THE WASTEWATER TECHNOLOGY CENTRE INTERLABORATORY STUDY FOR TOTAL CYANIDE:

PHASE 2: HIGH LEVEL TOTAL CYANIDE

Prepared for:

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1.0 EXECUTIVE SUMMARY

This study was carried out on behalf of the Conservation and Protection Laboratory Managers Committee of Environment Canada to evaluate the capability of Environment Canada labs to determine total cyanide in standards and industrial wastewaters. This is part of an ongoing program to prepare and distribute reference materials from industrial wastewaters and containing parameters of interest to Federal laboratories.

At the present time there are 12 Environment Canada laboratories. In order to allow comparison with other labs and to increase the sample size, a provincial government laboratory and non-government labs from the mining and commercial sectors were invited to participate. As a result, 31 laboratories across Canada and the USA participated in the study. Several laboratories submitted results determined by two different analytical methods.

The study was carried out in 2 phases; the first for low levels of cyanide (less than 5 ppm) and the second, for high levels (0-60 ppm). In the low level study, sample matrices included reagent water and gold mining tailing pond effluent. In the high level study, the matrices included Municipal STP effluent and steel industry biox effluent. In both cases the desired concentrations of cyanide were achieved by spiking with potassium ferricyanide. This report deals with the high level phase of the study.

All samples were prepared at the Wastewater Technology Centre laboratories. Target concentrations were developed by precise weight and volume measurements and all operations were subject to witness. During bottling of the standard samples, sets of samples were collected for immediate laboratory analysis (to develop empirical standard concentrations). These same samples were also analyzed over the period of the study to test sample stability over time.

The four techniques used to evaluate the data in this study include;

- Frequency analysis to check the distribution of results to determine whether parametric statistics (example: standard deviation, t-test) can be used.
- A two step flagging procedure to eliminate Grubbs outliers and flag imprecise data.
- Regression analysis to assess accuracy and precision.
- Ranking analysis to determine if any of the laboratories are consistently biased.

Since the standard solutions were prepared with reagent grade chemicals and are not traceable to a known standard, the Expected Value for each standard solution was calculated using the best data returned by participating laboratories rather than the Target Value (calculated from weights and measures). This Expected Value was used as the mean for statistical comparisons.

The key findings of this study are:

- Thirteen of the 351 results submitted in the high level cyanide study fell outside 3 standard deviations of the mean and were flagged as outliers. This represents only 3.7% of the data. A total of 23% of the results were identified as Grubbs outliers in the low level study.

- Forty one of the remaining 338 data or 13 percent of the total being identified as falling outside one standard deviation of the mean recalculated after removal of the Grubbs outliers. A total of 15 of the 31 labs (48%) earned at least one flagged result. A total of 67% of labs earned at least one flag in the low level study.

- According to the regression correlation coefficient test, 22 of the 35 data sets (63%) displayed good or satisfactory precision. Thirteen of 35 data sets showed poor precision. In 2 of these 13 cases, the laboratories had difficulty in the analysis of the biox effluents. A third lab was classified as having poor precision as the result of a single out of control value.

- No bias was detected in 25 of 35 data sets (71% of the participants) when the regression slope test was applied. Bias was detected in 10 laboratories by this test. Twice as many labs were biased high than were biased low. This was due to the tendency of several laboratories to overestimate the cyanide concentrations in the biox effluent samples. In the low level cyanide study, 72% of the data sets were assessed as unbiased by the regression slope test.

- No bias was detected by the Rank Sum test in 29 (88 percent of the total) of the 33 data sets. Laboratories CN011, CN021, CN007 and CN028 were assessed as biased high, meaning they consistently overestimated the concentration of the standard solutions and would do so more that 95 times out of 100. These labs were also assessed as biased high by the regression technique.

- None of the laboratories were assessed as biased low by the Rank Sum test, suggesting that, as with the regression results, more laboratories had difficulty with the overestimation of the samples than underestimation.

- Twenty seven of the 35 data sets (77%) displayed good or satisfactory regression intercept values. Eight labs fell into the poor category. This is about the same number as in the low level study. To establish the source of the problems in these cases, an examination of the regression curves is recommended to determine whether the errant Y-intercept values are the result of imprecision, method failure at high concentrations, overestimation of a single sample or inappropriate blank correction.

i. Acknowledgements

This report was prepared by Peter Child of Investigative Science Incorporated on behalf of the Wastewater Technology Centre. The technical aspects of the study including study design, sample preparation and distribution was carried out by a project team comprised of Jim Fraser, Mohammad Foroutan and Peter Fowlie of Wastewater Technology Centre and Peter Child of Investigative Science Incorporated. The authors wish to acknowledge the contributions of Marrianne Austen to the study.

ii. Abbreviations and Key Terms

The following abbreviations and key terms are used in this report. They have specific definitions which are summarized below as well as explained more fully in the body of the report.

Milli–Q Water:	Eighteen megohm quality water generated by a Millipore Milli–Q system.
Biox Effluent:	Final effluent from the biox reactor at a steel plant.
STP Effluent:	Final effluent from a municipal sewage treatment plant.
Standard Solutions:	The ten solutions or samples (labelled H1 through H10) sent to each participating laboratory.
Target Values:	The theoretical cyanide concentrations in the Standard Solution as calculated by weights and measures.
Expected Values:	The cyanide concentrations in the Standard Solutions statistically determined using data from the most accurate and precise participating laboratories.
mg/L:	Milligrams per litre, equal to parts per million (ppm).

- Comparison of the variability in the results for the water-based standards and effluents showed a substantial difference between the two. The coefficient of variation (standard deviation expressed as a percentage of the mean) for the biox effluent was 75%, the STP effluent; 57% and for samples having a water matrix was 31% before removal of the invalid data (Grubbs outliers). Once the outlying results were removed from the data set, the coefficient of variation for the biox effluent was 53%, the STP effluent; 40% and for samples having a water matrix; 17%. The results indicate that even when the extreme outlying results are removed from the data set, the effluent results were still more variable than results obtained with pure water standards.

2.0 INTRODUCTION

This study was carried out on behalf of the Conservation and Protection Laboratory Managers Committee of Environment Canada to evaluate the capability of Environment Canada labs to determine total cyanide in standards and industrial wastewaters. This is part of an ongoing program to prepare and distribute reference materials from industrial wastewaters and containing parameters of interest to Federal laboratories.

At the present time there are 12 Environment Canada laboratories. In order to allow comparison with other labs and to increase the sample size, non-government labs from the mining and commercial sectors were invited to participate. A total of 31 laboratories across Canada and the USA participated in the study.

The study was carried out in 2 phases; the first for low levels of cyanide (less than 5 ppm) and the second, for high levels (0–60 ppm). In the low level study, sample matrices included reagent water and gold mining tailing pond effluent. In the high level study, the matrices included Municipal STP influent and steel industry biox effluent. In both cases the desired concentrations of cyanide were achieved by spiking with potassium ferricyanide.

This report was prepared in 2 independent sections to reflect the 2 phases of the study.

3.0 TECHNICAL APPROACH

3.1 STUDY DESIGN

The study was designed to test laboratory proficiency in both pure water and industrial effluent matrices using ferricyanide ($Fe(CN)_6$) as the spike. The pure water matrix samples minimize potential interference whereas the effluent matrix samples provide the participating laboratories with samples containing interferences normally found in environmental analysis.

A total of ten samples were sent to each laboratory using ferricyanide ($Fe(CN)_6$) as the spike. Four samples were prepared with target concentrations of 10 to 40 mg/L CN^- in pure water, four samples covered the range of 25 to 85 mg/L CN^- in steel industry biox effluent, and three samples contained 0–11 mg/L CN^- in treated STP effluent. The background cyanide concentration was about 27 mg/L in the steel industry biox effluent and about 0.03 mg/L in the STP effluent.

Table 3.1 summarizes the target cyanide concentrations in the samples prepared for the study. The actual values determined in this study are summarized in Table 4.2.

