE

A "z-score" is calculated for each reported result as follows:

$$z = \frac{(x - \overline{X})}{s}$$

where: x = participant result;
$\overline{X}$ = the Assigned Value;
s = the Standard Deviation for Proficiency Assessment.

The assigned value $\overline{X}$ is generally estimated from the inter-laboratory Robust mean after outliers due to obvious gross errors (e.g., reported in wrong units) have been removed.

The Standard Deviation for Proficiency Assessment, s, is determined as follows:

- The inter-laboratory Robust standard deviation (stdev) is calculated using reported results, obvious outliers removed;
- The expected inter-laboratory standard deviation (s!) is estimated from regression equations derived from previous studies (see PROC11- *PT Regression Equations* for details);
- If s! is higher than stdev then si is used in the z score equation;
- If s! is lower than stdev then stdev is used in the z score equation;
- When a laboratory reports its detection limit, s will be estimated using a pooled variance procedure that uses both the inter-laboratory data and the reported detection limit.

3.2 COMPOSITE (PT) SCORE

Since each PT round involves four or two separate samples of distinct concentration for each test, it is necessary to calculate a composite PT score for each test to determine overall performance. The composite score is calculated by first averaging the absolute *z*-scores for the four results and then calculating a final score as 100 + (-15 x avg |z|).

Acceptable PT Scores equal or exceed 70.

3.3 IDENTIFYING BIAS

The proficiency testing report provides flags for bias. These are determined using the re-scaled *z*-score procedure.

$$RSZ = \frac{\sum z}{\sqrt{N}}$$

where z = the z- score
N = the number of samples

Flags are assigned for each test group/parameter combination as follows:

RSZ ≥ -2 and ≤ 2	no flag assigned
RSZ > 2	H (High)
RSZ > 3	VH (Very High)
RSZ < -2	L (LOW)
RSZ < -3	VL (Very Low)

3.4 DEVIATIONS FROM EVALUATION PROCEDURE

Other than changes to the Standard Deviation of Proficiency Assessment due to homogeneity or stability flags, any deviation from the published evaluation procedure is described on the cover page(s) of the final *PTC Proficiency Testing Report*.

4.0 PT Round Specific Data Summary

The following pages provide more detailed information about the PT round indicated in the cover page of this report than is found in the participant-specific PTC Proficiency Testing Report. The graphical representations and the statistical summaries are based upon the data after outliers have been removed.

4.1 SUMMARY STATISTICS

In addition to some of the statistics found in the customer reports, this table includes additional summary statistics such as Median, different measures of dispersion, the number of outliers removed, the number of results in the Questionable range (|z| between 2 and 3) and the Unacceptable range (z > 3), and whether a data set was flagged for Homogeneity or Stability. This section also includes sorted scatter plots of the data for each sample.

4.2 z- SCORE PLOTS

The z-scores for each sample are ranked in increasing order and plotted. When the data is normally distributed, the plot should show a slight sigmoidal curve, with an equal number of points above zero as below. Each bar in these plots is colour-coded to indicate the analytical method used by the participant.

4.3 KERNEL DENSITY PLOTS

Kernel density plots are generated for each data set. These plots are a graphical way to represent the overall data distribution and are used to visualize possible deviations from normality and unimodality.

4.4 STABILITY AND HOMOGENEITY PLOTS

Plots of reported result against analysis date, and reported result against order of bottling are displayed, along with the regression line. These regression analyses are used to determine if the SDPA should be adjusted due to homogeneity or stability.

4,4'-DDT (P,P'-DDT)

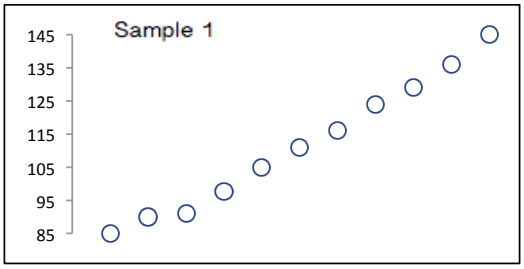
Summary Statistics

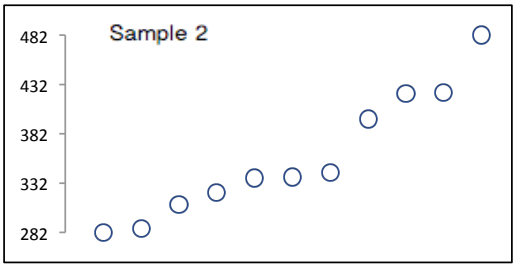
Statistic	C77-1	C77-2	C77-3	C77-4
N	11	11	11	11
Median	111	338	436	142
Robust Mean	112	356	443	141
U	8.6	26	20	12
Robust Standard Deviation	22.7	67.8	53.6	31.7
Regression Standard Deviation	27.7	82.6	102	34.2
Stability Flag				
Homogeneity Flag				
Standard Deviation Used	27.7	82.6	102	34.2
Outliers	1	1	1	1
|z|>3.0	0	0	0	0
2<|z|<3	0	0	1	0

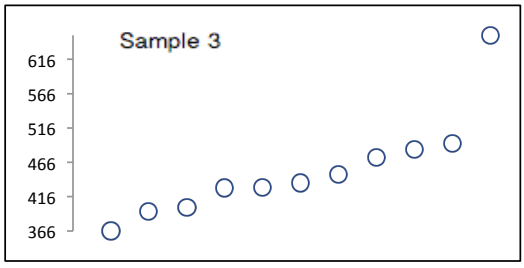
Methods Used

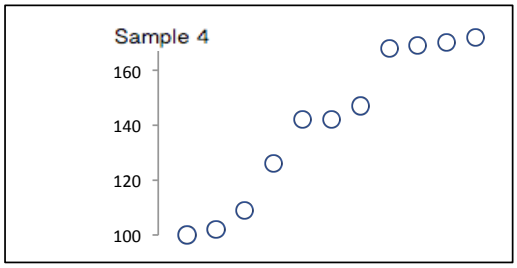
Method	C77-1	C77-2	C77-3	C77-4
GC/MS	4	4	4	4
GC/ECD	4	4	4	4
GC/MSHR	1	1	1	1
GC/MS/MS	1	1	1	1
GC/ECD/SHKE	1	1	1	1

All summary stats and the plots below are based on the data excluding any flagged outliers



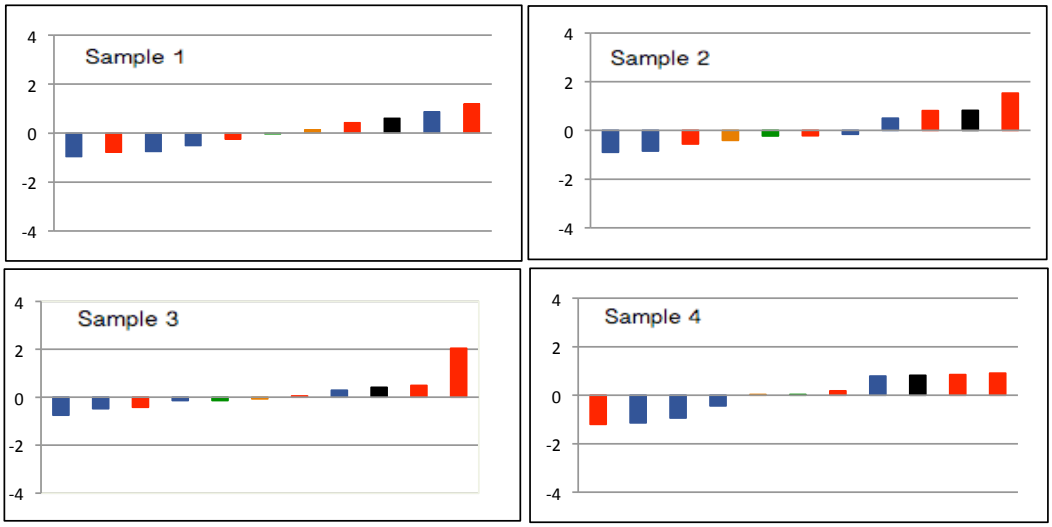




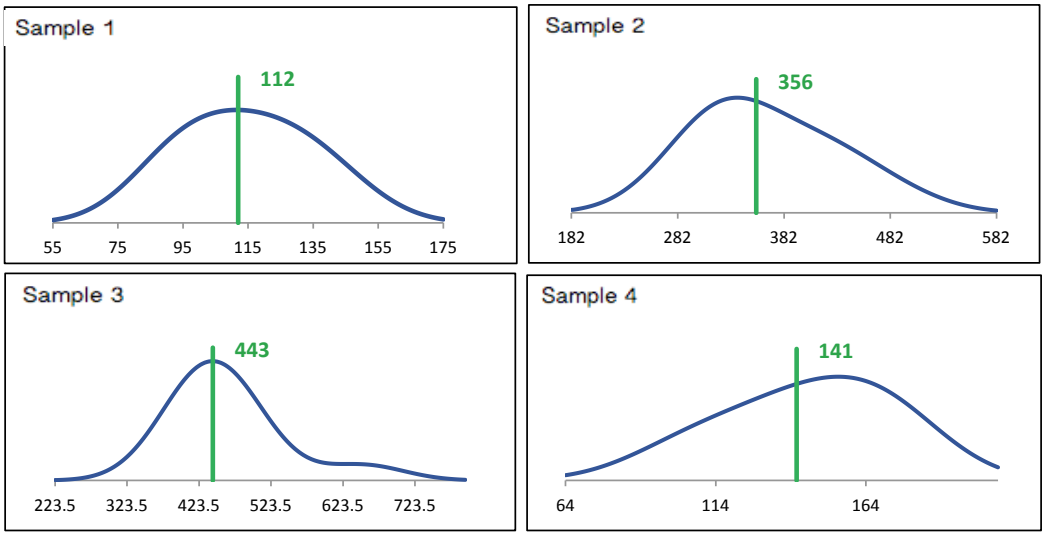


4,4'-DDT (P,P'-DDT)

z-Score Plots



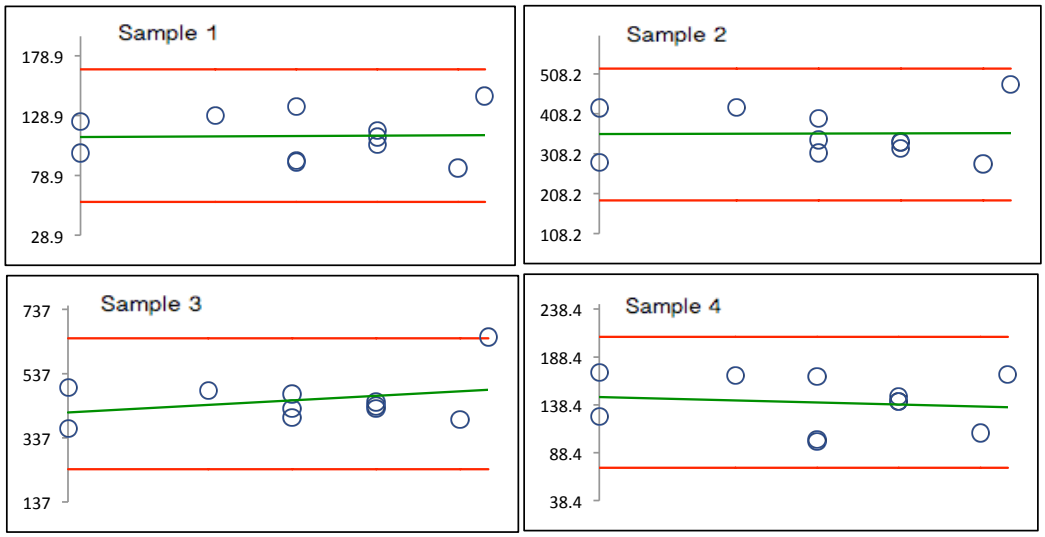
Kernel Density Plots



Annex A Summary by Analyte

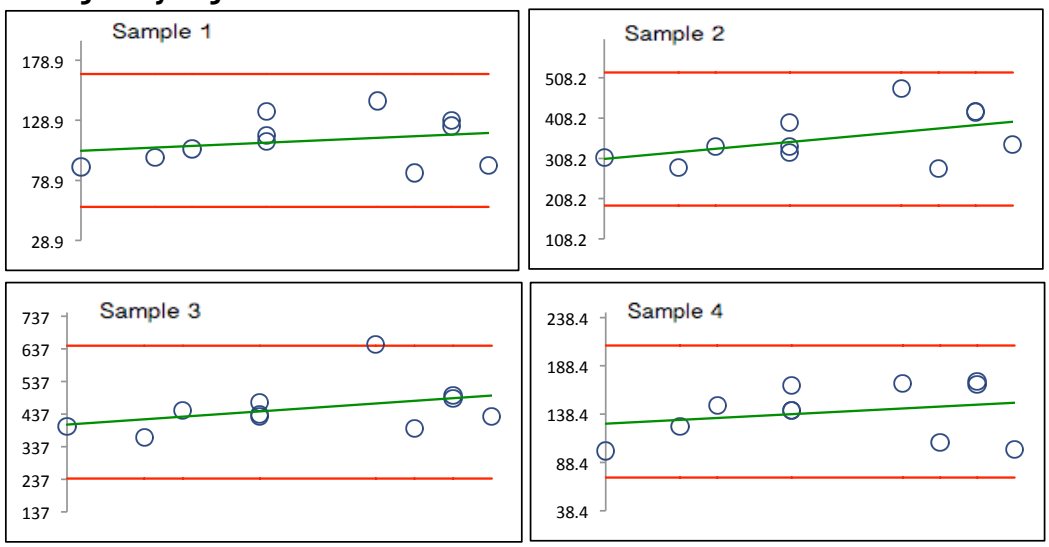
4,4'-DDT (P,P'-DDT)

Stability Regression



Reported results (Y-axis) plotted against reported analysis date (X-axis)

Homogeneity Regression



Reported results (Y-axis) plotted against bottling order (X-axis).

ALDRIN

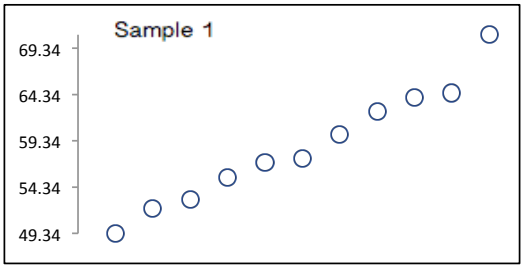
Summary Statistics

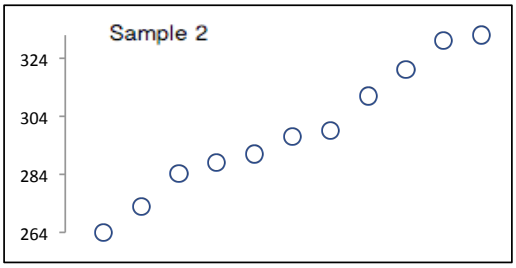
Statistic	C77-1	C77-2	C77-3	C77-4
N	11	11	11	11
Median	57.4	297	236	331
Robust Mean	58.5	299	235	324
U	2.6	10	9	10
Robust Standard Deviation	6.79	25.2	23.1	25.3
Regression Standard Deviation	13.7	62.4	49.5	67.5
Stability Flag				
Homogeneity Flag				
Standard Deviation Used	13.7	62.4	49.5	67.5
Outliers	1	1	1	1
|z|>3.0	0	0	0	0
2<|z|<3	0	0	0	0

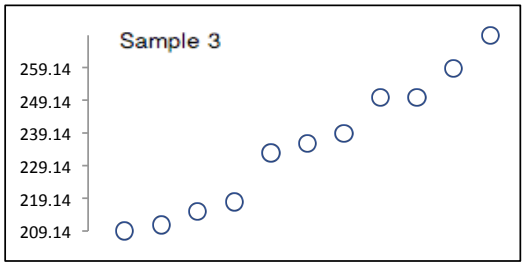
Methods Used

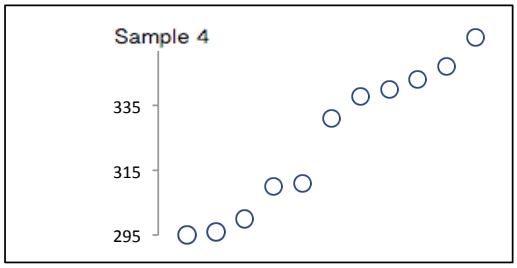
Method	C77-1	C77-2	C77-3	C77-4
GC/MS	4	4	4	4
GC/ECD/SHKE	1	1	1	1
GC/ECD	4	4	4	4
GC/MSHR	1	1	1	1
GC/MS/MS	1	1	1	1

All summary stats and the plots below are based on the data excluding any flagged outliers