The participating laboratories were each given a unique identification code number (CN001 through CN036). For labs submitting more than one data set, the letters A and B were appended to their codes. These code numbers were used in all subsequent correspondence to ensure the confidentiality of the results.

The samples were sent to the participants on Monday, February 17, 1992 by overnight courier. The ten samples were numbered randomly (as in table 3.1). The results were requested by March 31, 1992.

On April 27, 1992, a summary of the raw results were returned to each participant with a request that they check the results for data entry errors. The laboratories were advised at the outset that changes to results, other than data entry errors, could not be made at this time. Four laboratories requested corrections and these were made.

3.2 PREPARATION OF STANDARDS AND SAMPLES

3.2.1 OVERVIEW

A set of ten 30 litre standard cyanide solutions was prepared in 50 litre carboys for the study. Of these, seven were prepared in an effluent matrix and three in a pure water matrix. Initially a stock solution of 1000 mg/L CN^- was prepared with aliquots of this stock solution used to make up the standard solutions. The samples were bottled directly from the standard solution carboys.

In the preparation of the standard solutions and the samples, all weights, measurements, and records were witnessed by an observer to prevent mistakes by the analyst.

3.2.2 EQUIPMENT AND REAGENTS

The cyanide for the preparation of the stock solution was potassium ferricyanide ($K_4Fe(CN)_6 \cdot 3H_2O$) provided by Fisher (Certified ACS potassium ferricyanide, Cat. No. P-236, Lot 712095). Impurities in the reagent were 0.015% by weight and were accounted for in the preparation of the stock solution. No certified traceable source of pure cyanide salt (example: National Bureau of Standards, Canadian Standards Association, U.S. Environmental Protection Agency) could be found.

To stabilize the stock solutions and samples sodium hydroxide (NaOH) was added to bring the pH to 12. The sodium hydroxide was purchased from Fisher (Certified ACS sodium hydroxide, Cat. No. S-320. Lot 736976-60).

All water used for stock solution preparation and dilution of standards was 18 megohm produced by a Millipore Milli-Q water purification system. The effluents were biox effluent from local steel mill and treated effluent from a municipal sewage treatment plant.

Stock solutions were prepared using a balance and volumetric glassware. The balance calibration was checked with standard weights on November 18, 1991 and found to be accurate to ±0.001 gram. Volumetric dispensing of the stock solution to the standard solutions was done using volumetric pipettes.

The standard solutions were prepared in new 50 litre polypropylene carboys. The carboys were first washed with dilute sulphuric acid and triple rinsed with 18 megohm water. The samples were dispensed from the carboys through Tygon tubing into new 500 mL rectangular Nalgene bottles (high density polyethylene, Nalgene product number: 2007-0016).

3.2.3 PREPARATION OF STOCK WATER AND CYANIDE SOLUTIONS

The stock water or effluent was prepared in batches as required by putting 130 litres of water or effluent into a 200 litre plastic carboy and adding 480 ml of 20 % NaOH solution. This stock water was at pH 12 and was used as dilution water to make up the standard solutions.

The stock cyanide concentrate containing 10000 mg/L CN^- was prepared as follows: Into a 1 litre volumetric flask, 0.5 litre of water and 10 ml of 1 N NaOH were added and the pH tested with pH paper (pH 12.5). To this, 27.0624 g of $K_4Fe(CN)_6 \cdot 3H_2O$ was added and the volume brought up to below the 1 litre line. The pH was checked again and the solution made up to volume.

3.2.4 PREPARATION OF STANDARD SOLUTIONS

A set of ten cyanide solutions were prepared for the study with target concentrations shown in Table 3.1. The quantities of reagents used to prepare the standard solutions are also summarized in this table. All were prepared using the stock water, effluent and cyanide solutions discussed in the previous section.

The standards were prepared in 50 litre polypropylene carboys according to the following general protocol:

1) The carboys were washed with dilute sulphuric acid solution and rinsed three times with 18 megohm water.

2) Approximately 30 Kg of stock water was weighed into each carboy and this calibration level was marked for further reference. The exact weight of water was measured for each calibration level.

3) Stock water (Milli-Q water or effluent with NaOH to pH 12) was added to the carboy up to the calibration line (approximately 30 Kg). The exact weight of stock water was calculated using the measured density and calibrated mark on the carboy.

4) The required amount of 10,000 mg/L CN^- stock solution (see section 3.2.3) was added directly to the carboy using a volumetric pipette.

5) The contents were stirred for 1 minute with an electric mixer.

6) Each addition, weight or volume, was checked by a second analyst and the record initialled.

7) The solutions were bottled immediately and stored at room temperature until shipping.

Table 3.1

REAGENT QUANTITIES USED TO PREPARE THE HIGH LEVEL CYANIDE STANDARD SOLUTIONS

Sample Number (random)	Matrix	Cyanide Spike Level (mg/L)	Cyanide Stock† (ml)	Stock Water (kg)
H1	Biox Effluent	10	30.0	29.971
H2	STP Effluent	10	30.0	29.971
H3	STP Effluent	none	none	29.971
H4	Water	10	30.0	29.971
H5	Biox Effluent	40	120.0	30.094
H6	Biox Effluent	20	60.0	29.971
H7	Water	20	60.0	30.094
H8	Water	40	120.0	30.094
H9	Biox Effluent	none	none	29.971
H10	STP Effluent	5	15.0	30.094

†: 10,000 mg/L Stock Cyanide Solution

3.2.5 BOTTLING OF STANDARD SAMPLES

The samples were dispensed from the 50 litre carboys directly into new rectangular 500 mL Nalgene bottles through Tygon tubing immediately after preparation. All solutions were mechanically stirred for 1 minute prior to bottling. The bottled samples were capped and stored at room temperature until shipping. The filling sequence was recorded and three samples per sequence (starting, middle, and end) were retained for internal analysis.

3.3 VERIFICATION OF STANDARD CONCENTRATIONS

3.3.1 OVERVIEW

Verification of the standard concentrations was done using procedures to assure accurate target concentrations by weights and measures as well as by actual analysis of standard samples. Target concentrations were developed by precise weight and volume measurements (see Table 3.1) and all operations were subject to witness. During bottling of the standard samples, sets of samples were collected for immediate laboratory analysis (to develop empirical standard concentrations). These same samples were also analyzed over the period of the study to test sample stability over time.

No traceable source of pure cyanide salts were available for the study so Fisher Certified ACS potassium ferricyanide was used. The impurity content provided by the supplier (0.015%) was factored into the calculations for making up the cyanide standard solution but no independent verification of the purity was undertaken.

3.3.2 WITNESS SYSTEM

To reduce the chance of measurement, reading, or recording error a qualified witness observed all acts of weights and measures during the preparation of the stock and standard solutions. Laboratory notes were initialled by the witness throughout the procedure.

3.3.3 INTERNAL ANALYSIS OF STOCK REAGENTS

Internal analysis was performed on the stock reagents used. Analysis of the Stock Water (Milli-Q water with NaOH to pH 12) showed no detectable cyanide (less than 0.005 mg/L). Triplicate analysis of the steel industry biox effluent showed a cyanide concentration of 24.7 ± 0.6 mg/L. Triplicate analysis of the municipal treatment plant effluent showed a cyanide concentration of 0.033 ± 0.003 mg/L.

3.3.4 INTERNAL ANALYSIS OF FRESH STANDARD SOLUTIONS DURING BOTTLING

During the bottling of the standard solutions three 500 mL samples were collected for internal analysis. The samples collected were the first in the bottling series (bottle 1), one in the middle of the series (bottle 25), and one at the end of the series (bottle 53, 54, 55, or 56). Each of these samples was analyzed for cyanide concentration.

The results are shown in Table 3.2. From these data, we concluded that there were no systematic differences in cyanide concentration between the first and last samples bottled in each Standard Solution.

TABLE 3.2

ANALYSIS OF SAMPLES COLLECTED DURING THE BOTTLING RUN

Sample Number	Matrix	Position of Sample in Bottling Run			Mean	Standard Deviation
		Start	Middle	End		
H1	Biox Effluent	37	35	36	36.000	0.816
H2	STP Effluent	10	10	10	10.000	0.000
H3	STP Effluent	0	0	0	0.033	0.002
H4	Water	10	11	10	10.333	0.471
H5	Biox Effluent	67	67	64	66.000	1.732
H6	Biox Effluent	46	47	45	46.000	0.816
H7	Water	21	20	21	20.667	0.471
H8	Water	42	42	42	42.000	0.000
H9	Biox Effluent	25	25	24	24.667	0.471
H10	STP Effluent	5	5	5	5.317	0.109

3.3.5 INTERNAL ANALYSIS OF STANDARD SOLUTIONS FOR STABILITY

To determine if the standard samples were stable for the duration of the project, the samples retained for internal analysis were analyzed weekly for cyanide concentration. Each standard solution was tested three times between the start of the project and the date results were due from the participating laboratories.

The results are given in Table 3.3. From these results, we concluded that there was no evidence that the cyanide concentration in the bottled standard samples changed over the duration of the study.

TABLE 3.3

ANALYSIS OF BOTTLED STANDARDS OVER THE DURATION OF THE STUDY

Sample Number	Matrix	Cyanide Concentration (mg/L)				Mean	Standard Deviation
		Week 0	Week 2	Week 3	Week 4		
H1	Biox Effluent	36	35	36	34	35.250	0.829
H2	STP Effluent	10	10	11	10	10.250	0.433
H3	STP Effluent	0	0	0	0	0.035	0.002
H4	Water	10	10	10	10	10.083	0.143
H5	Biox Effluent	56	66	68	66	64.000	4.690
H6	Biox Effluent	46	45	46	45	45.500	0.500
H7	Water	21	21	20	19	20.175	0.769
H8	Water	42	42	42	42	42.000	0.000
H9	Biox Effluent	25	24	25	24	24.425	0.438
H10	STP Effluent	5	5	5	5	5.195	0.123

3.4 DATA EVALUATION

3.4.1 OVERVIEW

The purpose of assessing the data in this project is to identify values which differ significantly from the values expected and to characterize the status of laboratory analysis in general. Since the standard solutions were prepared with reagent grade chemicals and are not traceable to a known standard, the Expected Value for each standard solution was calculated using the best data returned by participating laboratories rather than the Target Value (calculated from weights and measures). This Expected Value is used as the mean for statistical comparisons. Its rationalization and calculation is described in section 4.2.3 of this report.

In addition to identifying outlying data and laboratories, the analysis techniques provide useful information as to why certain data or laboratories deviate significantly from the Expected Values. The interpretation of the statistical analysis is used to constructively review the performance of the participating laboratories.

The four techniques used in this study are:

- Frequency analysis to check the distribution of results to confirm that parametric statistics (example: standard deviation, t-test) can be used;
- A two step flagging procedure to eliminate Grubbs outliers and flag imprecise data;
- Regression analysis to compare each laboratory's results with the Expected Values and evaluate precision;
- Ranking analysis to determine if any of the laboratories are consistently biased.

Each technique is described in more detail below.

3.4.2 FREQUENCY DISTRIBUTION OF DATA

Round robin analytical data is expected to be distributed normally (ie. the data are distributed on a normal or "bell" curve) but there are cases such as consistent high or low end method failure where the data may appear skewed or even bi-modal. Frequency distribution is used to subjectively determine if the data are distributed normally.

To test the frequency distribution the data sets for each standard sample are arithmetically adjusted about a single mean. The frequency distribution of the entire data set is then plotted and visually interpreted.

3.4.3 FLAGGING PROCEDURE

The flagging procedure is done in two stages. In the flagging procedure the variability of the data is estimated using the standard deviation statistic calculated as a function of Quattro Pro 3.0® (Borland International). An explanation and definition of the statistic can be found in most introductory statistics texts such as Ostle and Mensing, 1975.

The first stage was to remove all invalid data generally referred to as Grubbs outliers (reference 1) and defined as all results which are more than three (3) standard deviations from the mean. Once the Grubbs outliers are removed, the means and standard deviations for each Standard Solutions are recalculated.

In the second stage of the flagging procedure the recalculated means and standard deviations are used to identify the data which lies outside one (1) standard deviation from the mean. The criteria of 1 standard deviation is arbitrary but considered reasonable by the authors for the purposes of this study.

To determine the Expected Values for each Standard Solution (the value deemed as correct) the outliers (ie. the data which lie outside one standard deviation from the mean) are removed from the data set and the means are recalculated. These means, which represent the results obtained by the central core of unflagged labs, are used as the Expected Values.

3.4.4 REGRESSION ANALYSIS

Linear regression analysis is done for the results of each participating laboratory. The analysis is done using the linear regression function (calculated using least squares) of Quattro Pro 3.0® (Borland International) . An explanation and definition of the statistic can be found in most introductory statistics texts such as Ostle and Mensing, 1975.

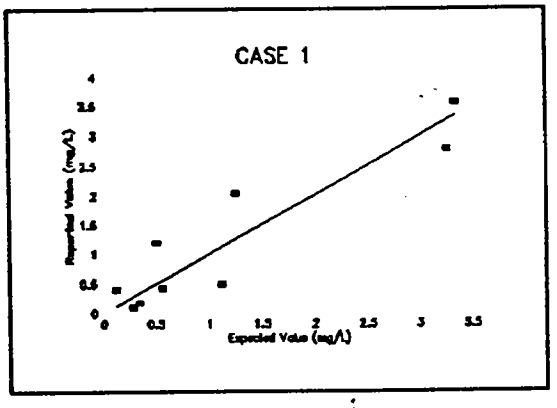
This analysis tests the performance of the laboratory by comparing the reported results of the laboratory to the Expected Values. Regression analysis provides both a visual representation of the data as well as descriptive statistics such as slope, regression coefficient, and $Y_{intercept}$. The results of regression analysis can be used to diagnose some of the typical problems found in laboratory performance studies. These problems, illustrated in Figure 3.1, include:

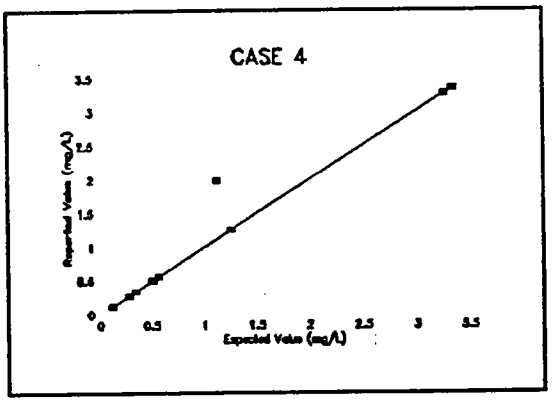
- Lack of precision (case 1)
- Calibration problems (high bias illustrated in case 2)
- Analytical blank problems (combined with high bias in case 3)
- Single sample outlier problems (case 4)
- Method failure (case 5)

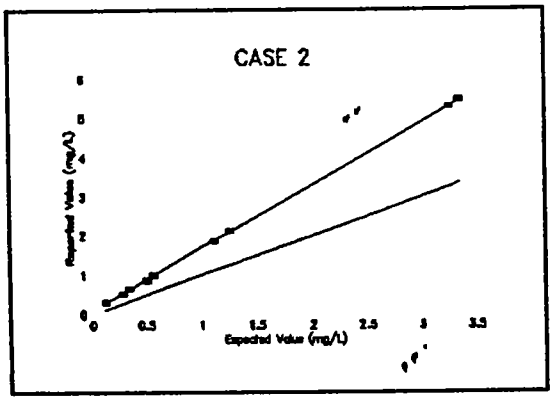
Case 6 in Figure 3.1 represents the ideal situation; perfect accuracy and precision. It should be noted that in Figure 3.1, the line passing through the data points represents the best fit regression line, while the other indicates the expected values.