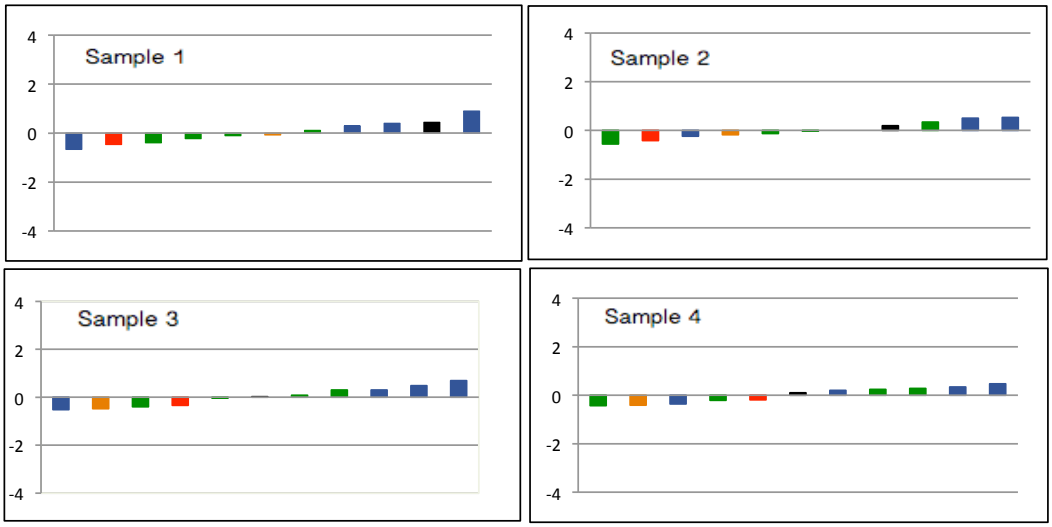




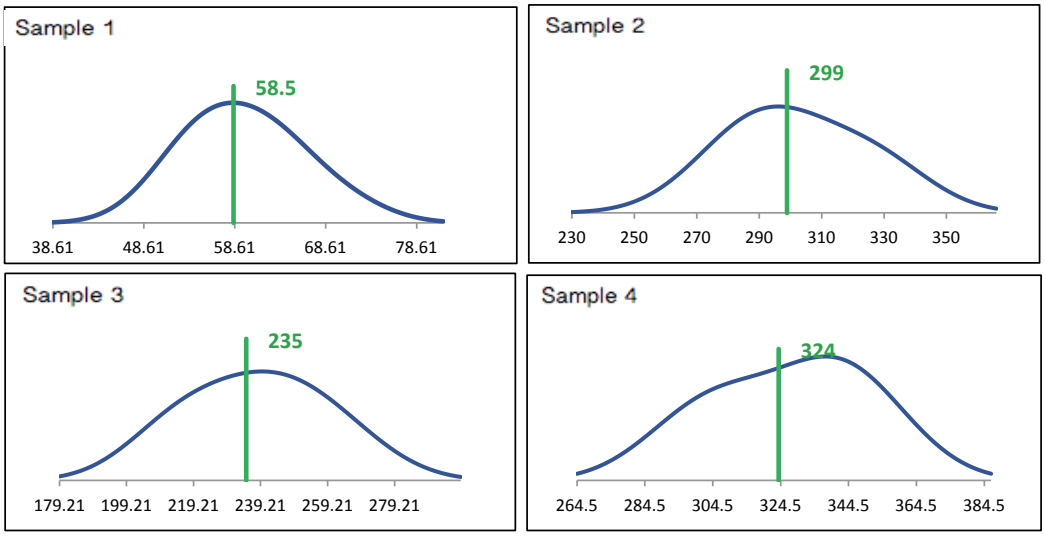


ALDRIN

z-Score Plots



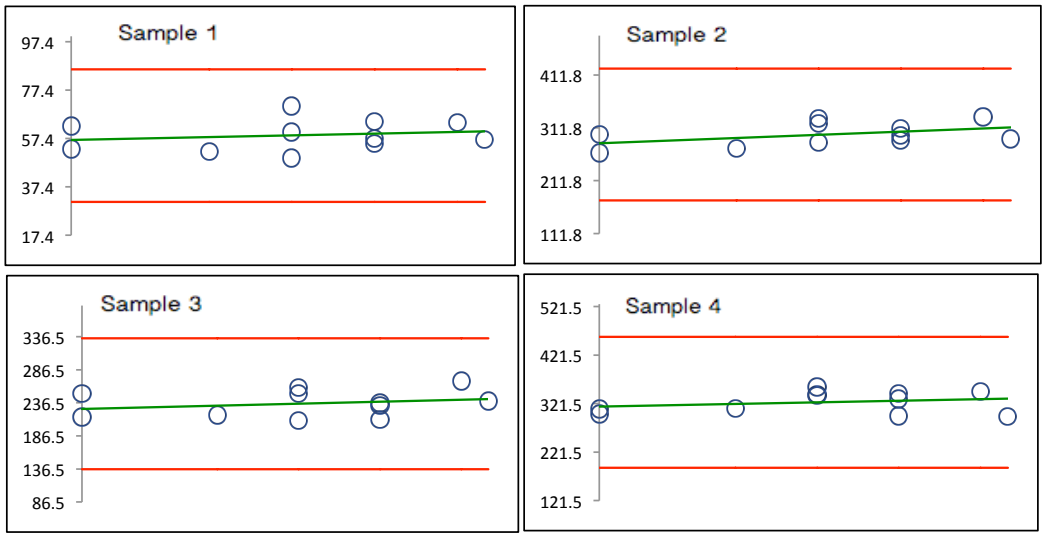
Kernel Density Plots



Annex A Summary by Analyte

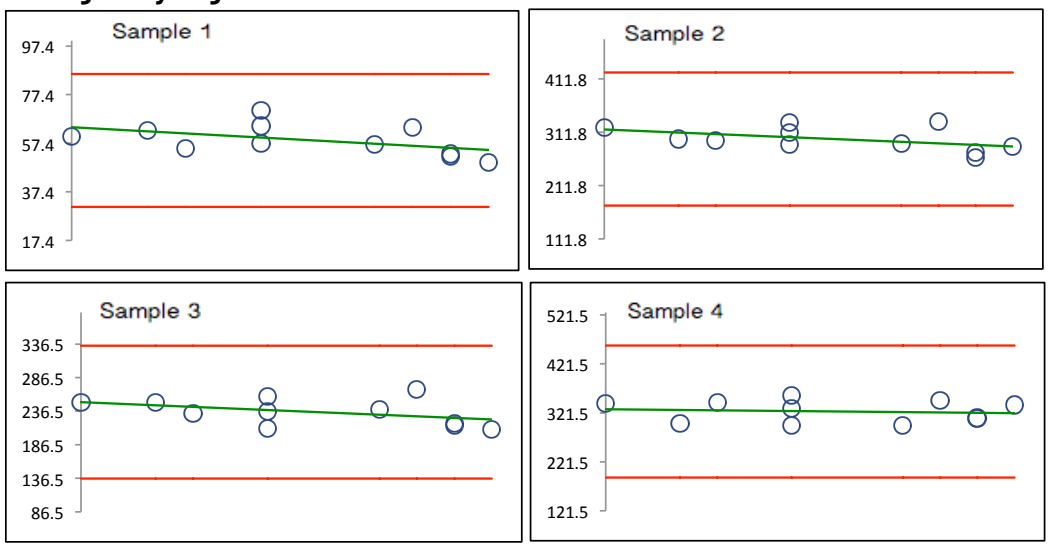
ALDRIN

Stability Regression



Reported results (Y-axis) plotted against reported analysis date (X-axis)

Homogeneity Regression



Reported results (Y-axis) plotted against bottling order (X-axis).

ALPHA-BHC

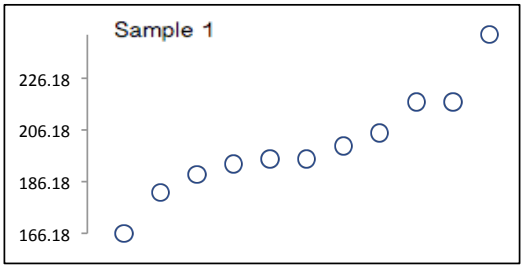
Summary Statistics

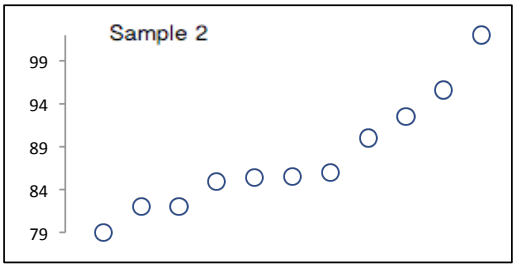
Statistic	C77-1	C77-2	C77-3	C77-4
N	11	11	11	11
Median	195	86	200	282
Robust Mean	199	87	201	283
U	7.0	2.5	5.7	4.9
Robust Standard Deviation	18.6	6.62	15.0	13.1
Regression Standard Deviation	43.1	20.7	43.4	60.0
Stability Flag				
Homogeneity Flag				
Standard Deviation Used	43.1	20.7	43.4	60.0
Outliers	1	1	1	1
|z|>3.0	0	0	0	0
2<|z|<3	0	0	0	0

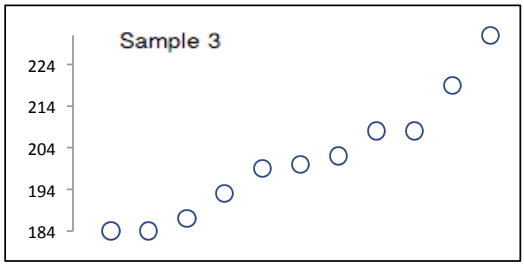
Methods Used

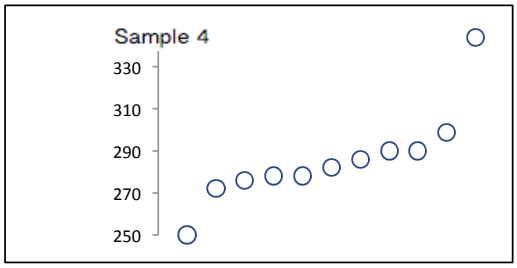
Method	C77-1	C77-2	C77-3	C77-4
GC/MS	4	4	4	4
GC/ECD/SHKE	1	1	1	1
GC/ECD	4	4	4	4
GC/MSHR	1	1	1	1
GC/MS/MS	1	1	1	1

All summary stats and the plots below are based on the data excluding any flagged outliers



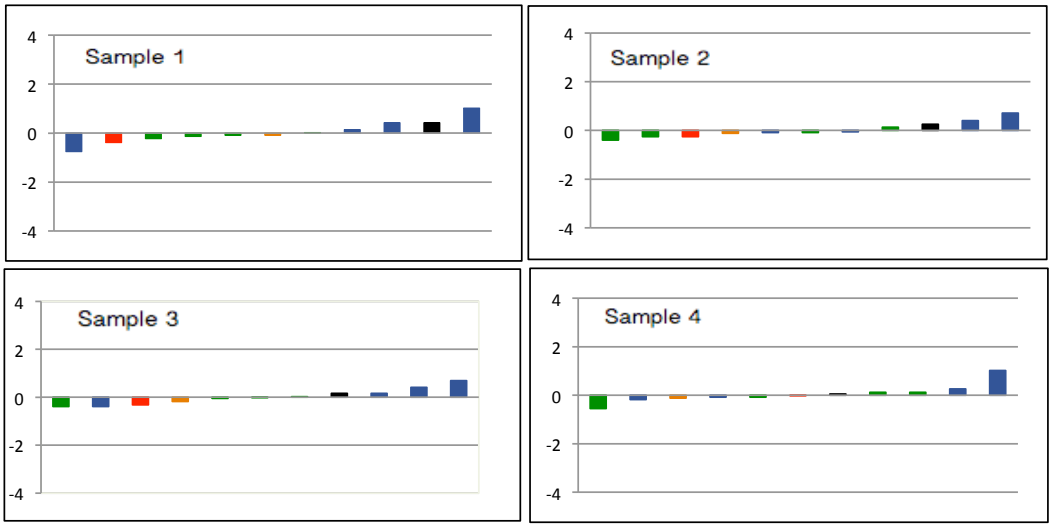




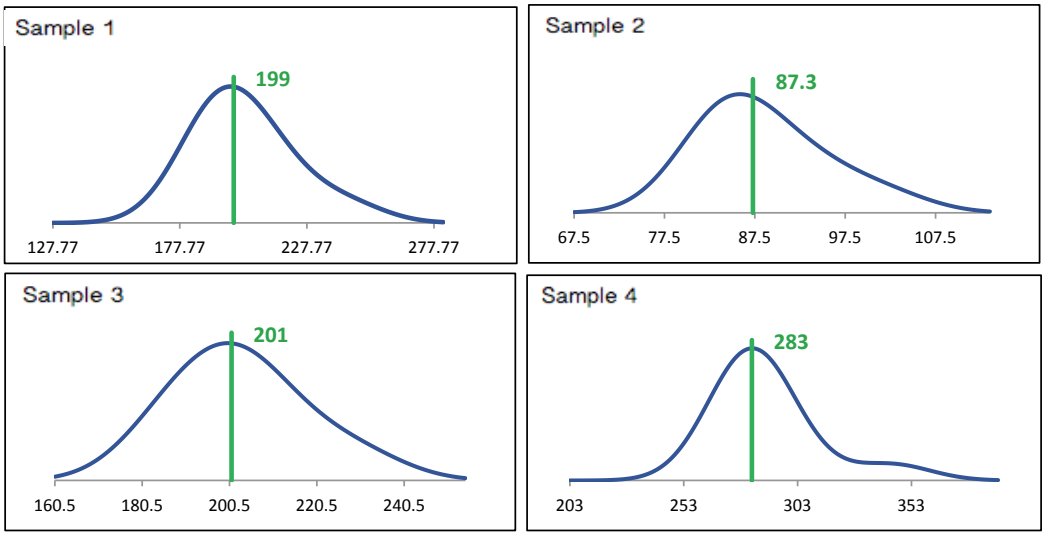


ALPHA-BHC

z-Score Plots



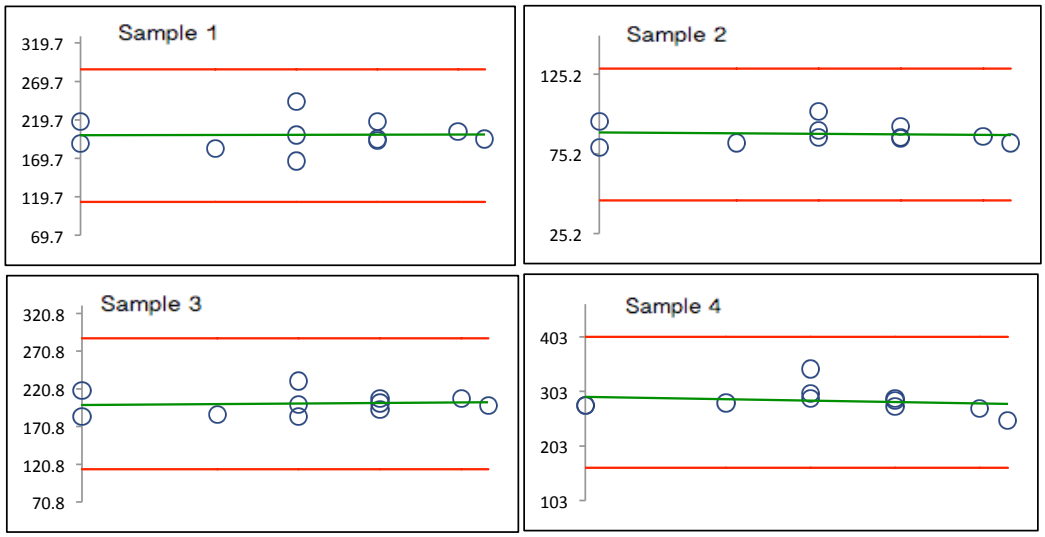
Kernel Density Plots



Annex A Summary by Analyte

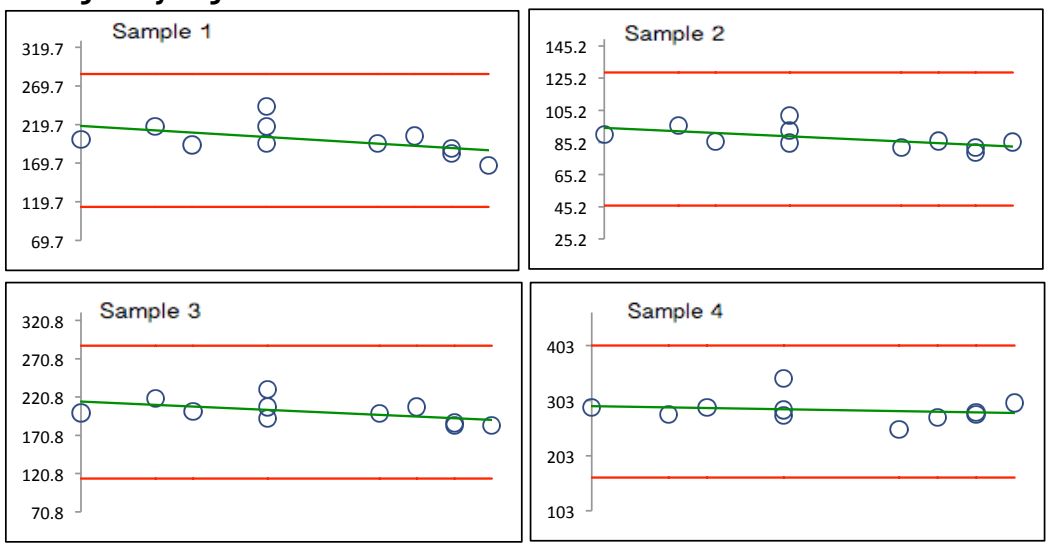
ALPHA-BHC

Stability Regression



Reported results (Y-axis) plotted against reported analysis date (X-axis)

Homogeneity Regression



Reported results (Y-axis) plotted against bottling order (X-axis).