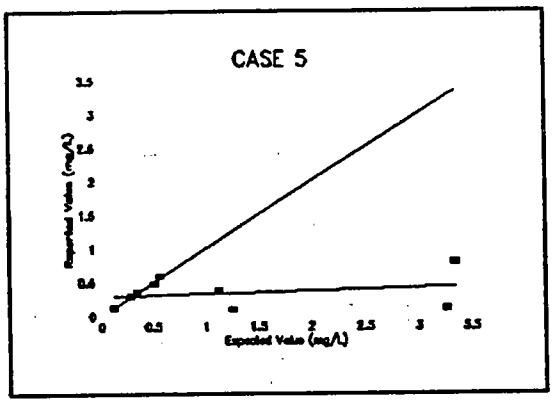
Figure 3.1

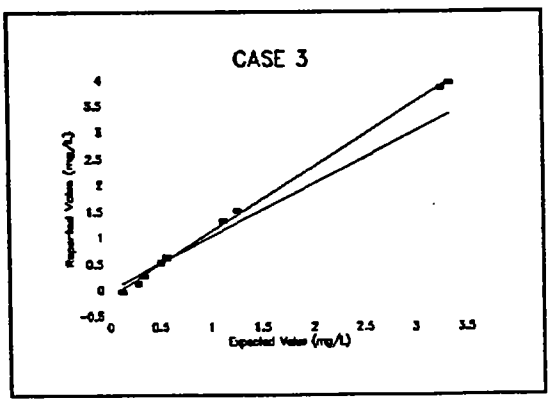
TYPICAL PROBLEMS ENCOUNTERED IN
LABORATORY PERFORMANCE STUDIES

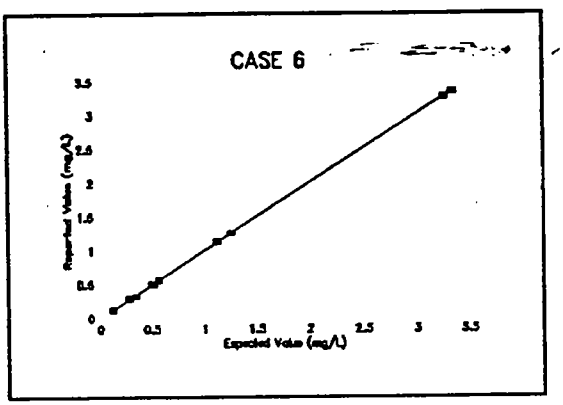












Using the descriptive statistics generated by regression analysis the precision of a laboratory is reflected in how close the reported data are to the regression line. This "quality of fit" is quantified by the regression coefficient R^2. For the purposes of this study the authors have arbitrarily chosen the following criteria: A regression coefficient (R^2) of greater than 0.995 to indicate good precision; An R^2 between 0.995 and 0.990 to indicate satisfactory precision; An R^2 of less than 0.990 to indicate poor precision.

The accuracy of each laboratory is reflected in the slope of the best fit line. The slope of the ideal line is 1.0 therefore lines which deviate significantly from this may indicate a calibration problem. For the purposes of this study the authors have arbitrarily chosen the following criteria: Laboratories with slopes falling between 0.85 and 1.15 are considered unbiased. Laboratories with slopes greater than 1.15 are designated as biased high. Laboratories with slopes less than 0.85 are designated as biased low.

A problem with the analytical blank may manifest itself as a deviation of the $Y_{intercept}$ from the origin. For the purposes of this study the authors have arbitrarily chosen the following criteria: A $Y_{intercept}$ within 0.3 mg/L of the origin is considered good; A $Y_{intercept}$ within 3 mg/L is considered satisfactory; A $Y_{intercept}$ greater than 3 mg/L from the origin is considered poor.

3.4.5 RANKING OF DATA TO DETECT BIAS

A Rank Sum Test (Youden and Steiner, 1975) is used to determine if any of the participating laboratories are consistently biased (ie. does a specific laboratory overestimate or underestimate all the Standard Solutions in a systematic manner). To calculate this statistic, the data from each laboratory for each Standard Solution are ranked. The rank 1 is given to the lowest result, a rank of 2 to the next lowest and so on. The rankings are then summed for each laboratory. The presumption is that a laboratory which ranked 1 for most or all standard solutions has a pronounced systematic bias towards underestimating the concentration.

The criterion for detecting bias is suggested by Youden as 5 percent. This criterion was adopted in the present study. This means that laboratories identified as biased by the test would be expected to be biased 19 times out of 20.

This statistic is useful in determining laboratories which are consistently producing either high or low results. Youden's rank test is non-parametric and can therefore be used without having normally distributed data. This makes it useful if the data are skewed or bi-modal in distribution. Like the paired t-test, however, Youden's rank test loses sensitivity if a laboratory's data is imprecise. It is, therefore, most useful for detecting slight biases in results from labs displaying a high degree of precision.

A summary of the strengths and weaknesses of the methods used to evaluate the results is given in Table 3.4

TABLE 3.4

SUMMARY OF DATA EVALUATION METHODS

Method	Features	Weaknesses	Requires Normal Data?
Outlier Analysis	-gives information on each individual result -recognizes differences between measured and expected values	-cannot distinguish inaccuracy from imprecision -flagging criteria depends upon entire group, therefore, if the entire group performs poorly, the flagging criteria are less strict	yes
Regression Analysis	-looks at pooled sample set -can distinguish imprecision from inaccuracy -indicates magnitude of biases -informative graphical format	-strongly affected by outliers	yes
Rank Sum Test	-detects bias -looks at pooled sample set -doesn't require normally distributed results	-may not detect bias in imprecise results or in cases where measured result line crosses the expected line -doesn't give magnitude of biases detected	no

4.0 RESULTS AND DISCUSSION

4.1 SUMMARY OF PARTICIPATING LABORATORIES

Thirty one laboratories participated in the study providing a total of 36 groups of results for analysis. A list of the participating laboratories is in Appendix 1. It should be noted that this listing is not in order of laboratory code.

4.2 ASSESSMENT OF LABORATORY PERFORMANCE

4.2.1 OVERVIEW

The purpose of the performance tests are to gain information concerning the accuracy and precision of each laboratory and to provide information as to why any specific laboratory had difficulty. It is the aim of these studies to provide constructive comments to the participants concerning potentially correctable problems such as calibration error, inappropriate blank correction, or method failure.

The laboratory performance is discussed in general terms in the following subsections. In addition, laboratory specific performance information is given in section 6.0. A complete table of the raw results is in Appendix 2.

4.2.2 DATA DISTRIBUTION

The overall distribution of the data was checked by developing a frequency distribution after arithmetically adjusting each standard sample result around a single mean. The purpose of this is to determine if there are any unusual skews in the data or if the data is bi-modal. Such non-normal distributions would indicate if there was a general method failure at the high end or near zero through the overall study. In addition, normally distributed data are necessary for the use of standard deviation statistics.

The frequency analysis, with and without the removal of Grubbs outliers, is shown in Figure 4.1. The shape of this distribution indicates the entire data set is probably normally distributed. There are small peaks at the high end of the distribution but these are largely accounted for when the Grubbs outlyers are removed (lower figure).

In addition to the frequency plot of the entire set of results, we tested each set of sample results using four standard normality tests. All four tests indicated that five of ten sets of results were normally distributed when outying values were removed. A further three sets were assessed as normal by at least one of the four tests after the removal of outliers. Two sets of results (H5 and H7) were not normal by any of the four tests under any conditions.

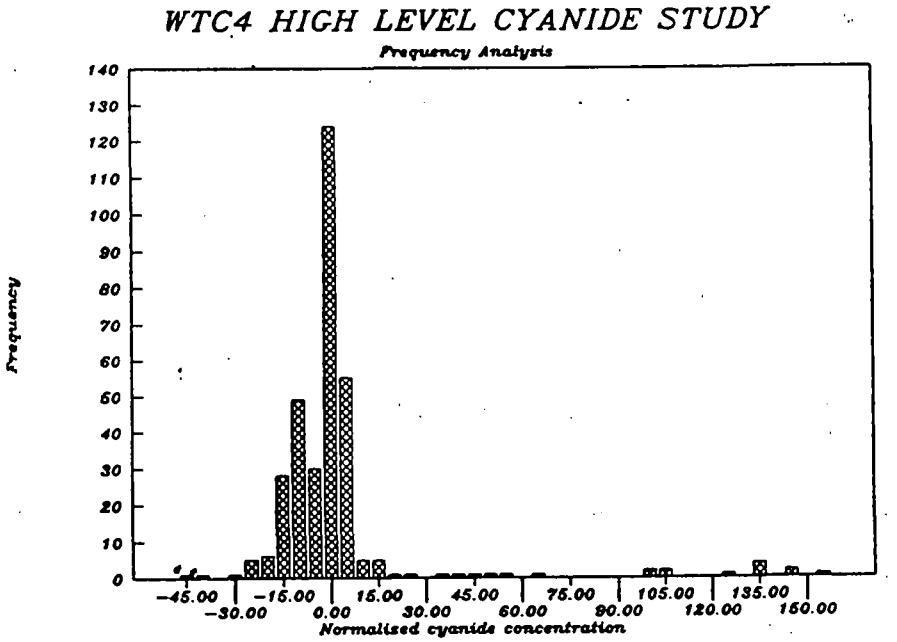
Several of the frequency plots for the individual sample result sets were skewed toward the right, or towards higher values. None were skewed to the left, or lower values. This indicates that for some samples, overestimation of the results was more common that underestimation. There was no correlation between the type of sample (eg. biox effluent, STP effluent or water-based sample) and the shape of the distribution of results.

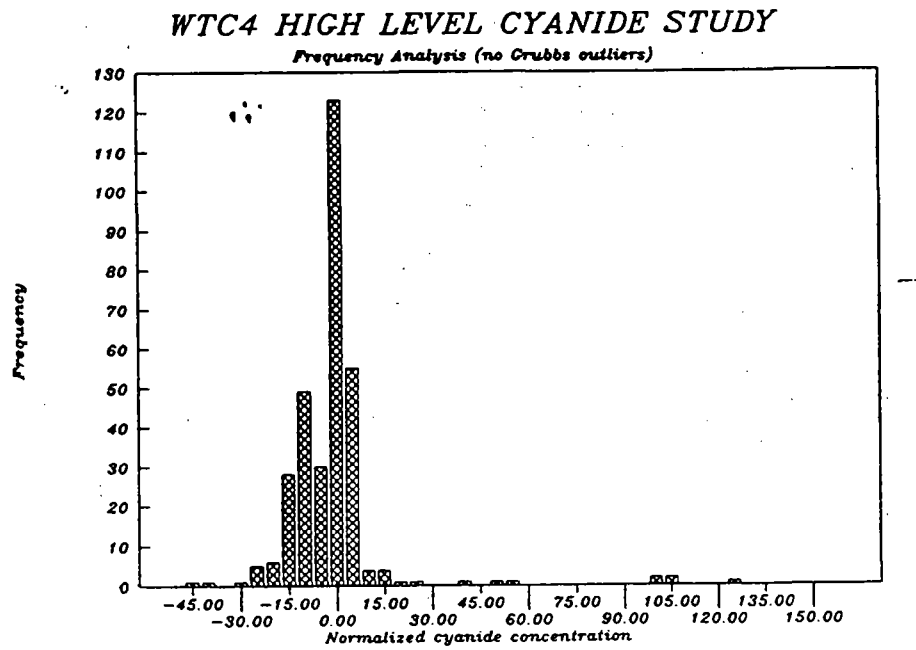
A non-normal distribution of results is not expected to influence the laboratory evaluations based on the regression analysis or the rank-sum test. The regression analysis uses only the slope, correlation coefficient and intercept of the best fit line and does not use the standard deviation of the data. The rank sum test is specifically used because it does not require a normal distribution of results.

The only test which is based solely on the mean and standard deviation is the assignment of flags. A non-normal distribution of results would influence the expected value and the standard deviation. We concluded that, in this case, the effect of non-normalcy would probably be only to widen the window into which "acceptable" results may fall. We recognize this limitation but, as the choice of a window defined by the mean plus or minus one standard deviation is itself arbitrary, we feel that the results of the flag assignment are still useful.

FIGURE 4.1

DISTRIBUTION OF STUDY RESULTS





4.2.3 EXPECTED VALUES

In this study the Expected Values are produced from the data submitted by the participating laboratories. The process is to use the full raw data set to calculate means and standard deviations (SD) for each Standard Solution. The Grubbs outliers (data more than 3 SD's from the mean) are then removed and the means and SD's are recalculated giving the valid data set. In the valid data set all data more than 1 SD from the mean are then rejected and the means again recalculated. These means are the Expected Values. The spike levels and resulting Expected values are shown in Table 4.2.

Table 4.2

INTERLABORATORY STUDY FOR LOW LEVEL TOTAL CYANIDE
TARGET AND EXPECTED VALUES FOR THE STANDARD SOLUTIONS

SAMPLE NUMBER	TARGET VALUE (mg/L) as CN^-	EXPECTED VALUE (mg/L) as CN^-
H1	10 mg/L + H9 value	36.40
H2	10 mg/L + H3 value	10.63
H3	unspiked STP effluent	0.025
H4	10 mg/L in Milli-Q water	10.66
H5	40 mg/L + H9 value	67.63
H6	20 mg/L + H9 value	46.51
H7	20 mg/L in Milli-Q water	21.13
H8	40 mg/L in Milli-Q water	42.46
H9	unspiked steel industry biox effluent	27.10
H10	5 mg/L + H3 value	5.39

4.2.4 ASSIGNING FLAGS

Flags were assigned in two stages. The first stage removed the invalid data (Grubbs outliers) falling outside three standard deviations of the mean. This resulted in the removal of 12 of the 350 results or 3.4 percent of the total. Table 4.3 shows the sample results classified as Grubbs outliers.

TABLE 4.3

SUMMARY OF RESULTS LYING OUTSIDE 3 STANDARD DEVIATIONS OF THE MEAN (GRUBBS OUTLIERS)

LABORATORY CODE	SAMPLE NUMBERS OUTSIDE 3 STD. DEV. OF THE MEAN
CN005	H1,H5,H6,H8,H9
CN007	H1,H6,H9
CN011	H2,H7,H8
CN015	H3
CN027	H10

Thirteen of the 351 results submitted fell outside 3 standard deviations of the mean and were flagged as outliers. This represents only 3.7% of the data. A total of 23% of the results were identified as Grubbs outliers in the low level study.

All of the sample numbers (ie. H1 to H10) appear to be evenly represented in the invalid data pool therefore no particular sample seemed to cause analytical difficulty. A table of the full data set with the invalid data removed is in Appendix 3.

The second stage of flagging was to identify results falling outside 1 standard deviation. This was done by tabulating the data with the Grubbs outliers removed (see appendix 6), recalculating the means and standard deviations for each of the Standard Solutions, and flagging all data which lie outside one standard deviation of the mean. This resulted in 41 of the remaining 338 data or 13 percent of the total being identified as outliers. Table 4.4 shows the laboratories and sample numbers which are outside 1 standard deviation of the mean.

Table 4.4

SUMMARY OF RESULTS LYING OUTSIDE 1 STANDARD DEVIATION OF THE MEAN

LABORATORY CODE	SAMPLE NUMBERS FALLING OUTSIDE 3 STD.DEV. OF THE MEAN
CN005	H2, H4, H7, H10
CN007	H3, H4, H5, H7, H8
CN008	H3, H8
CN009	H1, H5, H6, H8, H9
CN011	H1, H4, H5, H6, H10
CN013	H10
CN017	H7, H8
CN018	H3
CN020	H2, H3, H4, H7, H8
CN021	H2, H4, H8
CN022	H10
CN027	H8
CN028	H8
CN029	H2, H3, H4
CN031	H7, H8
CN032	H6

A total of 15 of the 31 labs (48%) earned at least one flagged result. A total of 67% of labs earned at least one flag in the low level study. No particular sample seemed to cause analytical difficulty. A table of the full data set with all outliers removed is in Appendix 4.