ALPHA-CHLORDANE

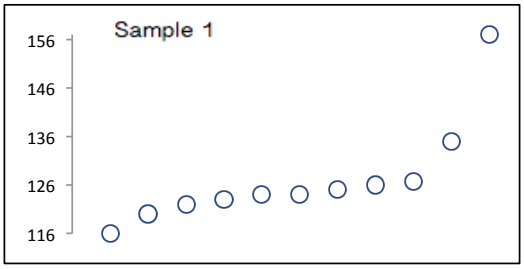
Summary Statistics

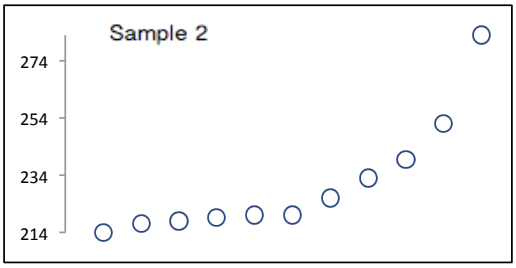
Statistic	C77-1	C77-2	C77-3	C77-4
N	11	11	11	11
Median	124	220	394	63
Robust Mean	125	228	398	64
U	2.3	5.9	9.9	2.3
Robust Standard Deviation	6.19	15.6	26.3	6.2
Regression Standard Deviation	24.1	43.5	75.4	12.7
Stability Flag				
Homogeneity Flag				
Standard Deviation Used	24.1	43.5	75.4	12.7
Outliers	1	1	1	1
|z|>3.0	0	0	0	0
2<|z|<3	0	0	0	0

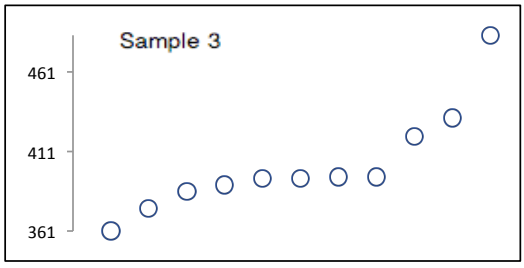
Methods Used

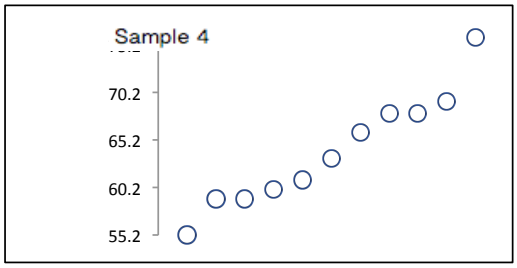
Method	C77-1	C77-2	C77-3	C77-4
GC/ECD	4	4	4	4
GC/MSHR	1	1	1	1
GC/MS/MS	1	1	1	1
GC/ECD/SHKE	1	1	1	1
GC/MS	4	4	4	4

All summary stats and the plots below are based on the data excluding any flagged outliers



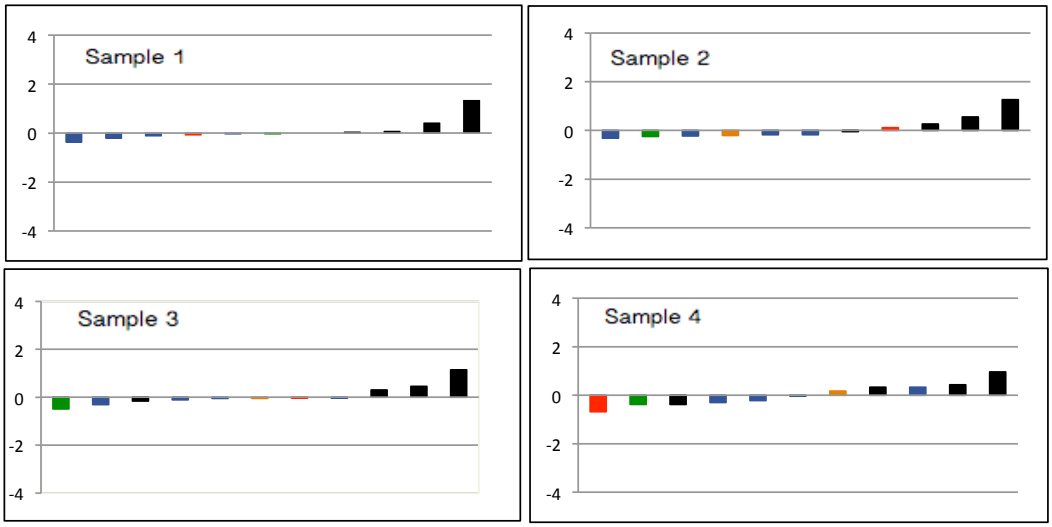




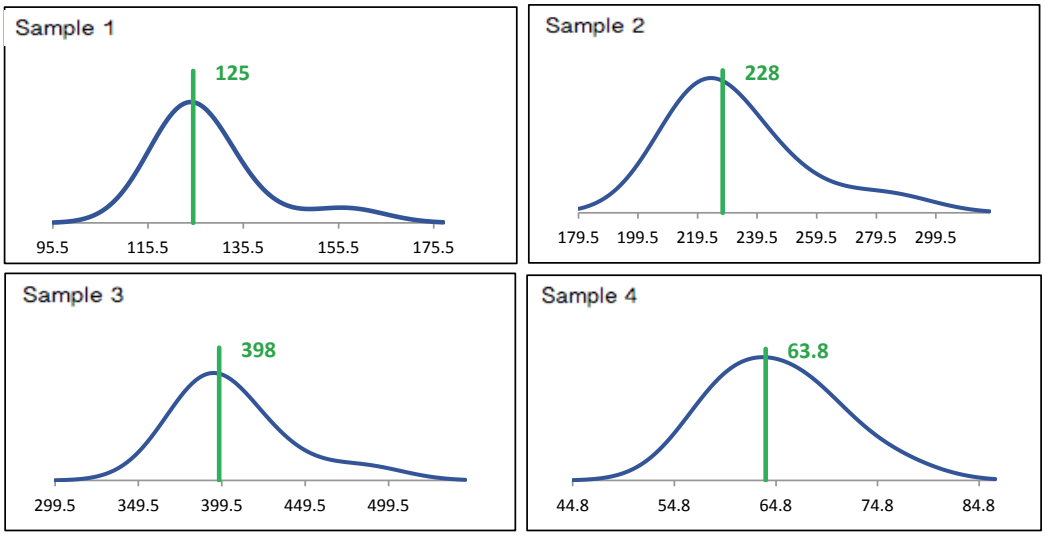


ALPHA-CHLORDANE

z-Score Plots

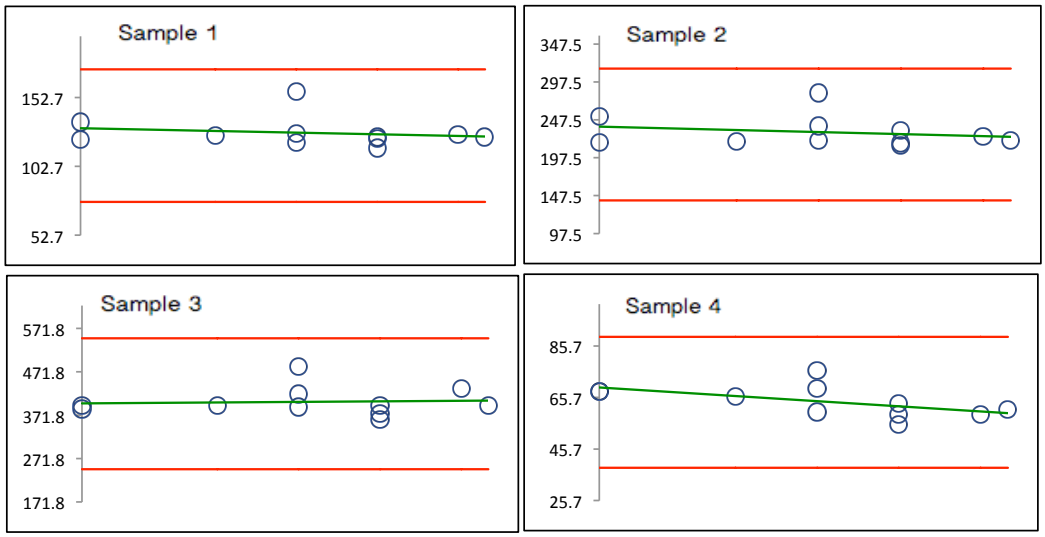


Kernel Density Plots



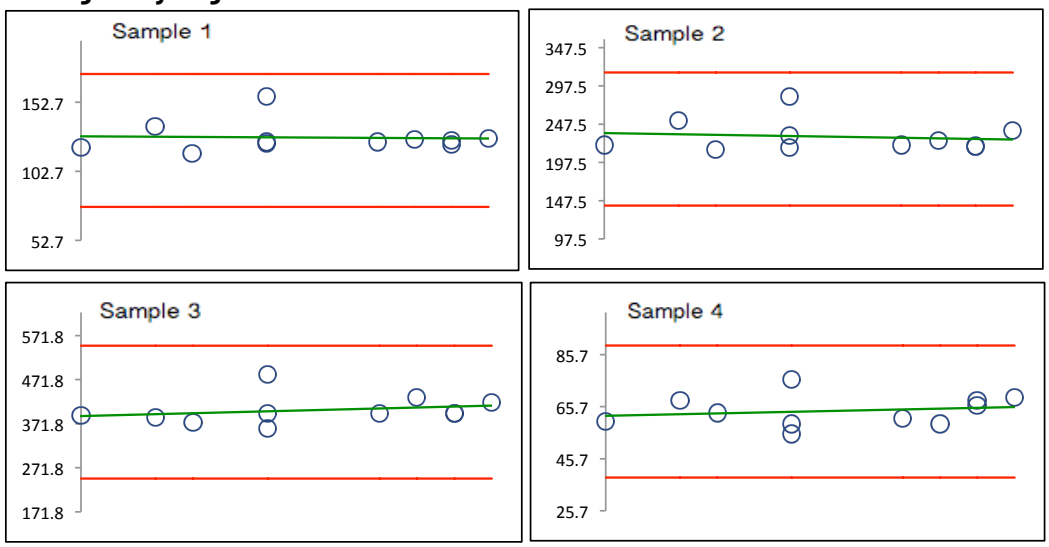
ALPHA-CHLORDANE

Stability Regression



Reported results (Y-axis) plotted against reported analysis date (X-axis)

Homogeneity Regression



Reported results (Y-axis) plotted against bottling order (X-axis).

BETA-BHC

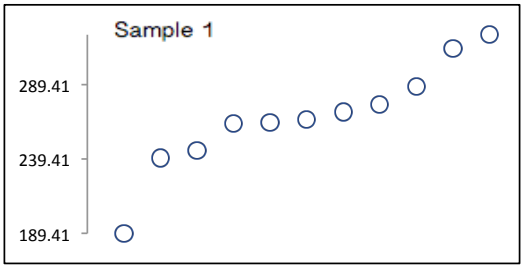
Summary Statistics

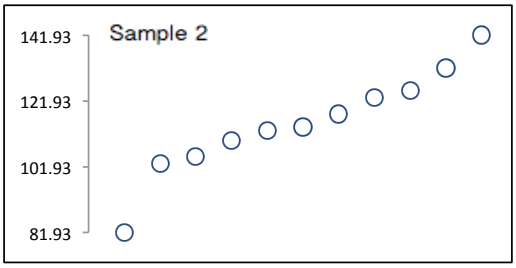
Statistic	C77-1	C77-2	C77-3	C77-4
N	11	11	11	11
Median	266	114	73	137
Robust Mean	270	116	72	135
U	13.0	5.6	2.6	6.0
Robust Standard Deviation	34.5	14.9	6.79	15.8
Regression Standard Deviation	57.6	30.1	22.3	33.5
Stability Flag				
Homogeneity Flag				
Standard Deviation Used	57.6	30.1	22.3	33.5
Outliers	1	1	1	1
|z|>3.0	0	0	0	0
2<|z|<3	0	0	0	0

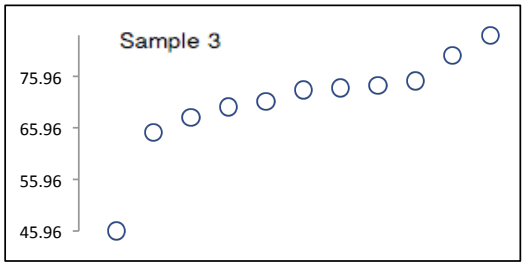
Methods Used

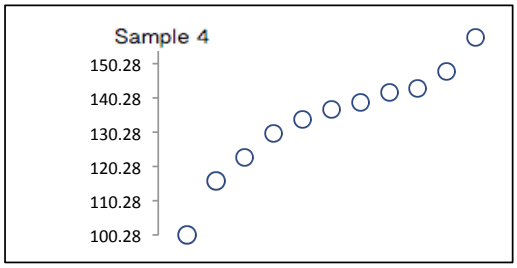
Method	C77-1	C77-2	C77-3	C77-4
GC/MS	4	4	4	4
GC/ECD	4	4	4	4
GC/ECD/SHKE	1	1	1	1
GC/MS/MS	1	1	1	1
GC/MSHR	1	1	1	1

All summary stats and the plots below are based on the data excluding any flagged outliers



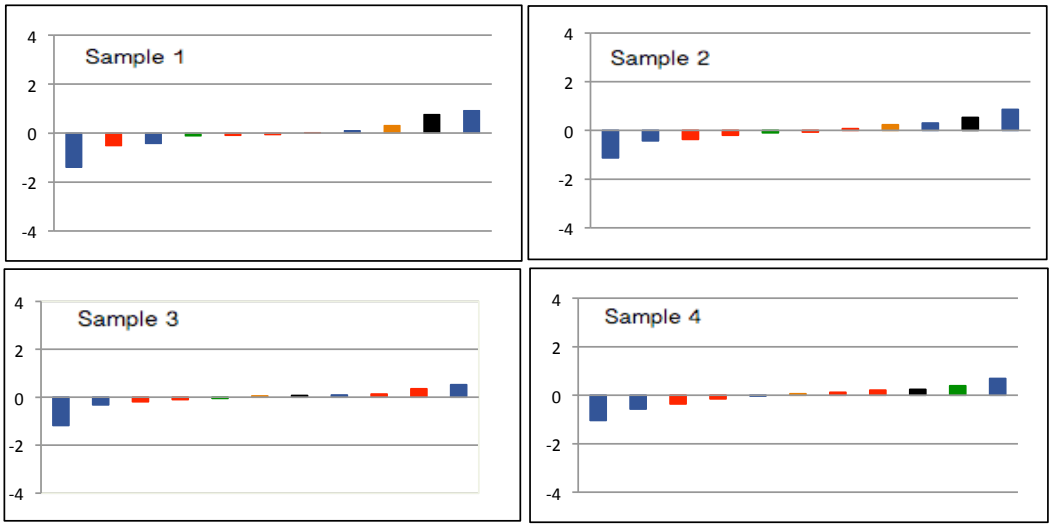




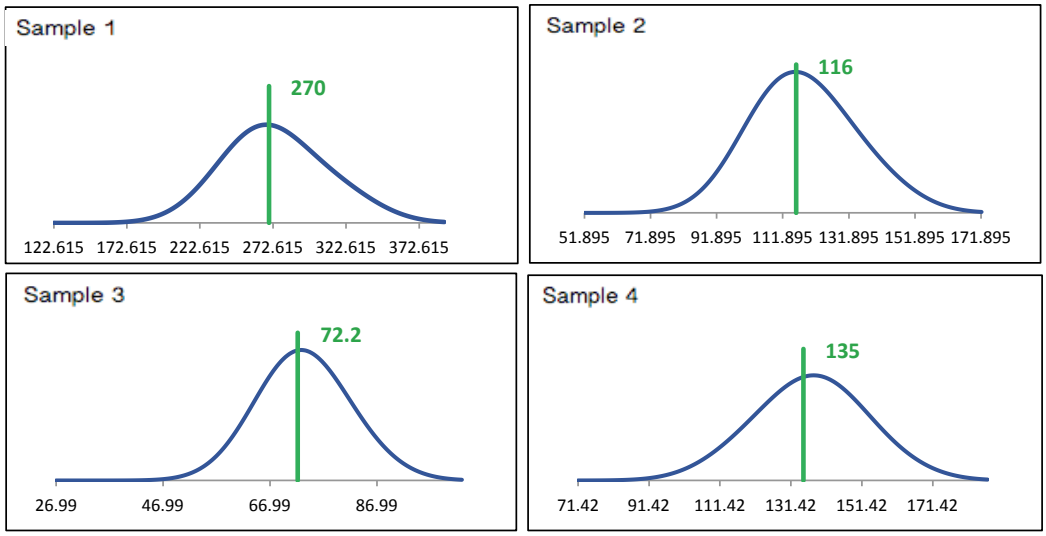


BETA-BHC

z-Score Plots

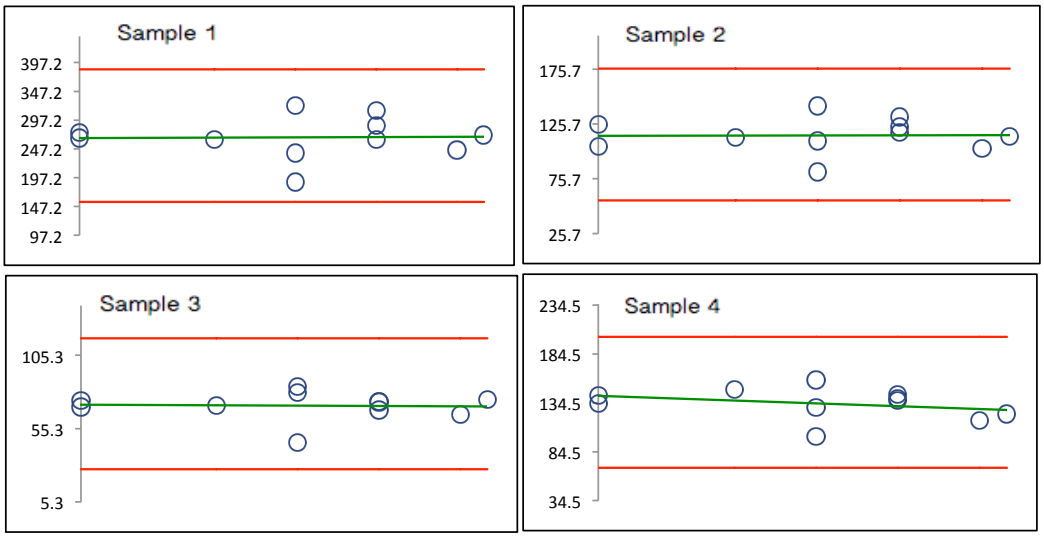


Kernel Density Plots



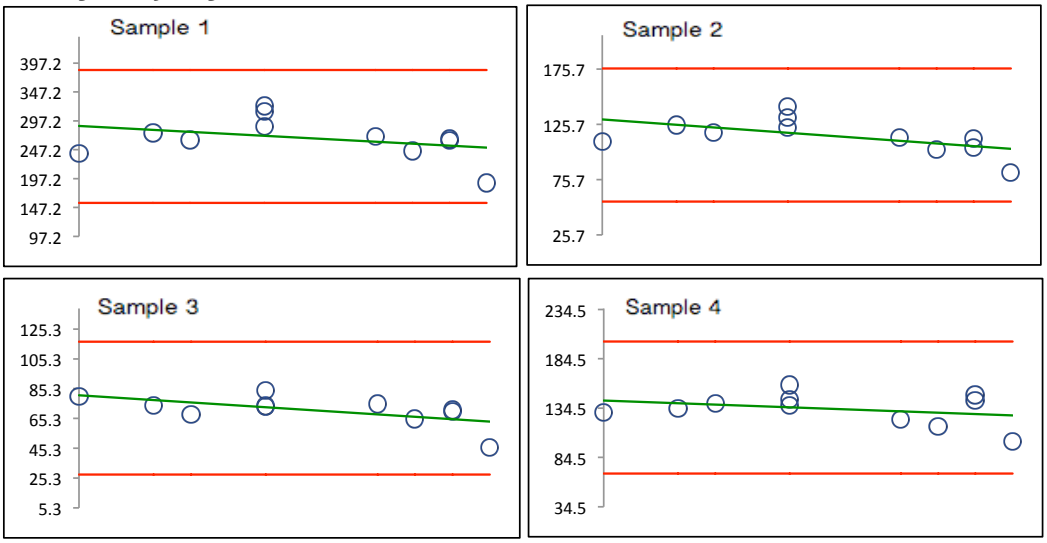
BETA-BHC

Stability Regression



Reported results (Y-axis) plotted against reported analysis date (X-axis)

Homogeneity Regression



Reported results (Y-axis) plotted against bottling order (X-axis).