4.2.5 REGRESSION ANALYSIS

Linear regression analysis was done for each participating laboratory. The results submitted by the laboratory were regressed against the Expected Values. A best fit line, slope, and $Y_{intercept}$ were calculated for the submitted results. A summary of the findings are given below and the actual regression curves are included in the lab-specific summaries in Section 6.0.

This analysis is very useful in trouble-shooting analytical problems. Inferences can be made about precision, calibration problems, blank problems, and overall accuracy. In addition, the graphical representation of the data on the regression plot provides an intuitive picture of the overall laboratory performance.

4.2.5.1 Precision Evaluated by the Regression Coefficient, R^2

The precision of each laboratory is reflected in how well the data fit on the regression line. This "quality of fit" is quantified by the regression coefficient R^2. In this study we have assumed that a regression coefficient (R^2) of greater than 0.995 indicates good precision and an R^2 between 0.995 and 0.980 indicates satisfactory precision. An R^2 of less than 0.980 indicates poor precision.

Table 4.5 shows the participating laboratories with regression coefficients in descending order of R^2.

Table 4.5

REGRESSION COEFFICIENTS OF PARTICIPATING LABORATORIES

LAB CODE	REGRESSION COEFFICIENT	INFERENCE	LAB CODE	REGRESSION COEFFICIENT	INFERENCE
CN036B	0.999296	Good Precision	CN010	0.990012	Satisfactory Precision
CN017	0.999215	"	CN026	0.989339	"
CN003	0.9980	"	CN012A	0.989229	"
CN035B	0.998420	"	CN036A	0.989169	"
CN015	0.997463	"	CN014	0.9880	"
CN004B	0.997395	"	CN022	0.985970	"
CN024	0.997355	"	CN012B	0.979710	Poor Precision
CN013	0.997326	"	CN028	0.9740	"
CN019	0.997184	"	CN031	0.967676	"
CN004A	0.997047	"	CN018	0.9423	"
CN032	0.996805	"	CN027	0.935437	"
CN008	0.996274	"	CN011	0.870992	"
CN002	0.9960	"	CN029	0.850852	"
CN025	0.994447	Satisfactory Precision	CN020	0.812075	"
CN030	0.993237	"	CN005	0.743736	"
CN035A	0.992910	"	CN009	0.683174	"
CN021	0.991992	"	CN007	0.653349	"
CN016	0.991057	"	CN032	0.6060	"

Twenty two of the 35 data sets (63%) displayed good or satisfactory precision according to these criteria. Thirteen of 35 data sets displayed poor precision. Of the latter group, 2 labs showed difficulty in the analysis of the biox effluents. One lab was classified as having poor precision as the result of a single out of control value.

4.2.5.2 Use of the Regression Slope to Detect Bias

The accuracy of each laboratory is reflected in the slope of the best fit line. The slope of the ideal line is 1.0. Lines which deviate significantly from this may usually reflect bias caused by a calibration problem. Laboratories with slopes within 0.15 of 1 (ie between 1.15 and 0.85) are considered unbiased in this study. Laboratories with slopes above 1.15 were flagged as biased high. Laboratories with slopes less than 0.85 were flagged as biased low.

Table 4.6 lists the laboratories, regression slopes and bias assessments.

TABLE 4.6

REGRESSION SLOPES AND BIAS ASSESSMENTS OF PARTICIPATING LABORATORIES

LAB CODE	REGRESSION SLOPE	INFERENCE	LAB CODE	REGRESSION SLOPE	INFERENCE
CN005	3.890118	High bias	CN004A	1.014322	No bias detected
CN007	3.460992	"	CN016	1.011841	"
CN009	2.934032	"	CN010	1.007789	"
CN011	1.924867	"	CN012A	1.005004	"
CN028	1.370	"	CN013	0.997703	"
CN021	1.328293	"	CN012B	0.989312	"
CN032	1.264	"	CN004B	0.982840	"
CN026	1.113900	No bias detected	CN022	0.945191	"
CN031	1.078905	"	CN024	0.944919	"
CN002	1.078000	"	CN025	0.926946	"
CN036A	1.069937	"	CN030	0.916147	"
CN019	1.067757	"	CN014	0.9110	"
CN018	1.0603	"	CN027	0.902649	"
CN036B	1.054070	"	CN017	0.891481	"
CN003	1.040	"	CN008	0.832274	Low bias
CN035A	1.034224	"	CN020	0.736724	"
CN015	1.026113	"	CN029	0.636213	
CN035B	1.015720	"			

No bias was detected in 25 of 35 data sets (71 percent of the participants) listed in Table 4.6. Bias was detected in 10 laboratories. In the low level cyanide study, 10 labs were also flagged as biased. In the present study, twice as many labs were biased high than were biased low. Several laboratories displayed major difficulties in the handling of biox effluent samples. One assessment of high bias arose from the gross overestimation of one sample concentration. The remaining 9 results displayed no bias.

4.2.5.3 Evaluation of the Regression Intercept

Deviation of the $Y_{intercept}$ from the origin may indicate an analytical blank problem, poor precision or method failure at high concentrations. In this study, a $Y_{intercept}$ less than ± 0.30 mg/L is considered good and those within ± 3.0 mg/L are considered satisfactory. A $Y_{intercept}$ greater than 3.0 mg/L is designated as poor.

Table 4.7 lists the laboratories and regression Y intercepts sorted from highest to lowest.

TABLE 4.7

REGRESSION Y INTERCEPTS OF PARTICIPATING LABORATORIES LISTED IN DESCENDING ORDER

LAB CODE	REGRESSION Y-INTERCEPT	INFERENCE	LAB CODE	REGRESSION Y-INTERCEPT	INFERENCE
CN011	5.708505	Poor	CN017	-0.111517	Good
CN029	5.484535	Poor	CN035A	-0.235334	Good
CN020	4.735902	Poor	CN016	-0.283938	Good
CN027	2.124377	Satisfactory	CN035B	-0.430869	Satisfactory
CN010	1.987220	Satisfactory	CN036A	-0.573802	Satisfactory
CN031	1.606632	Satisfactory	CN004B	-0.598912	Satisfactory
CN008	0.982687	Satisfactory	CN036B	-0.680016	Satisfactory
CN014	0.7754	Satisfactory	CN004A	-0.708153	Satisfactory
CN030	0.721138	Satisfactory	CN002	-0.899966	Satisfactory
CN022	0.680941	Satisfactory	CN012A	-1.134451	Satisfactory
CN024	0.376211	Satisfactory	CN026	-1.202626	Satisfactory
CN025	0.373905	Satisfactory	CN012B	-1.247627	Satisfactory
CN003	0.3179	Satisfactory	CN021	-1.259016	Satisfactory
CN019	0.275670	Good	CN032	-1.891	Poor
CN018	0.2443	Good	CN028	-1.3567	Poor
CN013	-0.076603	Good	CN007	-4.902544	Poor
CN015	-0.088846	Good	CN009	-7.080923	Poor
			CN005	-9.796815	Poor

Twenty seven of the 35 data sets (77%) displayed good or satisfactory regression intercept values. Eight labs fell into the poor category. This is about the same number as in the low level study. To establish the source of the problems in these cases, an examination of the regression curves is recommended to determine whether the errant Y-intercept values are the result of imprecision, method failure at high concentrations, overestimation of a single sample or inappropriate blank correction.

4.2.6 RANKING FOR BIAS

The Rank Sum Test (Youden et al, 1975) was used to determine if any of the participating laboratories were consistently biased (ie. did a specific laboratory overestimate or underestimate all the standard solutions in a systematic manner). This test complements the regression slope analysis but does not require a normal distribution of results in order to be valid. In this test, the data from each laboratory for each standard solution are ranked. The rank 1 is given to the lowest result, a rank of 2 to the next lowest and so on. The rankings are then summed for each laboratory giving the Rank Sum statistic. Laboratories with unusually low or high rank sums are designated as biased low or biased high, respectively.

The results of the Rank Sum test are shown in ascending order in Table 4.8 with the Laboratory code, the Rank Sum, and inference. The results for laboratories CN005 and CN017 were incomplete and were omitted from this analysis. This left a total of 33 data sets. Using a linear extrapolation of Youden's assessment criteria (Youden et al, 1975), laboratories are considered unbiased if their Rank sums fall between 82 and 258.

No bias was detected by the rank sum test in 29 (88 percent of the total) of the 33 data sets. Laboratories CN011, CN021, CN007 and CN028 were assessed as biased high, meaning they consistently overestimated the concentration of the standard solutions and would do so more that 95 times out of 100. These labs were also assessed as biased high by the regression technique.

None of the laboratories were assessed as biased low, suggesting that, as with the regression results, more laboratories had difficulty with the overestimation of the samples than underestimation.

TABLE 4.8

RANK SUM TEST RESULTS FOR PARTICIPATING LABORATORIES

LABORATORY CODE	RANK SUM	INFERENCE	LABORATORY CODE	RANK SUM	INFERENCE
CN011	296	Biased High	CN014	146	No Bias Detected
CN021	284	"	CN035B	144	"
CN007	279	"	CN016	143	"
CN028	269	"	CN029	143	"
CN010	249	No Bias Detected	CN032	126	"
CN031	246	"	CN018	121	"
CN019	242	"	CN022	118	"
CN003	203	"	CN012A	118	"
CN015	200	"	CN024	117	"
CN026	197	"	CN012B	114	"
CN002	195	"	CN027	114	"
CN020	188		CN025	113	"
CN013	180	"	CN004A	106	"
CN036B	168	"	CN004B	86	"
CN036A	166	"	CN008	83	"
CN009	150	"			
CN035A	149	"			
CN030	147	"			

4.3 PERFORMANCE WITH EFFLUENTS vs WATER MATRIX

The spiked samples analyzed by the participating laboratories were provided in both effluent and pure water matrices. The water matrix samples (H4,H7,H8) were a matrix of Milli–Q water at pH 12. The effluent matrix samples were obtained from steel industry biox reactor (H1,H5,H6,H9) and from a municipal sewage treatment plant (H2,H3,H10) and were adjusted to pH 12.

The means and standard deviations of the raw data set and of the data set with the laboratories having Grubbs outliers removed were calculated to determine if there was a trend towards more

variability in effluent samples. These calculations are summarized in the Table 4.9 below.

TABLE 4.9

WATER vs EFFLUENT MATRIX EFFECTS

		RAW DATA			GRUBBS OUTLIERS REMOVED		
SAMPLE NUMBER	MATRIX	MEAN	SD	COEFF. VAR.	MEAN	SD	COEFF. VAR.
H1	Biox eff.	48.74	40.83	84	40.09	22.32	56
H2	STP eff.	11.18	2.50	22	10.89	1.87	17
H3	STP eff.	0.036	0.039	108	0.031	0.026	84
H4	Water	11.19	2.58	23	11.19	2.58	23
H5	Biox eff.	81.75	42.04	51	77.08	32.84	43
H6	Biox eff.	62.68	42.59	68	54.01	25.42	47
H7	Water	24.24	11.84	49	22.33	4.16	19
H8	Water	45.52	10.08	22	43.28	4.38	10
H9	Biox eff.	38.77	38.02	98	30.51	19.35	63
H10	STP eff.	6.03	2.55	42	5.64	1.13	20

SD: Standard deviation.
COEFF VAR: Coefficient of variation; equals (100 x standard deviation)/mean
GRUBBS REMOVED: The data set with laboratories having Grubbs outliers (ie. data outside of 3 SD's of the mean) removed.

The coefficient of variation of the raw data without and without Grubbs outlying labs removed shows a substantial difference between effluent and water matrices. The coefficient of variation for the biox effluent was 75%, the STP effluent; 57% and for samples having a water matrix was 31%. Once the outlying results were removed from the data set, the coefficient of variation for the biox effluent was 53%, the STP effluent; 40% and for samples having a water matrix; 17%.

The results indicate that even when the extreme outlying results are removed from the data set, laboratories still produced effluent results that were more variable than with pure water standards. This cannot simply be a function of the cyanide concentrations present because the water standards contained higher cyanide concentrations than the STP effluents. It is unlikely that the higher variability in the biox effluents is related to the higher concentrations present in those samples as the relative variability in measurements usually decreases or does not change with increasing concentration. It rarely increases. Furthermore, several labs had obvious difficulty in estimating the concentrations present in the biox effluents. The results presented in this section indicate that even when the extreme results are removed from the data set, a large proportion of labs overestimated the actual concentrations in the biox samples.

5.0 SUMMARY AND CONCLUSIONS

The key findings of this study are:

- Thirteen of the 351 results submitted in the high level cyanide study fell outside 3 standard deviations of the mean and were flagged as outliers. This represents only 3.7% of the data. A total of 23% of the results were identified as Grubbs outliers in the low level study.

- Forty one of the remaining 338 data or 13 percent of the total being identified as falling outside one standard deviation of the mean recalculated after removal of the Grubbs outliers. A total of 15 of the 31 labs (48%) earned at least one flagged result. A total of 67% of labs earned at least one flag in the low level study.

- According to the regression correlation coefficient test, 22 of the 35 data sets (63%) displayed good or satisfactory precision. Thirteen of 35 data sets showed poor precision. In 2 of these 13 cases, the laboratories had difficulty in the analysis of the biox effluents. A third lab was classified as having poor precision as the result of a single out of control value.

- No bias was detected in 25 of 35 data sets (71% of the participants) when the regression slope test was applied. Bias was detected in 10 laboratories by this test. Twice as many labs were biased high than were biased low. This was due to the tendency of several laboratories to overestimate the cyanide concentrations in the biox effluent samples. In the low level cyanide study, 72% of the data sets were assessed as unbiased by the regression slope test.

- No bias was detected by the Rank Sum test in 29 (88 percent of the total) of the 33 data sets. Laboratories CN011, CN021, CN007 and CN028 were assessed as biased high, meaning they consistently overestimated the concentration of the standard solutions and would do so more that 95 times out of 100. These labs were also assessed as biased high by the regression technique.

- None of the laboratories were assessed as biased low by the Rank Sum test, suggesting that, as with the regression results, more laboratories had difficulty with the overestimation of the samples than underestimation.

- Twenty seven of the 35 data sets (77%) displayed good or satisfactory regression intercept values. Eight labs fell into the poor category. This is about the same number as in the low level study. To establish the source of the problems in these cases, an examination of the regression curves is recommended to determine whether the errant Y-intercept values are the result of imprecision, method failure at high concentrations, overestimation of a single sample or inappropriate blank correction.

- Comparison of the variability in the results for the water–based standards and effluents showed a substantial difference between the two. The coefficient of variation (standard deviation expressed as a percentage of the mean) for the biox effluent was 75%, the STP effluent; 57% and for samples having a water matrix was 31% before removal of the invalid data (Grubbs outliers). Once the outlying results were removed from the data set, the coefficient of variation for the biox effluent was 53%, the STP effluent; 40% and for samples having a water matrix; 17%. The results indicate that even when the extreme outlying results are removed from the data set, the effluent results were still more variable than results obtained with pure water standards.The key findings of this study are:

6.0 LABORATORY SPECIFIC REPORTS

The following pages are reports for each of the participating laboratories giving a summary of their results and statistical analysis, the inferences which can be made form these analyses, and recommendations for corrective action. These reports provide each laboratory with the essential results pertaining to their specific situation on one page.