DIELDRIN

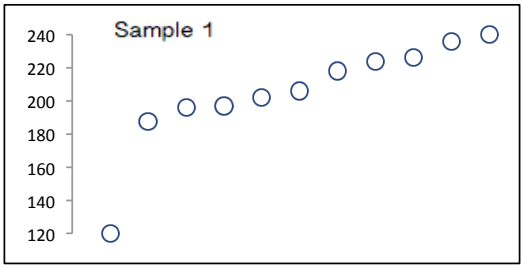
Summary Statistics

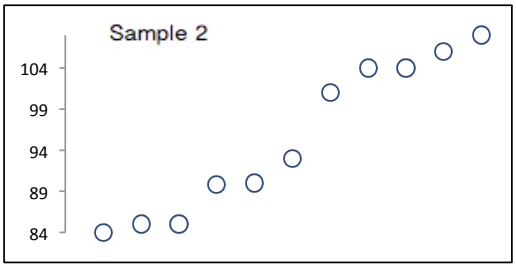
Statistic	C77-1	C77-2	C77-3	C77-4
N	11	11	11	11
Median	206	92.9	522	210
Robust Mean	210	95.4	514	209
U	8.9	4.0	18.5	7.2
Robust Standard Deviation	23.6	10.5	49.10	19.2
Regression Standard Deviation	39.1	20.0	90.0	38.9
Stability Flag				
Homogeneity Flag				
Standard Deviation Used	39.1	20.0	90.0	38.9
Outliers	1	1	1	1
|z|>3.0	0	0	0	0
2<|z|<3	1	0	0	0

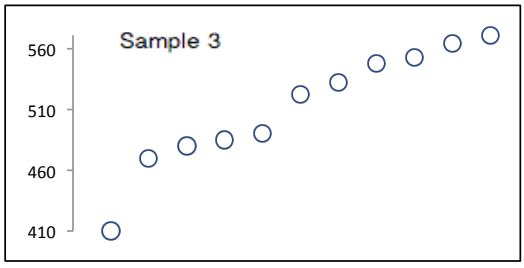
Methods Used

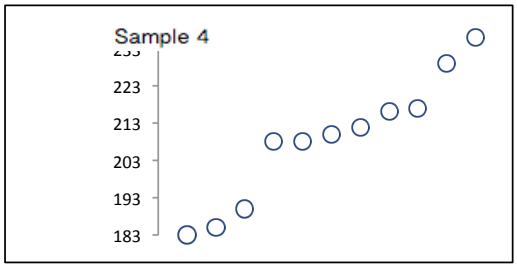
Method	C77-1	C77-2	C77-3	C77-4
GC/ECD	5	5	5	5
GC/MS	3	3	3	3
GC/ECD/SHKE	1	1	1	1
GC/MS/MS	1	1	1	1
GC/MSHR	1	1	1	1

All summary stats and the plots below are based on the data excluding any flagged outliers



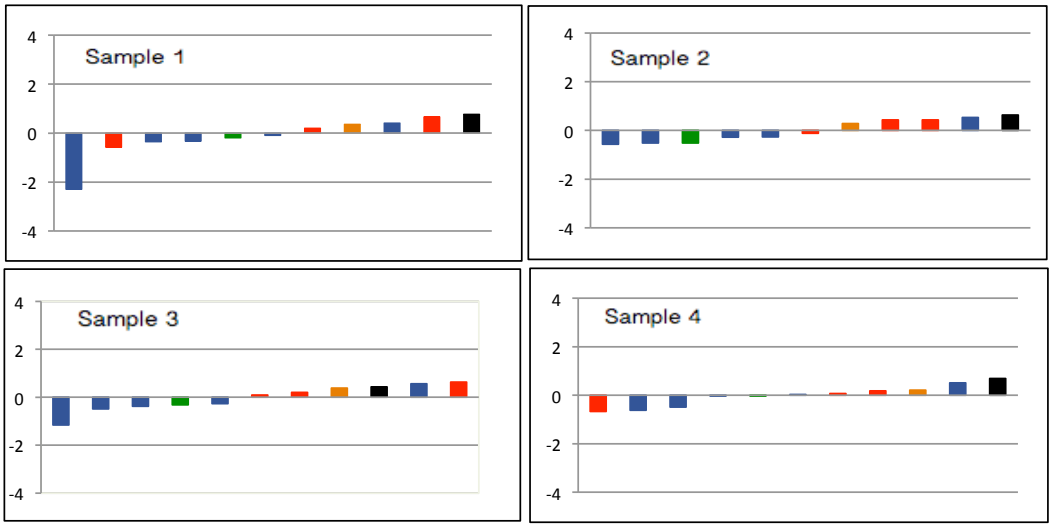




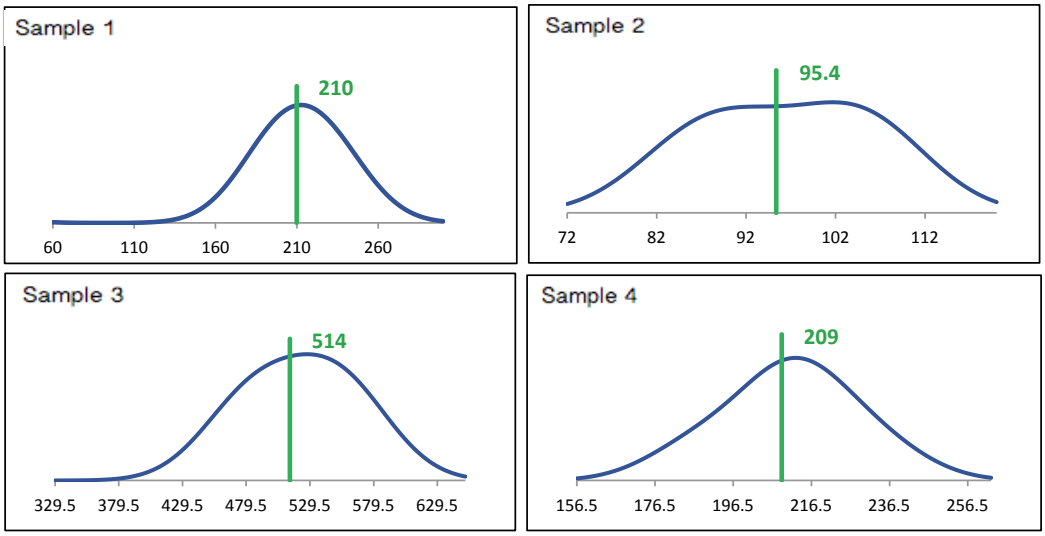


DIELDRIN

z-Score Plots

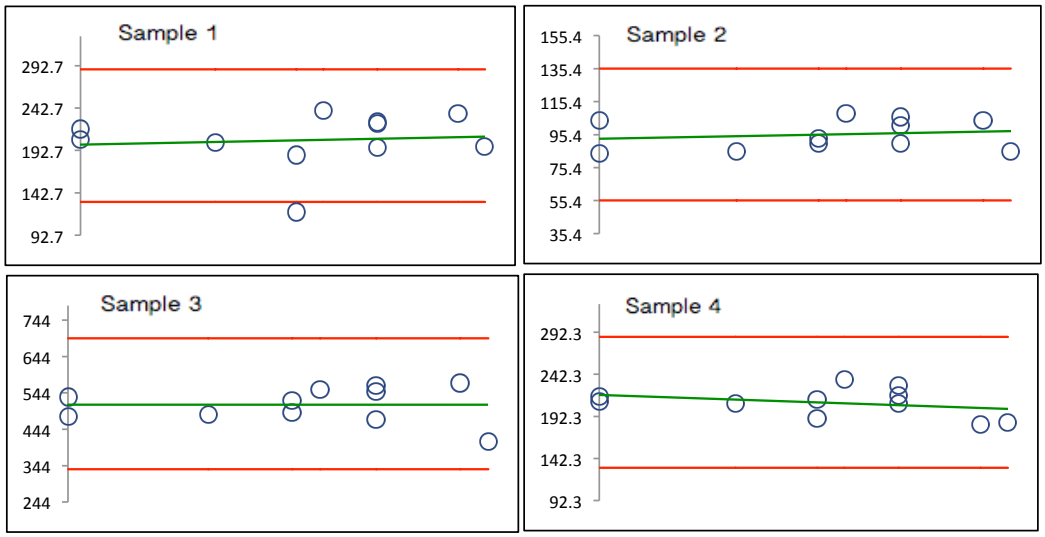


Kernel Density Plots



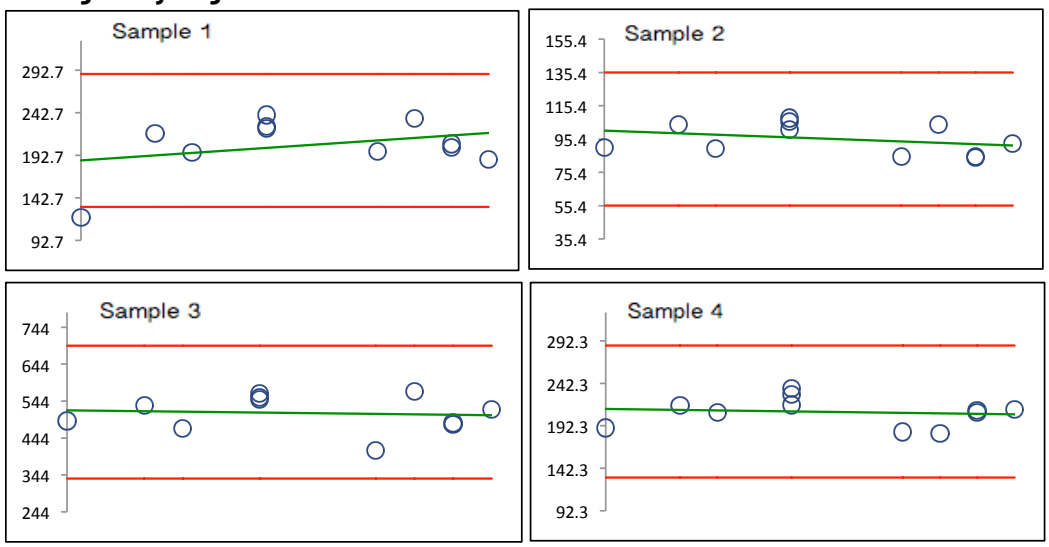
DIELDRIN

Stability Regression



Reported results (Y-axis) plotted against reported analysis date (X-axis)

Homogeneity Regression



Reported results (Y-axis) plotted against bottling order (X-axis).

ENDOSULFAN I (A-ENDOSULFAN)

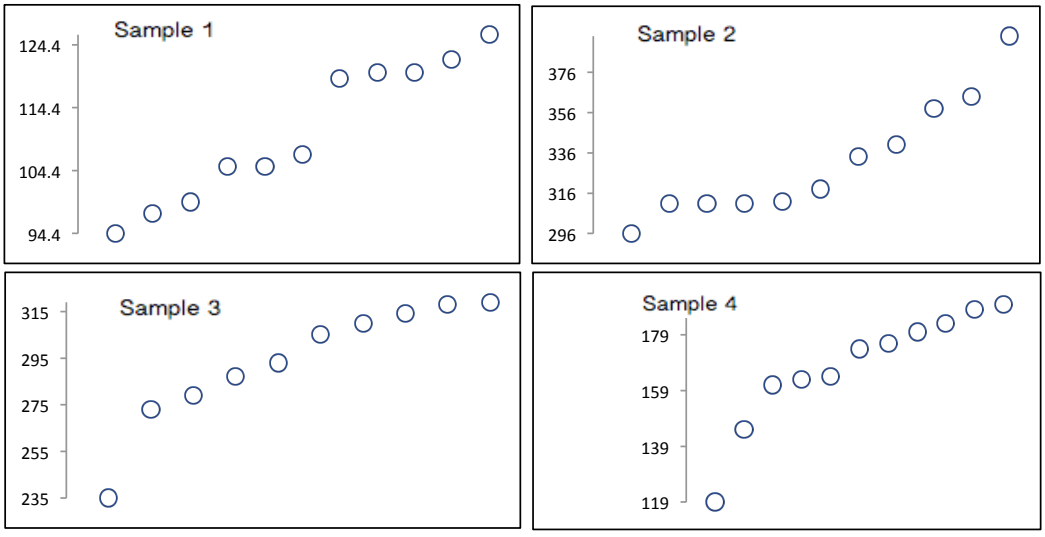
Summary Statistics

Statistic	C77-1	C77-2	C77-3	C77-4
N	11	11	10	11
Median	107	318	299	174
Robust Mean	110	330	296	170
U	4.8	11.1	9.1	6.9
Robust Standard Deviation	12.7	29.4	23.1	18.3
Regression Standard Deviation	25.2	65.3	59.1	36.0
Stability Flag				
Homogeneity Flag				
Standard Deviation Used	25.2	65.3	59.1	36.0
Outliers	1	1	2	1
|z|>3.0	0	0	0	0
2<|z|<3	0	0	0	0

Methods Used

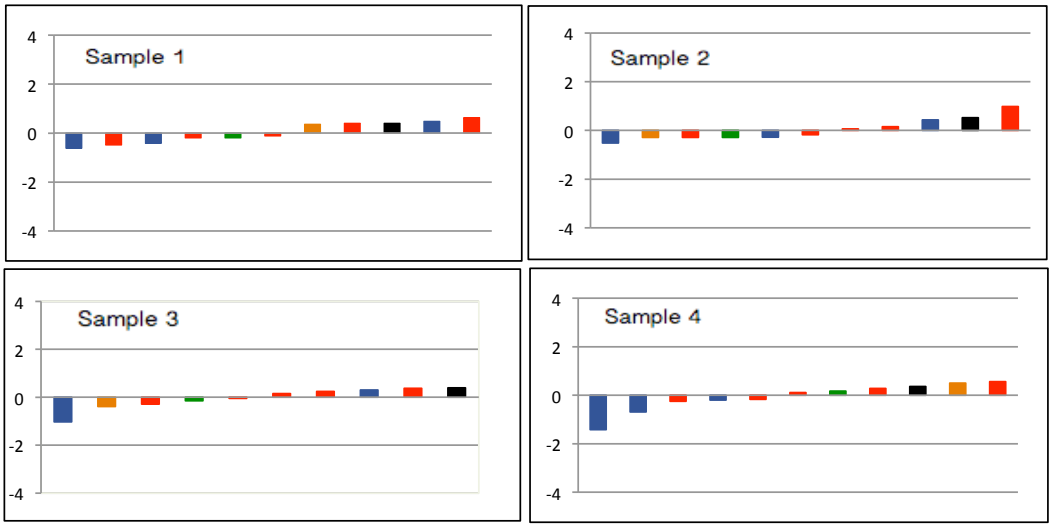
Method	C77-1	C77-2	C77-3	C77-4
GC/MS	3	3	2	3
GC/ECD	5	5	5	5
GC/ECD/SHKE	1	1	1	1
GC/MSHR	1	1	1	1
GC/MS/MS	1	1	1	1

All summary stats and the plots below are based on the data excluding any flagged outliers

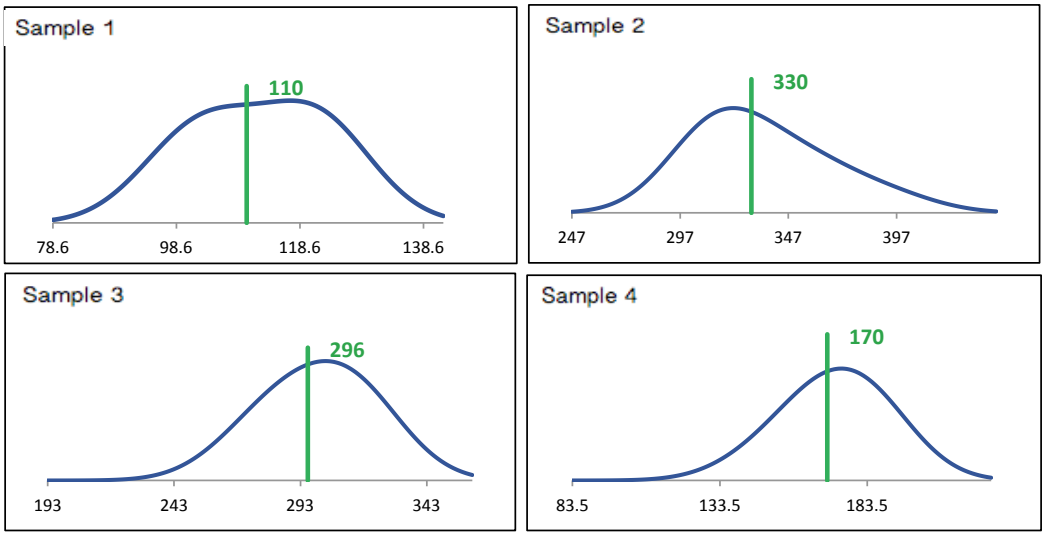


ENDOSULFAN I (A-ENDOSULFAN)

z-Score Plots

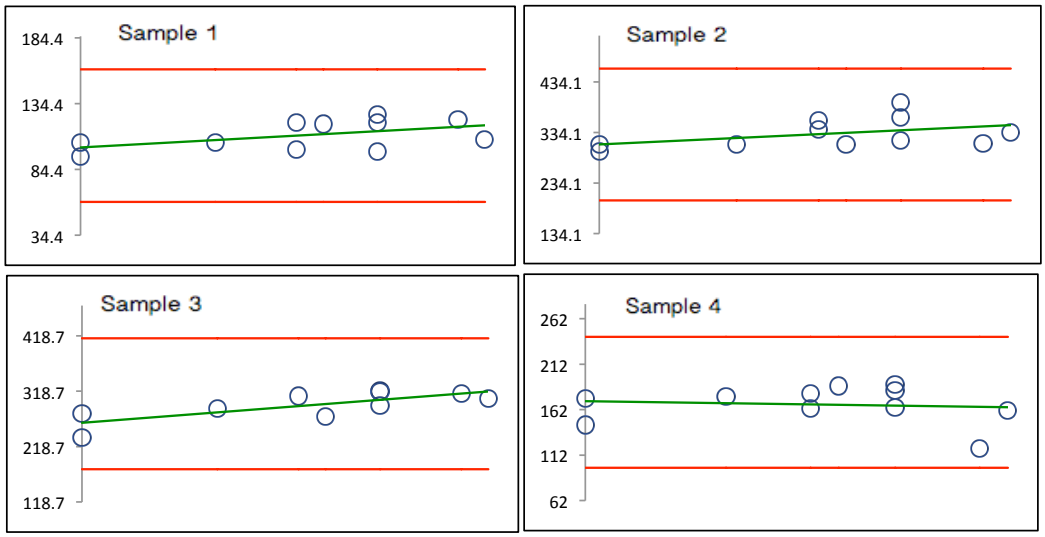


Kernel Density Plots



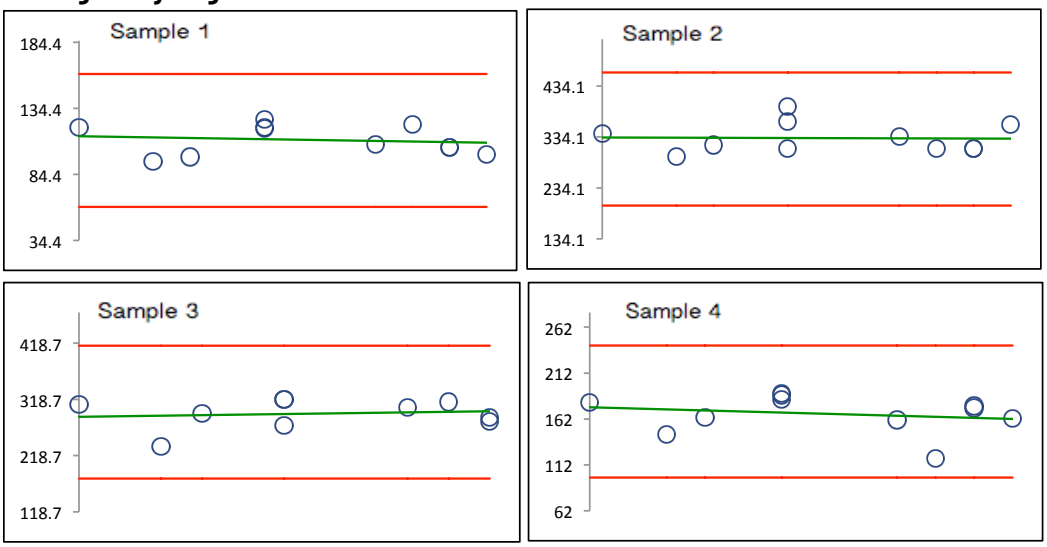
ENDOSULFAN I (A-ENDOSULFAN)

Stability Regression



Reported results (Y-axis) plotted against reported analysis date (X-axis)

Homogeneity Regression



Reported results (Y-axis) plotted against bottling order (X-axis).

ENDOSULFAN II (B-ENDOSULFAN)

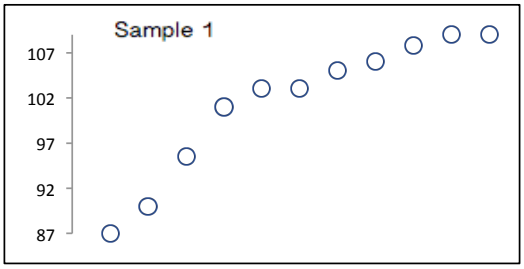
Summary Statistics

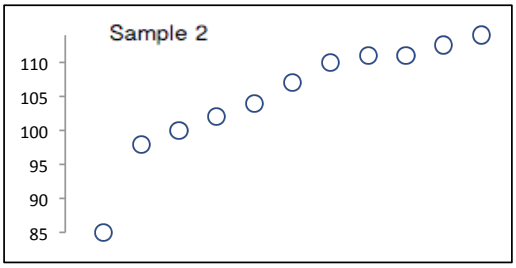
Statistic	C77-1	C77-2	C77-3	C77-4
N	11	11	11	11
Median	103	107	320	142
Robust Mean	102	106	317	139
U	3.0	2.8	10.0	5.2
Robust Standard Deviation	7.98	7.35	26.4	13.7
Regression Standard Deviation	23.8	24.7	67.4	31.5
Stability Flag				
Homogeneity Flag				
Standard Deviation Used	23.8	24.7	67.4	31.5
Outliers	1	1	1	1
|z|>3.0	0	0	0	0
2<|z|<3	0	0	0	0

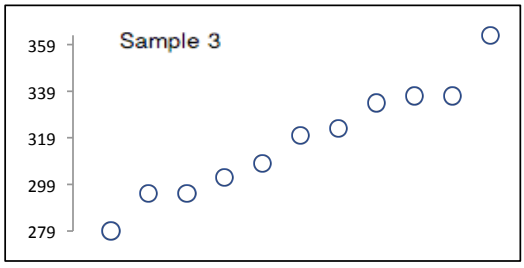
Methods Used

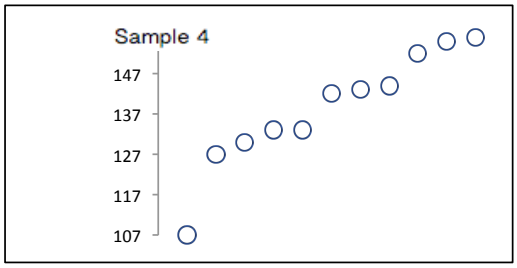
Method	C77-1	C77-2	C77-3	C77-4
GC/MS	3	3	3	3
GC/ECD	5	5	5	5
GC/MS/MS	1	1	1	1
GC/MSHR	1	1	1	1
GC/ECD/SHKE	1	1	1	1

All summary stats and the plots below are based on the data excluding any flagged outliers



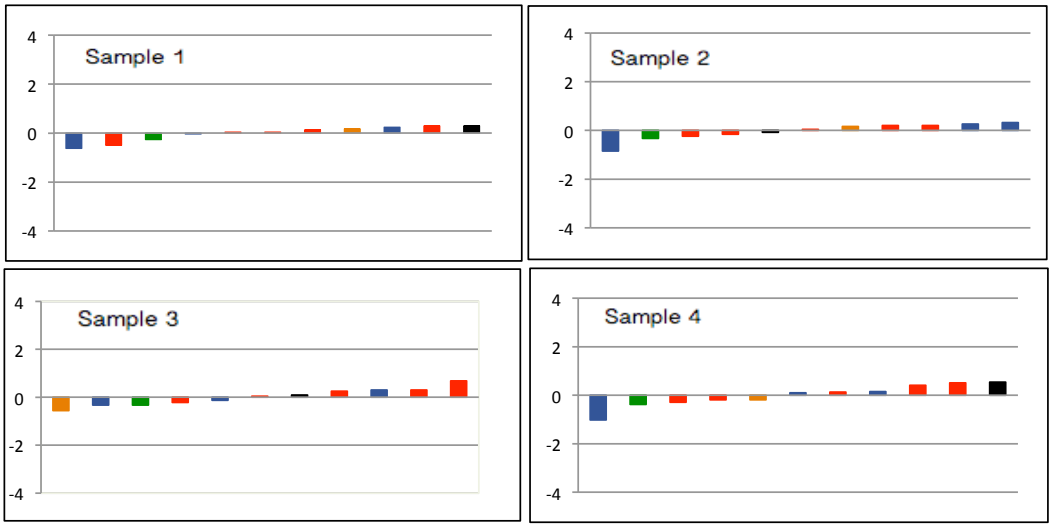




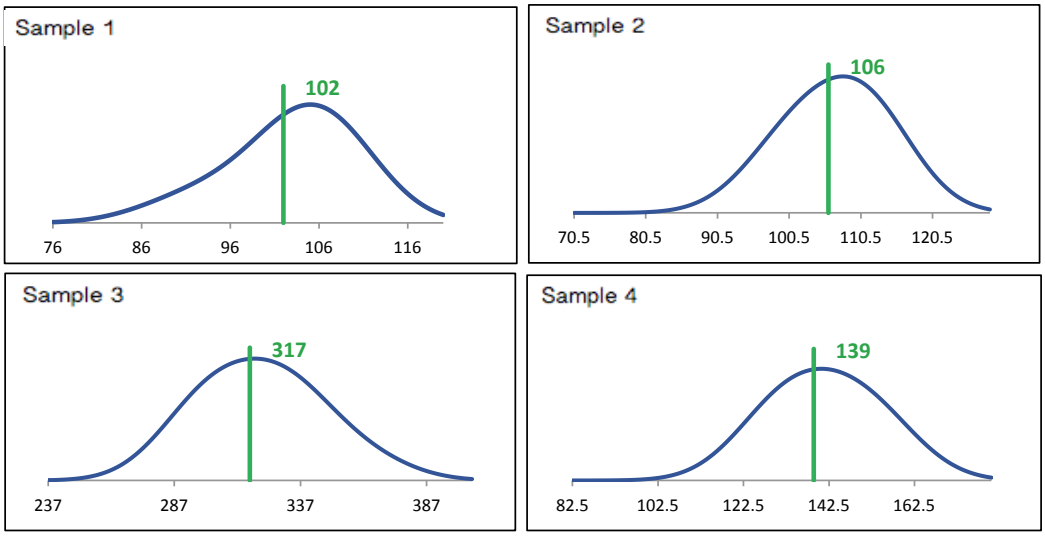


ENDOSULFAN II (B-ENDOSULFAN)

z-Score Plots

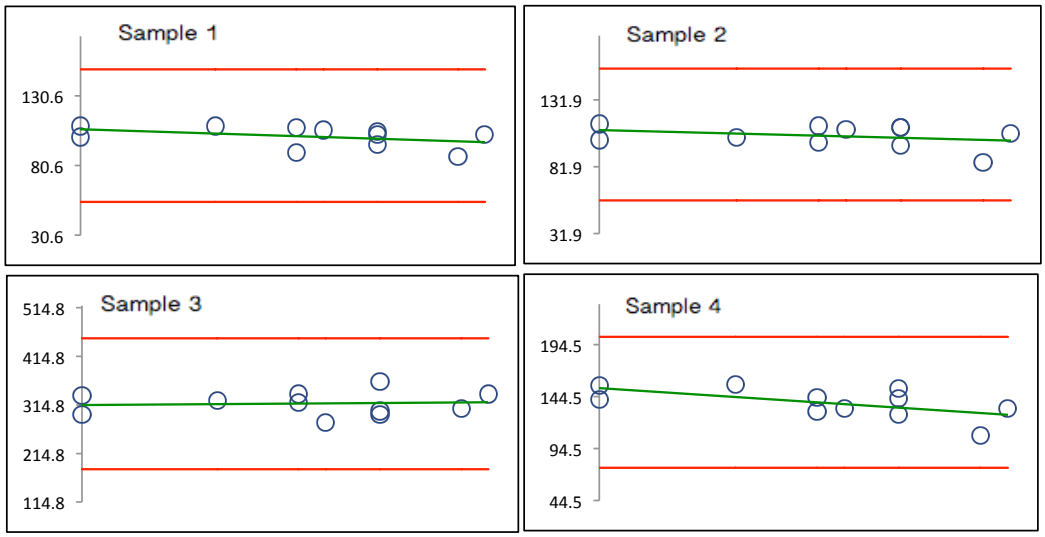


Kernel Density Plots



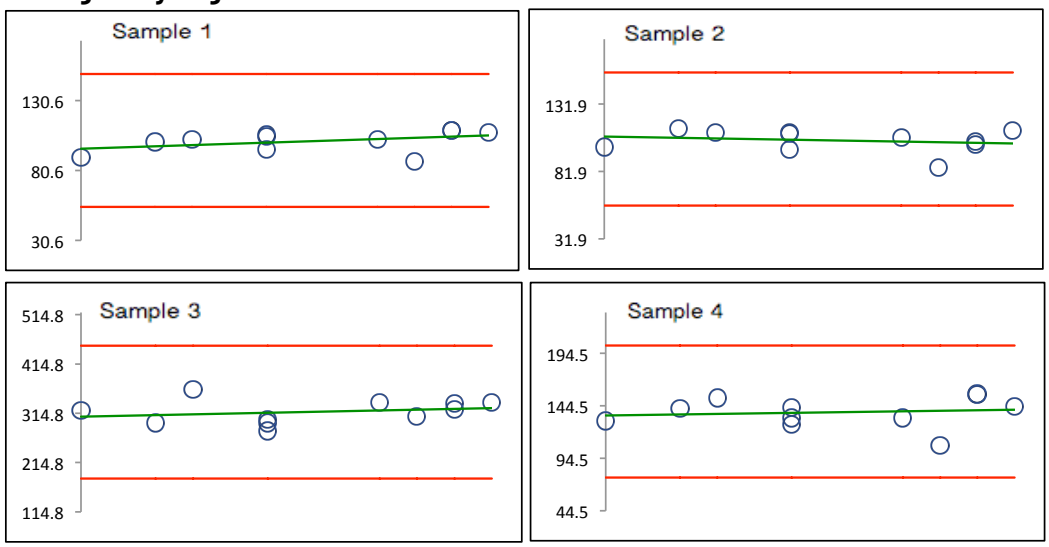
ENDOSULFAN II (B-ENDOSULFAN)

Stability Regression



Reported results (Y-axis) plotted against reported analysis date (X-axis)

Homogeneity Regression



Reported results (Y-axis) plotted against bottling order (X-axis).

ENDRIN

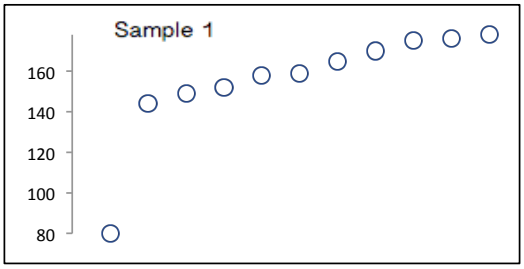
Summary Statistics

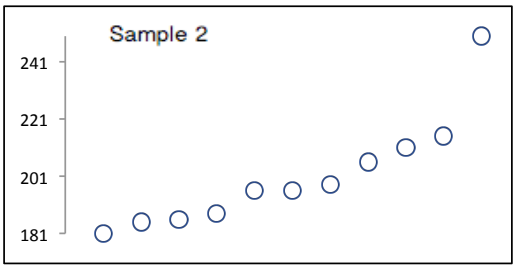
Statistic	C77-1	C77-2	C77-3	C77-4
N	11	11	11	11
Median	159	196	193	246
Robust Mean	160	198	199	253
U	5.9	5.7	8.0	13.2
Robust Standard Deviation	15.7	15.1	21.2	35.0
Regression Standard Deviation	30.2	35.6	35.7	43.5
Stability Flag				
Homogeneity Flag		Homogeneity	Homogeneity	
Standard Deviation Used	30.2	37.8	38.3	43.5
Outliers	1	1	1	1
|z|>3.0	0	0	0	0
2<|z|<3	1	0	0	0

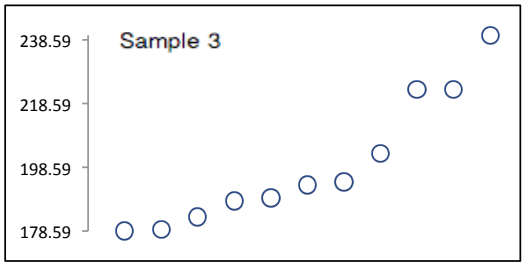
Methods Used

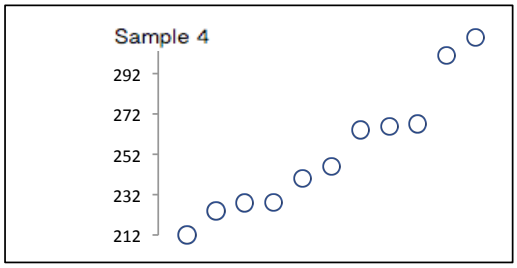
Method	C77-1	C77-2	C77-3	C77-4
GC/ECD	5	5	5	5
GC/ECD/SHKE	1	1	1	1
GC/MS	3	3	3	3
GC/MSHR	1	1	1	1
GC/MS/MS	1	1	1	1

All summary stats and the plots below are based on the data excluding any flagged outliers



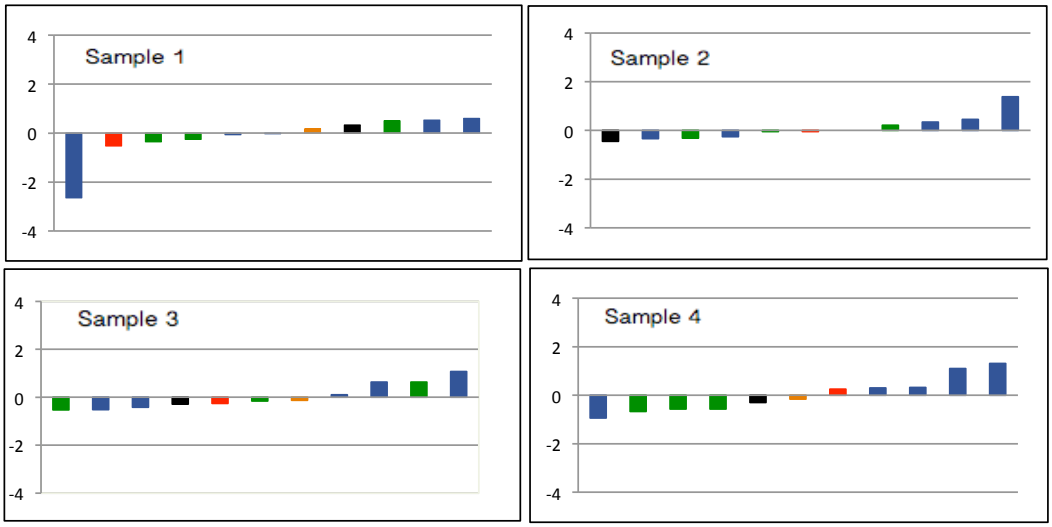




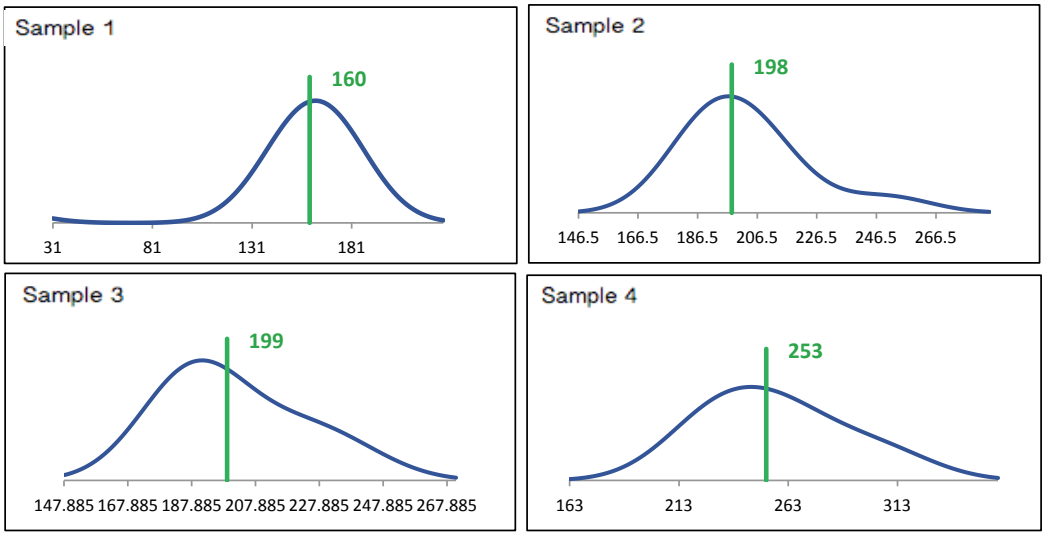


ENDRIN

z-Score Plots

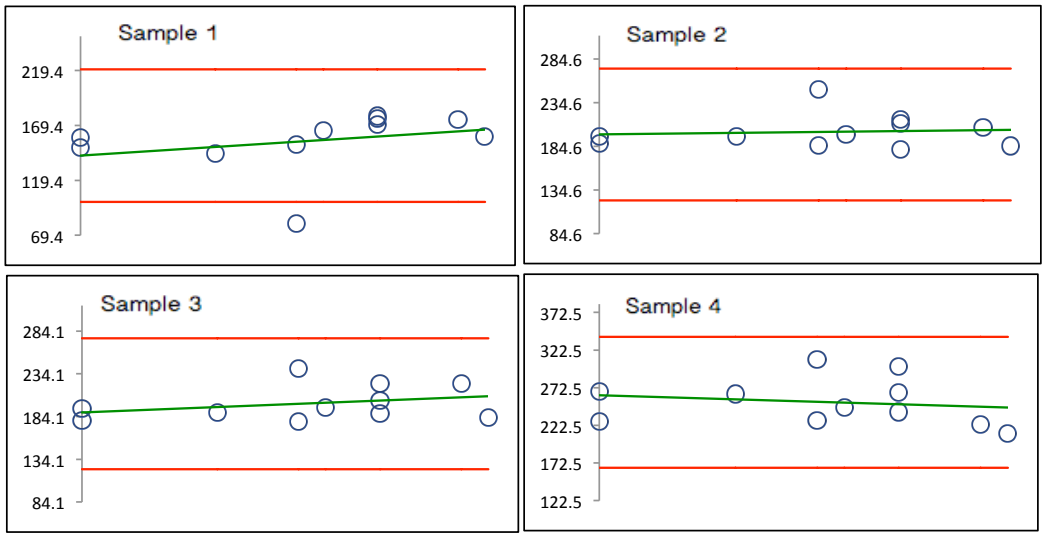


Kernel Density Plots



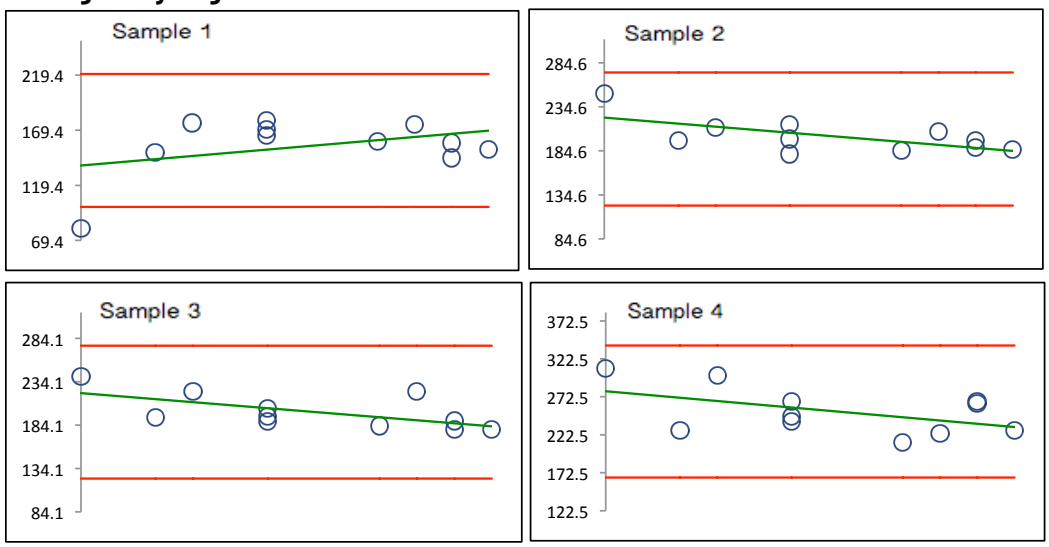
ENDRIN

Stability Regression



Reported results (Y-axis) plotted against reported analysis date (X-axis)

Homogeneity Regression



Reported results (Y-axis) plotted against bottling order (X-axis).

LINDANE (GAMMA-BHC)

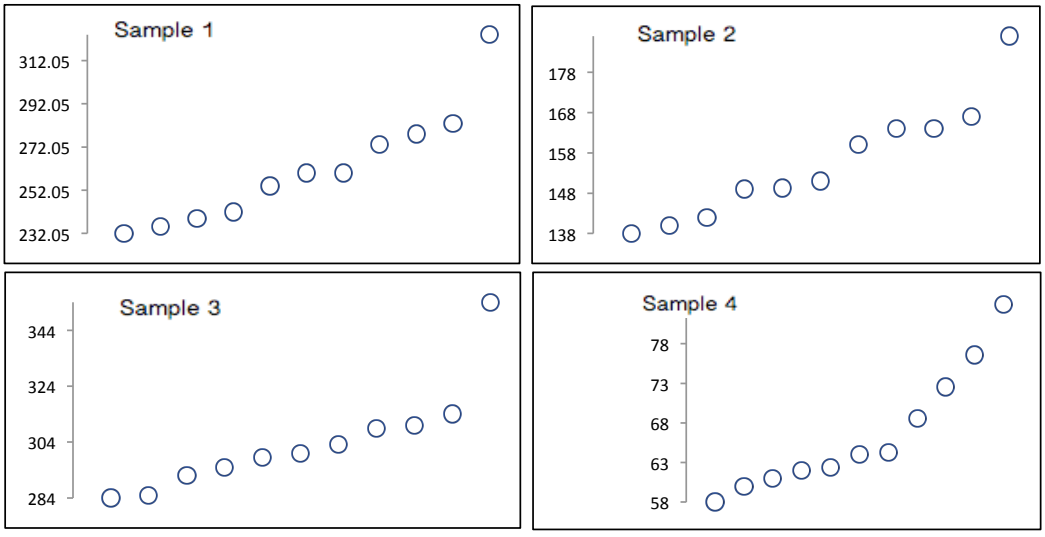
Summary Statistics

Statistic	C77-1	C77-2	C77-3	C77-4
N	11	11	11	11
Median	260	151	300	64
Robust Mean	259	155	301	66
U	9.0	5.3	5.1	2.9
Robust Standard Deviation	23.9	14.0	13.4	7.7
Regression Standard Deviation	56.7	36.2	64.9	18.9
Stability Flag				
Homogeneity Flag				
Standard Deviation Used	56.7	36.2	64.9	18.9
Outliers	1	1	1	1
|z|>3.0	0	0	0	0
2<|z|<3	0	0	0	0

Methods Used

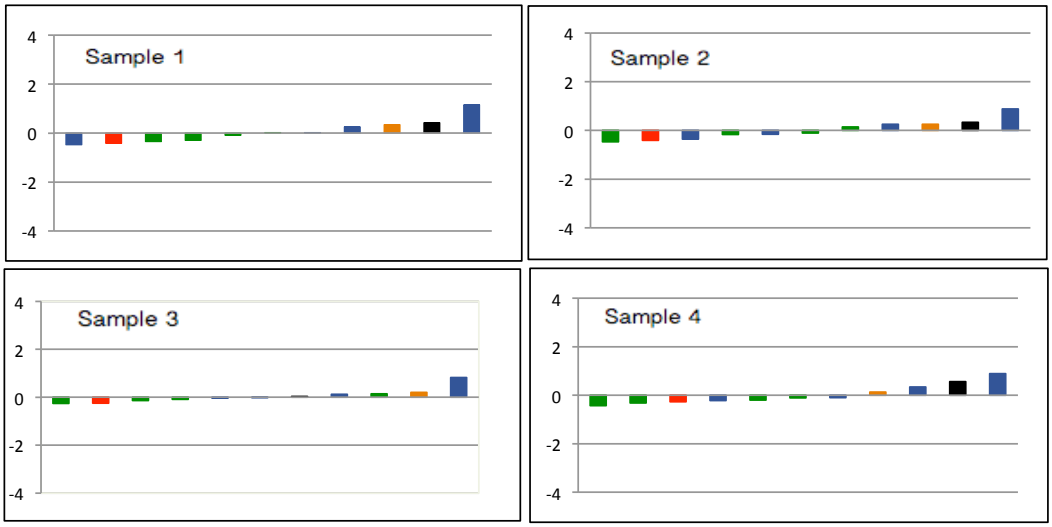
Method	C77-1	C77-2	C77-3	C77-4
GC/MS	4	4	4	4
GC/ECD/SHKE	1	1	1	1
GC/ECD	4	4	4	4
GC/MS/MS	1	1	1	1
GC/MSHR	1	1	1	1

All summary stats and the plots below are based on the data excluding any flagged outliers

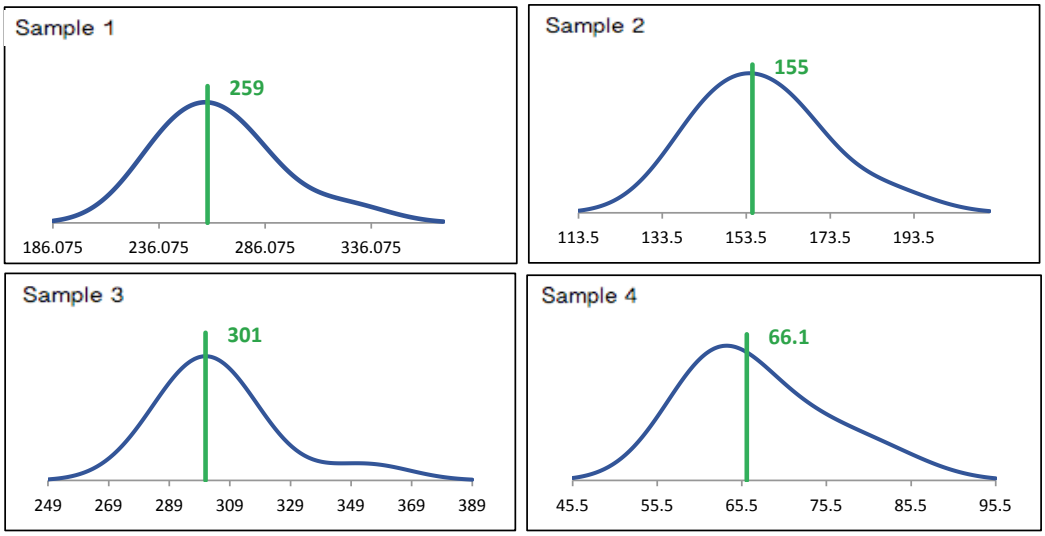


LINDANE (GAMMA-BHC)

z-Score Plots

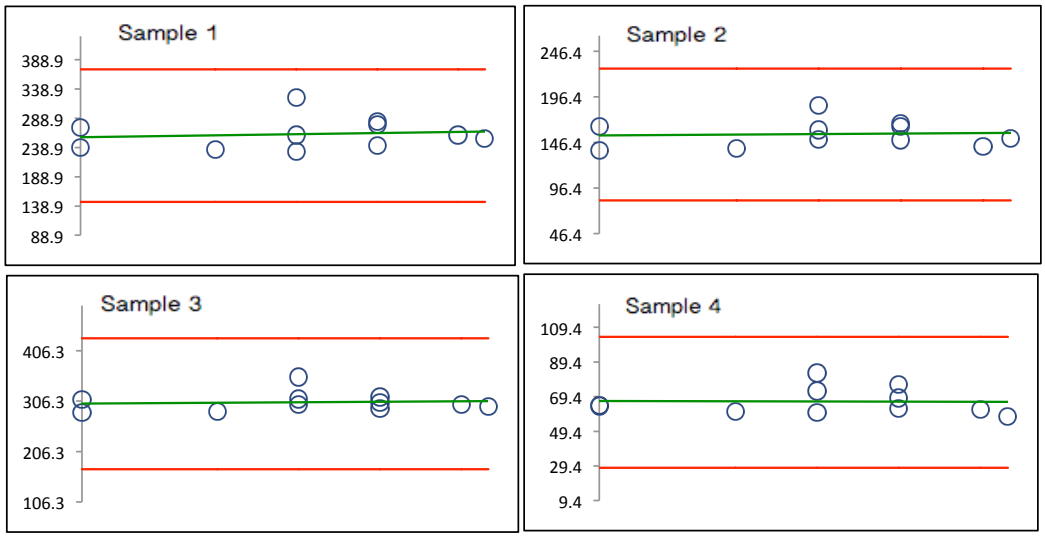


Kernel Density Plots



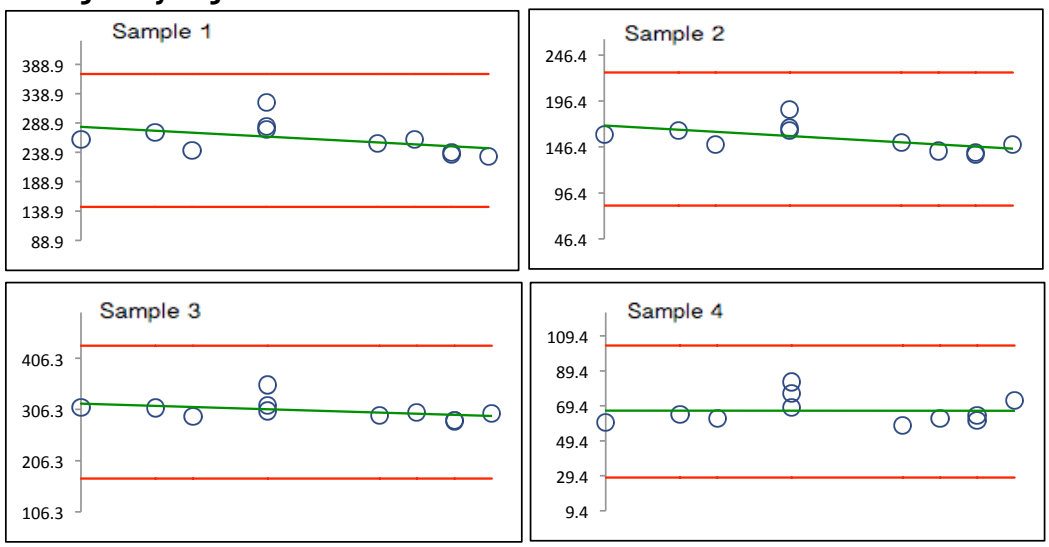
LINDANE (GAMMA-BHC)

Stability Regression



Reported results (Y-axis) plotted against reported analysis date (X-axis)

Homogeneity Regression



Reported results (Y-axis) plotted against bottling order (X-axis).

GAMMA-CHLORDANE

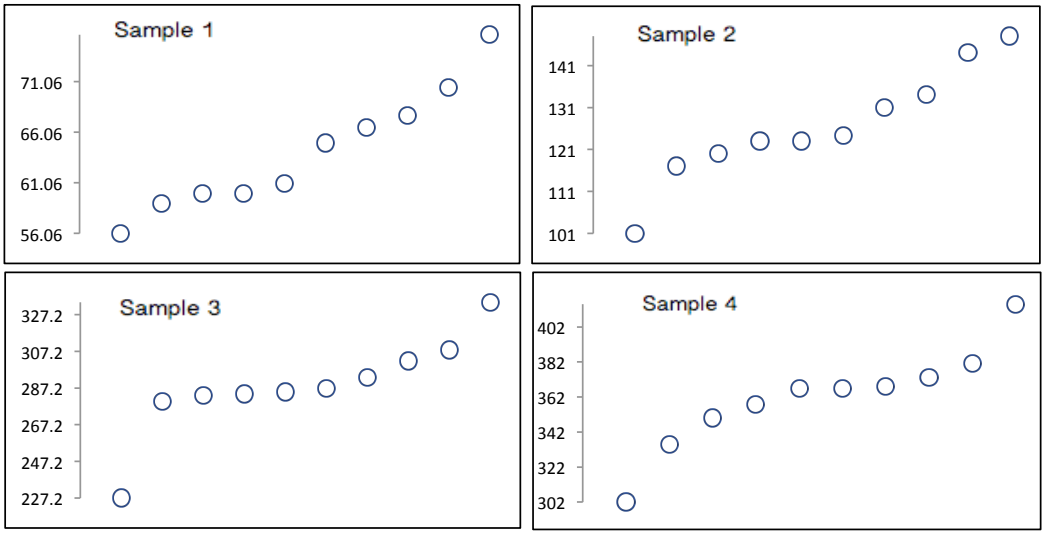
Summary Statistics

Statistic	C77-1	C77-2	C77-3	C77-4
N	10	10	10	10
Median	63.0	124	286	367
Robust Mean	63.9	127	290	362
U	2.5	5.7	6.5	9.5
Robust Standard Deviation	6.34	14.4	16.4	24.0
Regression Standard Deviation	12.7	23.2	50.4	62.4
Stability Flag				
Homogeneity Flag				
Standard Deviation Used	12.7	23.2	50.4	62.4
Outliers	1	1	1	1
|z|>3.0	0	0	0	0
2<|z|<3	0	0	0	0

Methods Used

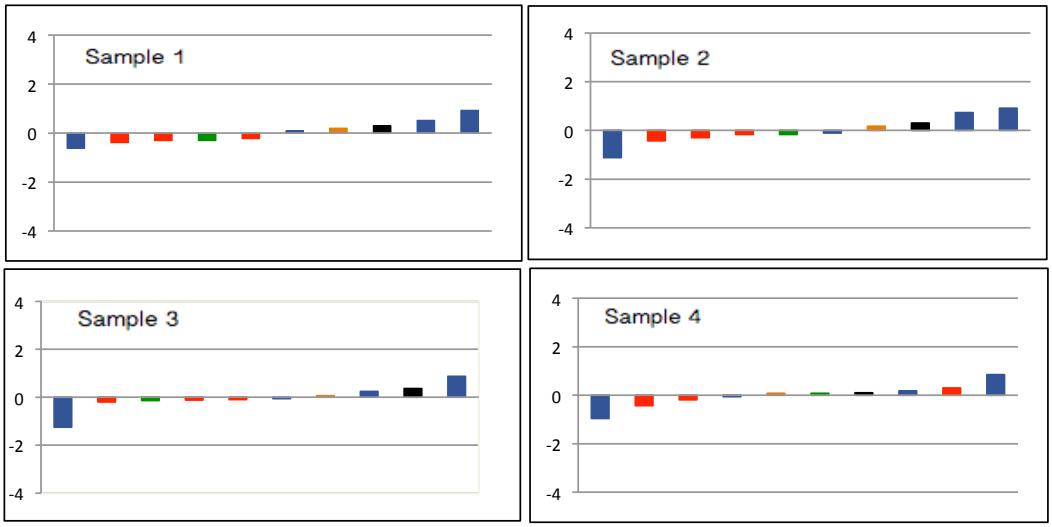
Method	C77-1	C77-2	C77-3	C77-4
GC/MS	4	4	4	4
GC/ECD	3	3	3	3
GC/ECD/SHKE	1	1	1	1
GC/MS/MS	1	1	1	1
GC/MSHR	1	1	1	1

All summary stats and the plots below are based on the data excluding any flagged outliers

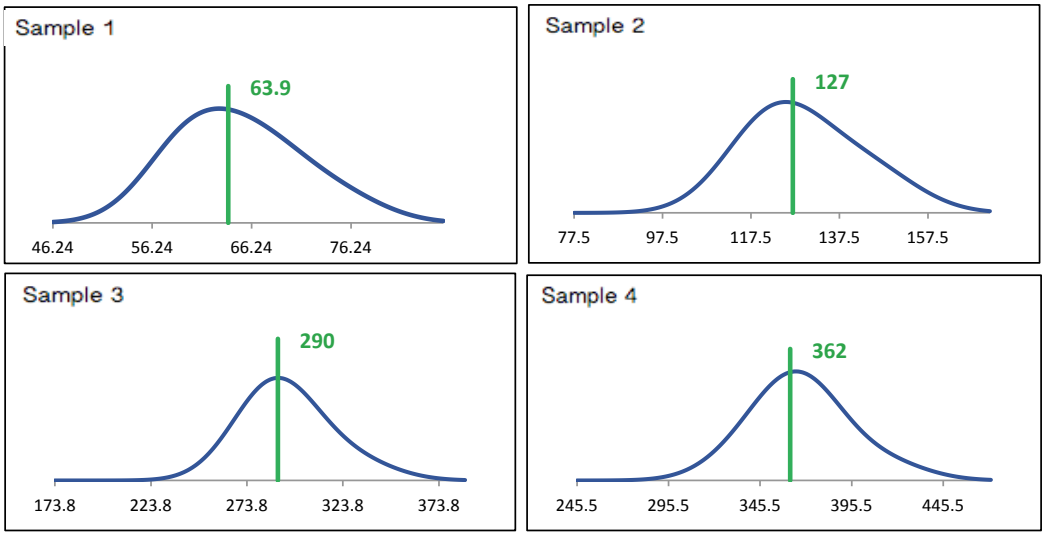


GAMMA-CHLORDANE

z-Score Plots

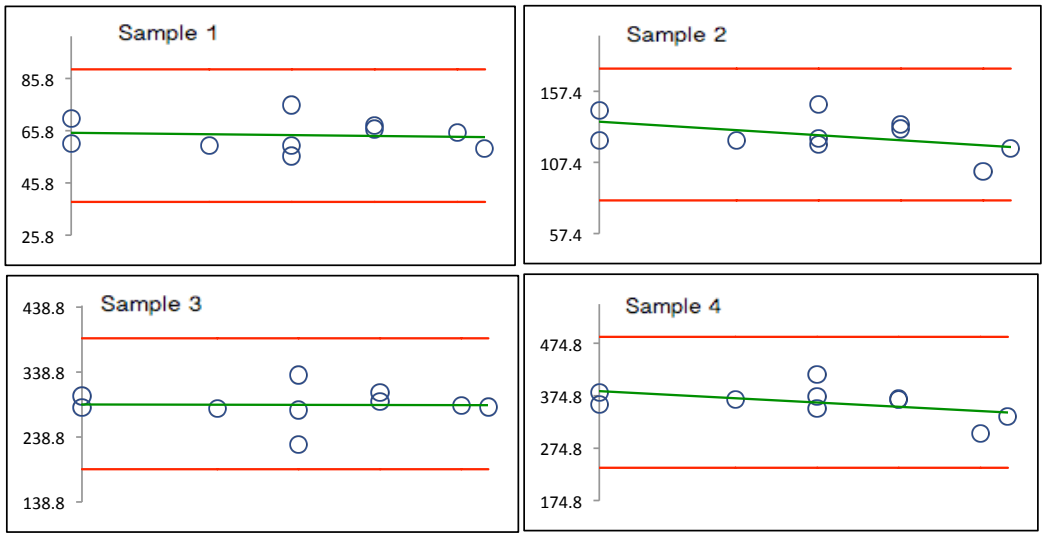


Kernel Density Plots



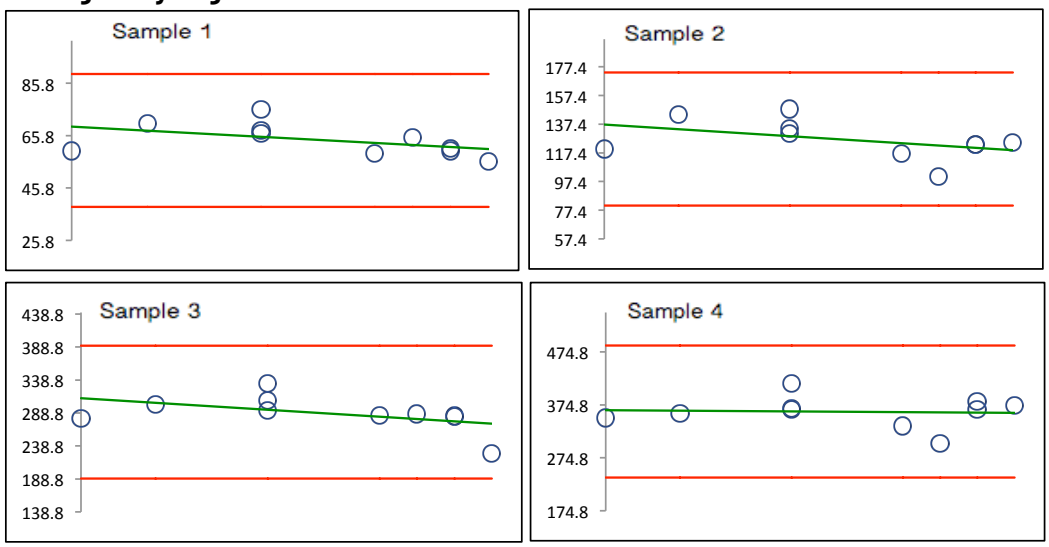
GAMMA-CHLORDANE

Stability Regression



Reported results (Y-axis) plotted against reported analysis date (X-axis)

Homogeneity Regression



Reported results (Y-axis) plotted against bottling order (X-axis).

HEPTACHLOR

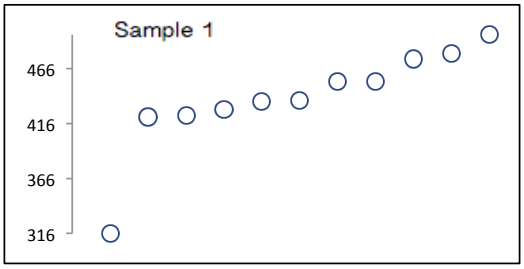
Summary Statistics

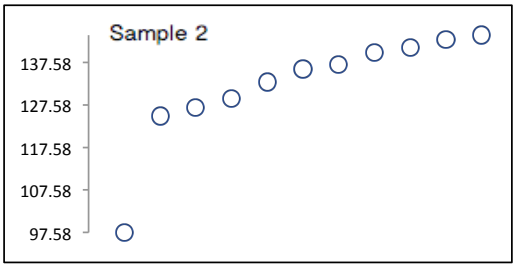
Statistic	C77-1	C77-2	C77-3	C77-4
N	11	11	11	11
Median	437	136	78.5	142
Robust Mean	446	134	79.4	144
U	12.6	3.3	1.8	3.1
Robust Standard Deviation	33.4	8.82	4.81	8.33
Regression Standard Deviation	87.7	28.2	17.7	30.0
Stability Flag				
Homogeneity Flag				
Standard Deviation Used	87.7	28.2	17.7	30.0
Outliers	1	1	1	1
|z|>3.0	0	0	0	0
2<|z|<3	0	0	0	0

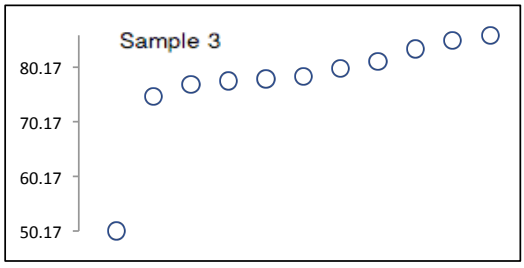
Methods Used

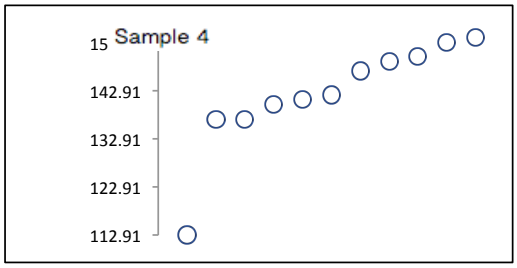
Method	C77-1	C77-2	C77-3	C77-4
GC/MS	4	4	4	4
GC/ECD	4	4	4	4
GC/ECD/SHKE	1	1	1	1
GC/MSHR	1	1	1	1
GC/MS/MS	1	1	1	1

All summary stats and the plots below are based on the data excluding any flagged outliers



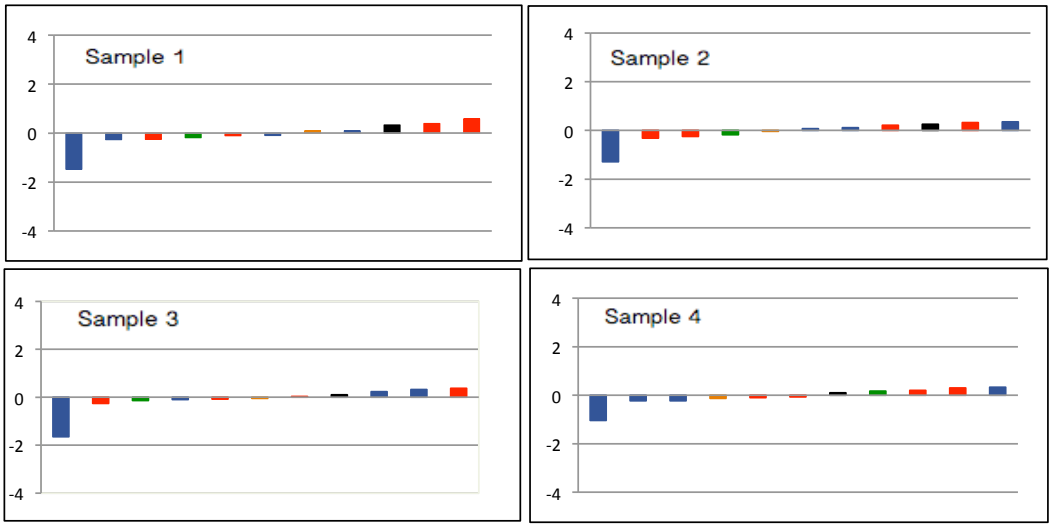




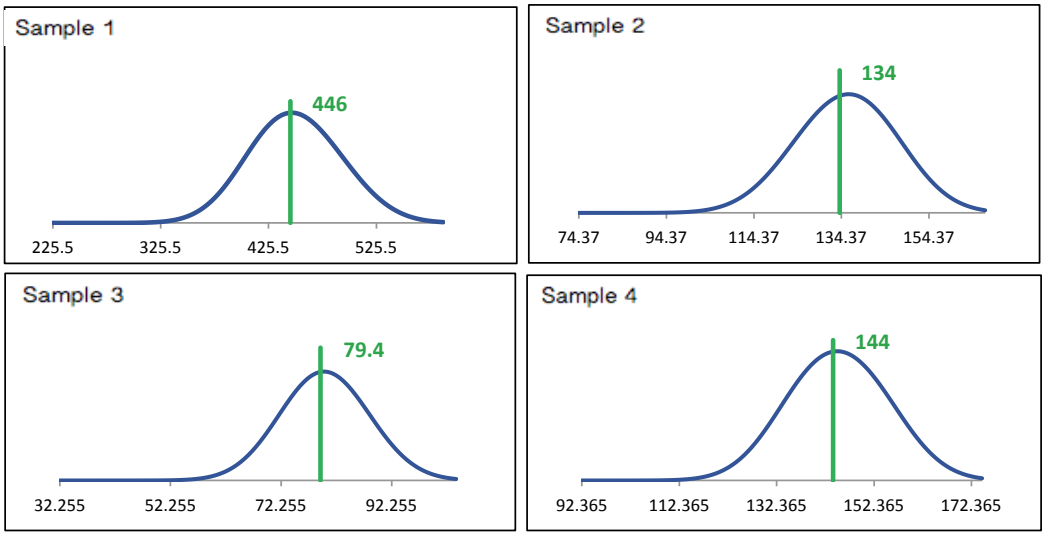


HEPTACHLOR

z-Score Plots

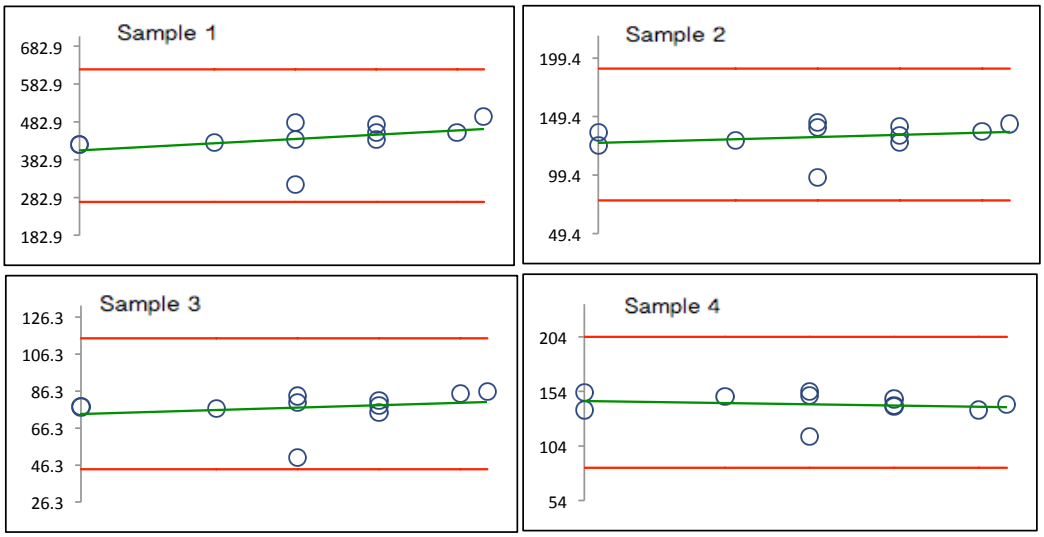


Kernel Density Plots



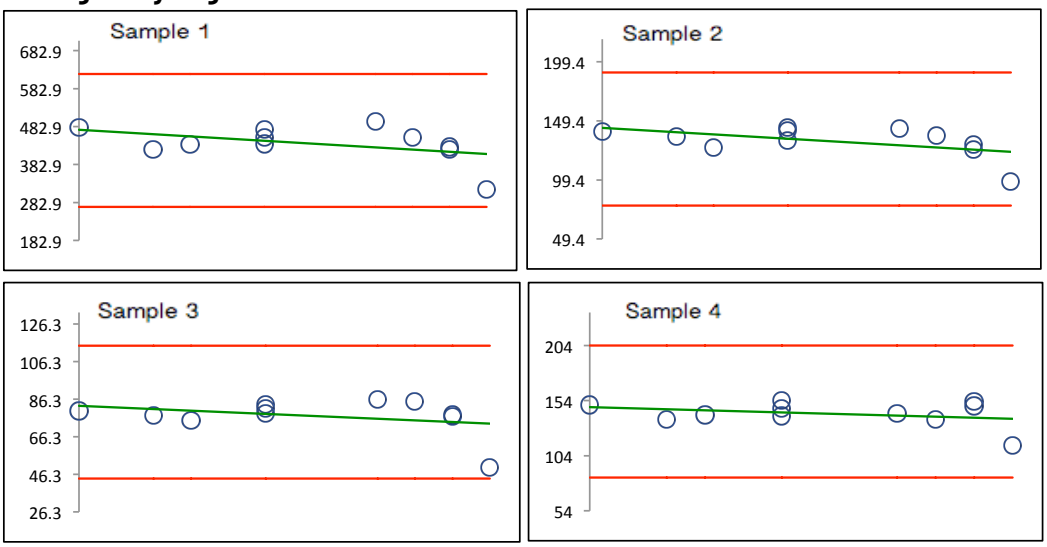
HEPTACHLOR

Stability Regression



Reported results (Y-axis) plotted against reported analysis date (X-axis)

Homogeneity Regression



Reported results (Y-axis) plotted against bottling order (X-axis).

HEPTACHLOR EPOXIDE

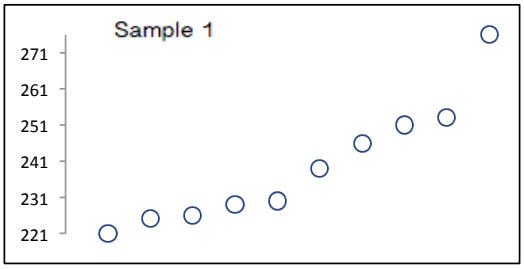
Summary Statistics

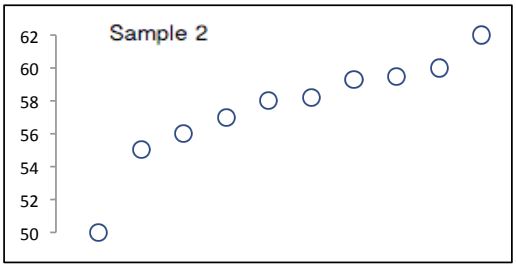
Statistic	C77-1	C77-2	C77-3	C77-4
N	10	10	10	10
Median	235	58.1	167.0	272
Robust Mean	238	57.9	166.0	264
U	6.3	1.1	3.5	11.5
Robust Standard Deviation	16.0	2.86	8.89	29.00
Regression Standard Deviation	45.0	12.8	32.0	49.7
Stability Flag				
Homogeneity Flag				
Standard Deviation Used	45.0	12.8	32.0	49.7
Outliers	1	1	1	1
|z|>3.0	0	0	0	0
2<|z|<3	0	0	0	0

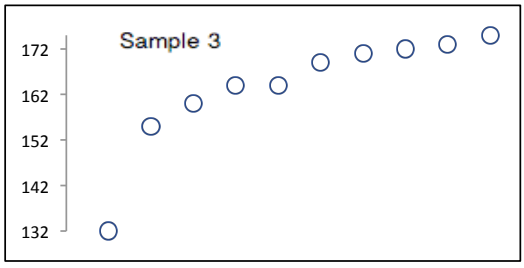
Methods Used

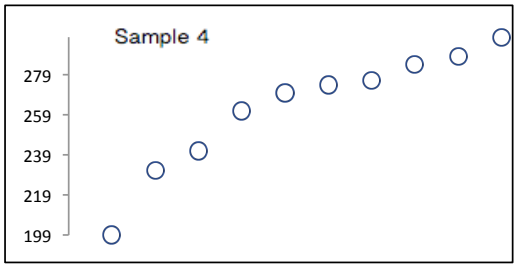
Method	C77-1	C77-2	C77-3	C77-4
GC/ECD	4	4	4	4
GC/ECD/SHKE	1	1	1	1
GC/MS	3	3	3	3
GC/MS/MS	1	1	1	1
GC/MSHR	1	1	1	1

All summary stats and the plots below are based on the data excluding any flagged outliers



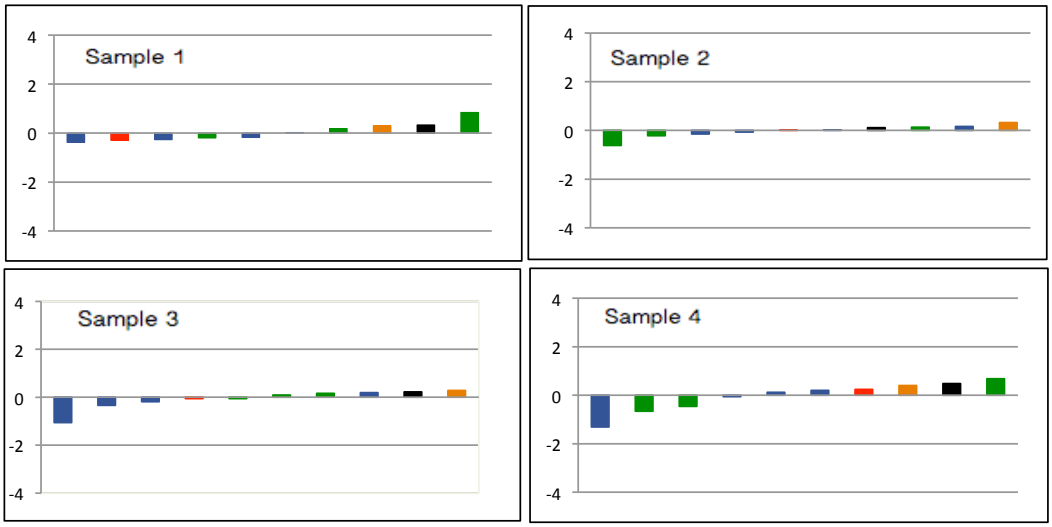




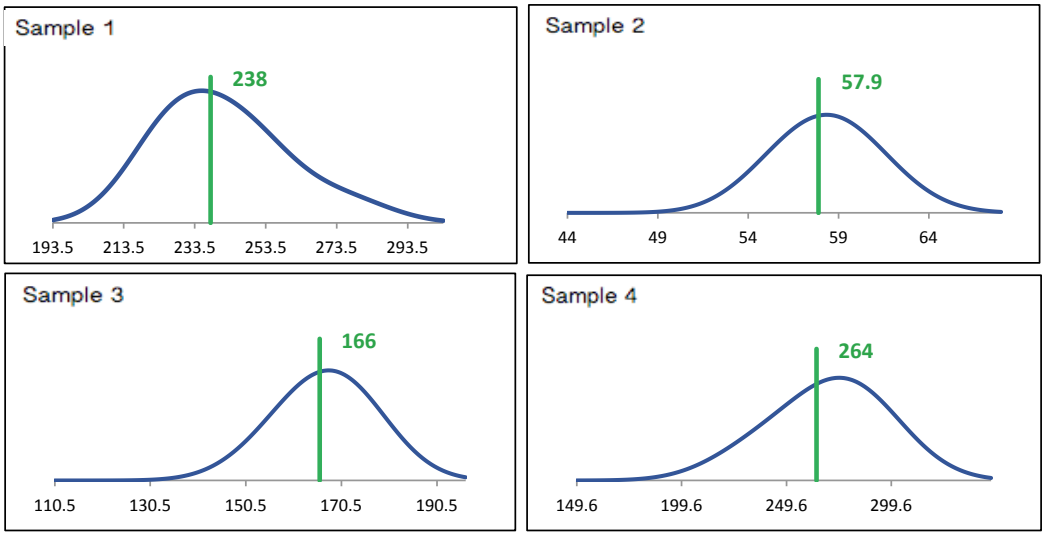


HEPTACHLOR EPOXIDE

z-Score Plots

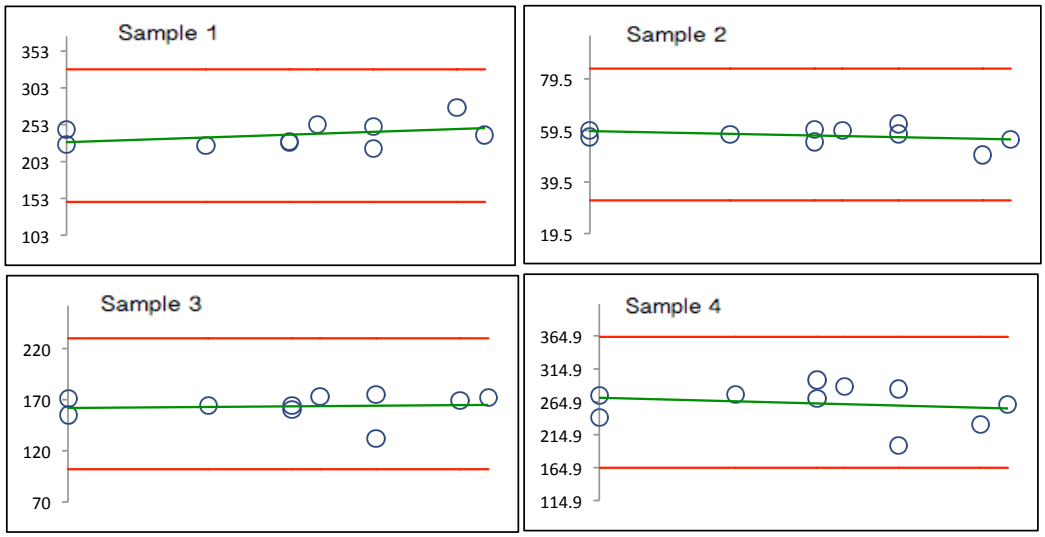


Kernel Density Plots



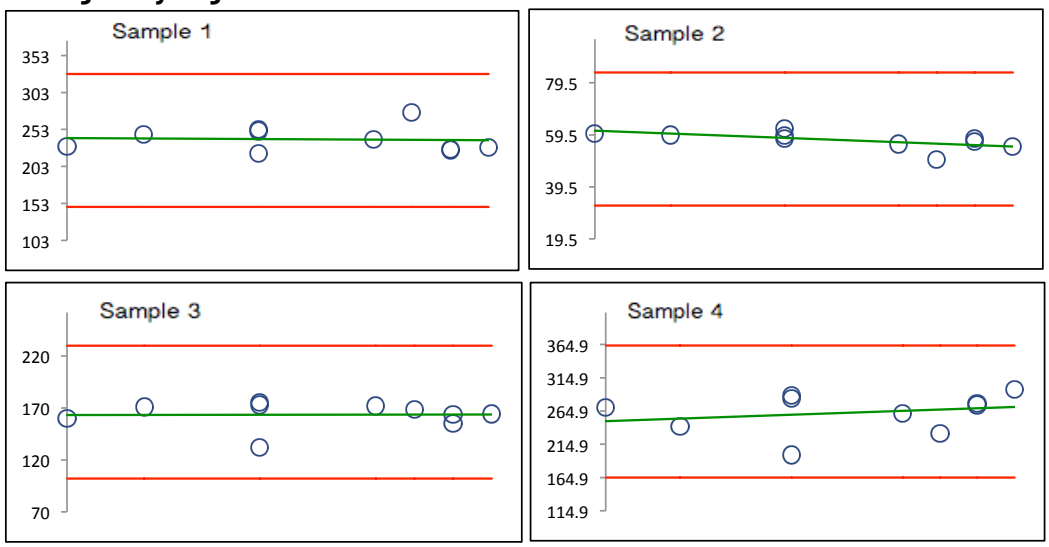
HEPTACHLOR EPOXIDE

Stability Regression



Reported results (Y-axis) plotted against reported analysis date (X-axis)

Homogeneity Regression



Reported results (Y-axis) plotted against bottling order (X-axis).

4,4'-METHOXYCHLOR (P,P'-METHOXYCHLOR)

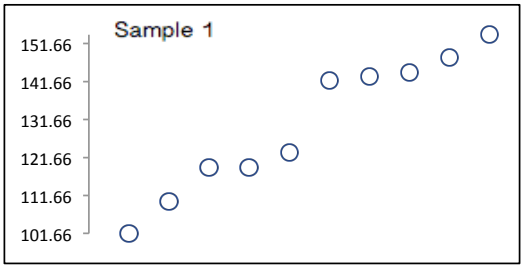
Summary Statistics

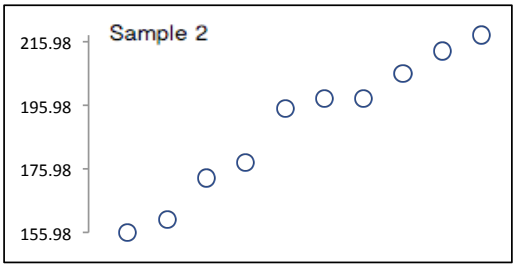
Statistic	C77-1	C77-2	C77-3	C77-4
N	10	10	10	10
Median	133	197	476	77
Robust Mean	130	189	469	78
U	8.1	9.7	21.0	6.6
Robust Standard Deviation	20.4	24.5	53.1	16.7
Regression Standard Deviation	41.2	57.2	132	27.0
Stability Flag				
Homogeneity Flag				
Standard Deviation Used	41.2	57.2	132	27.0
Outliers	0	0	0	0
|z|>3.0	0	0	0	0
2<|z|<3	0	0	0	0

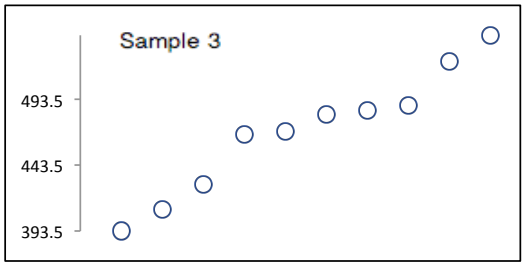
Methods Used

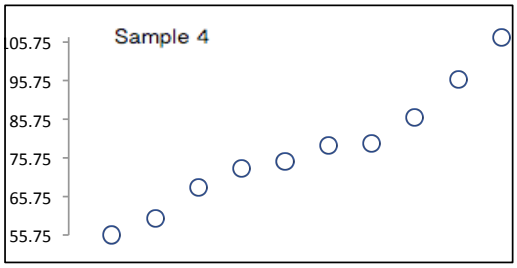
Method	C77-1	C77-2	C77-3	C77-4
GC/MS	3	3	3	3
GC/ECD	4	4	4	4
GC/MS/MS	1	1	1	1
GC/ECD/SHKE	1	1	1	1
GC/MSHR	1	1	1	1

All summary stats and the plots below are based on the data excluding any flagged outliers



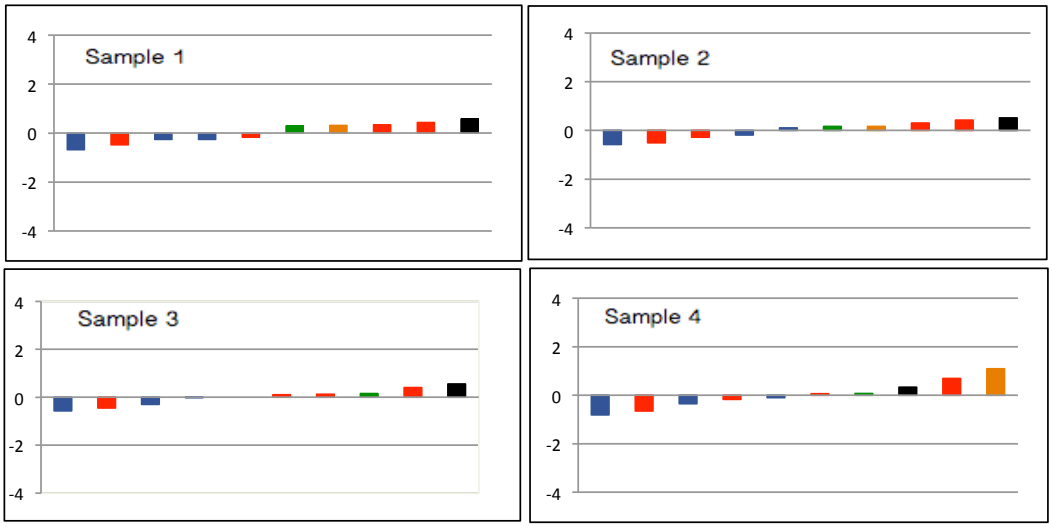




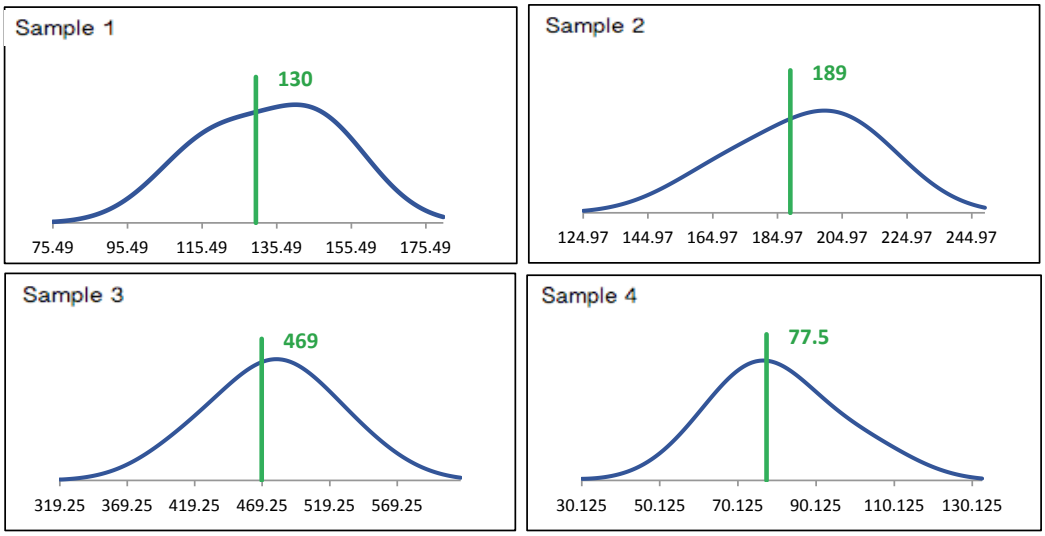


4,4'-METHOXYCHLOR (P,P'-METHOXYCHLOR)

z-Score Plots

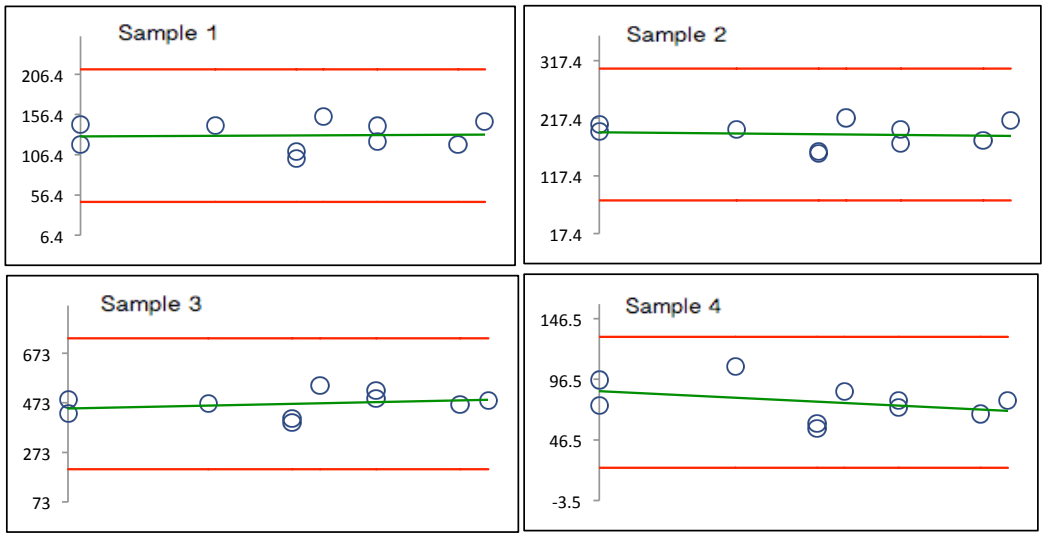


Kernel Density Plots



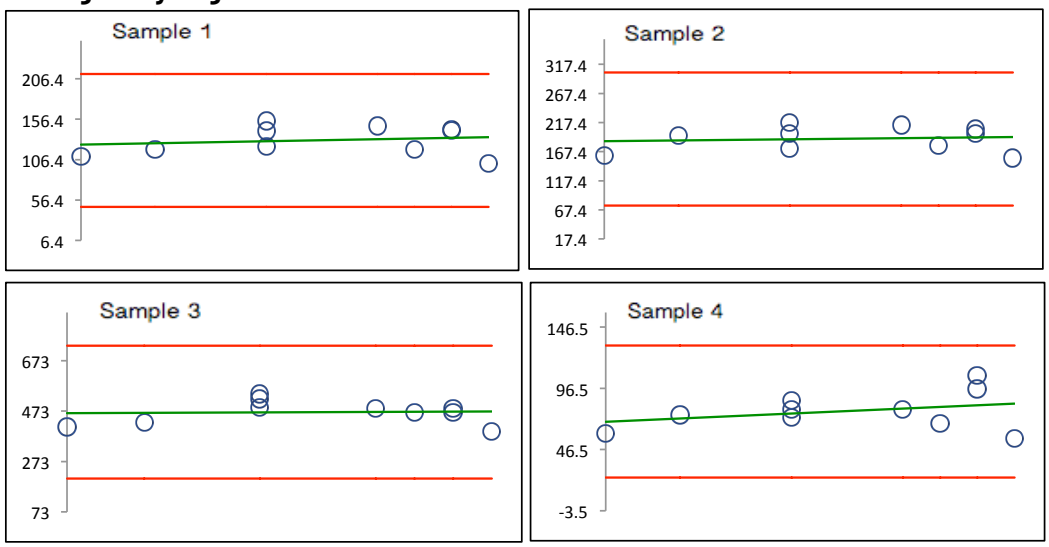
4,4'-METHOXYCHLOR (P,P'-METHOXYCHLOR)

Stability Regression



Reported results (Y-axis) plotted against reported analysis date (X-axis)

Homogeneity Regression



Reported results (Y-axis) plotted against bottling order (X-axis).