REPORT FOR LABORATORY CN002

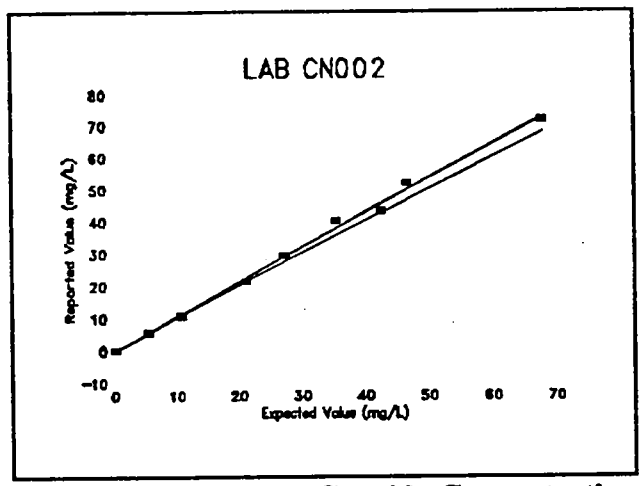
RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN002 Value (mg/L)	40.10	10.60	0.01	10.40	71.60	51.60	21.30	43.00	29.30	5.27

STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 1 standard deviation of the mean expected values. The absence of flags and the high regression coefficient (R^2=0.996) indicate good precision.

The slope of the regression line (m=1.078, see figure) indicates a no bias. The rank sum test detected a high bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

INFERENCE:

The statistical analysis of your data indicates that your laboratory has good precision in high level cyanide analysis. This is indicated by the high regression coefficient and with the absence of flags.

A high bias was detected by the rank sum test but a visual inspection of the above figure shows that this is very slight. The rank sum test is capable of detecting very small biases, but only in very precise results such as those from your laboratory. The regression slope criteria did not detect bias in your results.

REPORT FOR LABORATORY CN025

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN025 Value (mg/L)	36.80	10.60	0.04	9.91	61.80	43.00	19.60	40.60	23.70	5.09

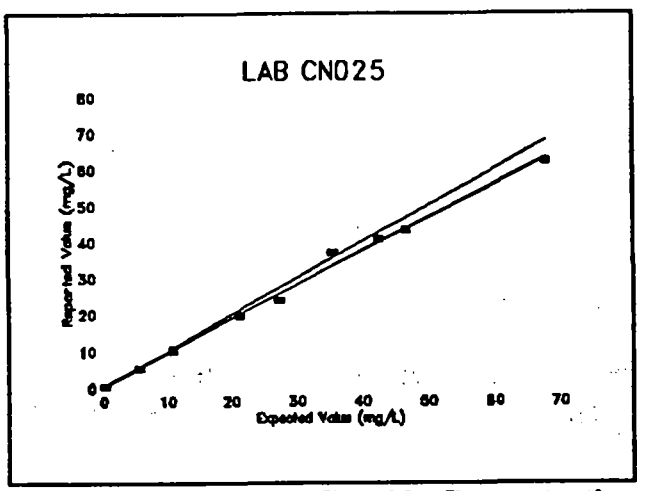
STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 1 standard deviation of the mean expected values. This observation and the regression coefficient (R^2=0.994) indicate satisfactory to good precision.

The slope of the regression line (m=0.9269, see figure) indicates no bias. The rank sum test also indicates no bias.

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed satisfactory to good precision with no bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

REPORT FOR LABORATORY CN026

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN026 Value (mg/L)	39.84	11.83	0.03	11.44	78.18	45.34	20.88	44.96	27.89	4.88

STATISTICAL SUMMARY:

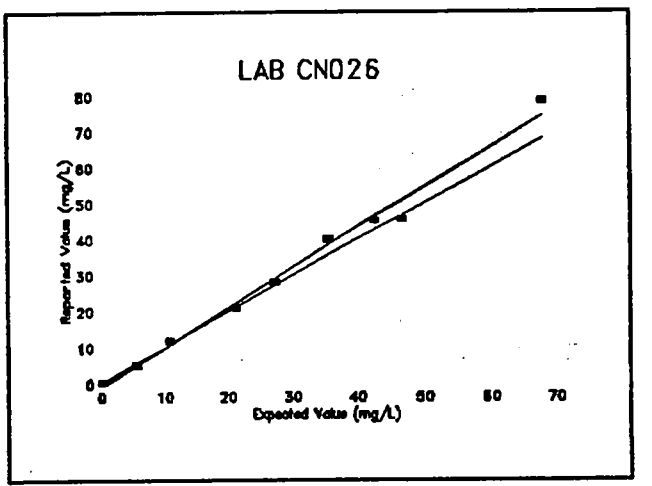
The flagging procedure indicated that no samples fell outside 1 standard deviation of the mean expected values.

The regression coefficient (R^2=0.989) indicated satisfactory precision.

The slope of the regression line (m=1.1139, see figure) indicates no bias. The rank sum test also indicates no bias.

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed satisfactory precision with no bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

REPORT FOR LABORATORY CN014

RESULTS:

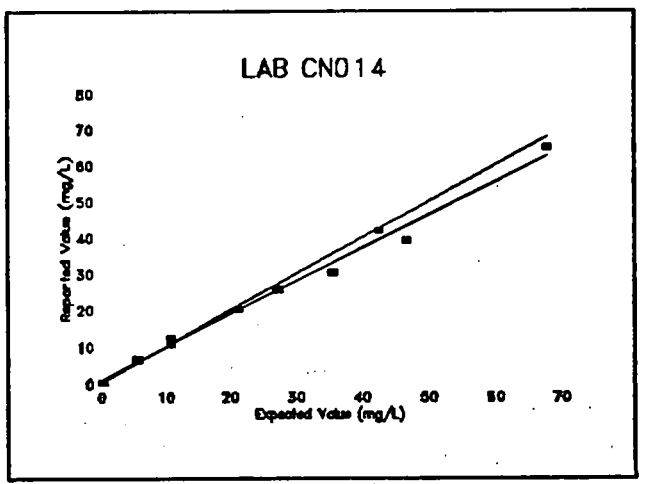
Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN014 Value (mg/L)	30.20	12.30	0.03	10.60	64.70	39.10	20.00	41.80	25.70	6.46

STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 1 standard deviation of the mean expected values.

The regression coefficient (R^2=0.988) indicated satisfactory precision.

The slope of the regression line (m=0.911, see figure) indicates no bias. The rank sum test also indicates no bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed satisfactory precision. Although the regression slope and rank sum tests indicate no bias, visual inspection of the above graphs indicates a possible underestimation of higher concentrations of cyanide./ This is particualrily evident in the biox effluent samples.

REPORT FOR LABORATORY CN015

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN015 Value (mg/L)	37.50	10.50	0.20	10.60	69.00	45.90	21.20	45.70	26.80	5.58

STATISTICAL SUMMARY:

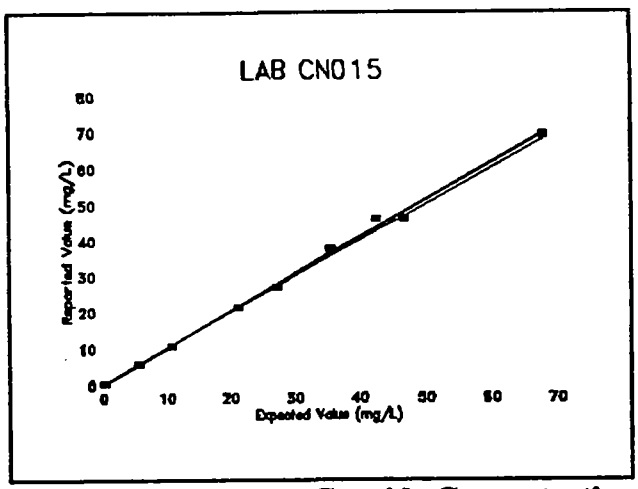
The flagging procedure indicated that sample H3 fell outside 3 standard deviations of the mean expected value.

The regression coefficient (R^2=0.997) indicated good precision.

The slope of the regression line (m=1.026, see figure) indicates no bias. The rank sum test also indicates no bias.

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed generally good precision with no bias. One sample, the unspiked STP effluent, was flagged as falling outside three standard deviations of the mean expected value.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

REPORT FOR LABORATORY CN022

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN022 Value (mg/L)	34.50	9.29	0.02	13.30	62.30	47.80	23.60	41.70	22.30	4.27

STATISTICAL SUMMARY:.

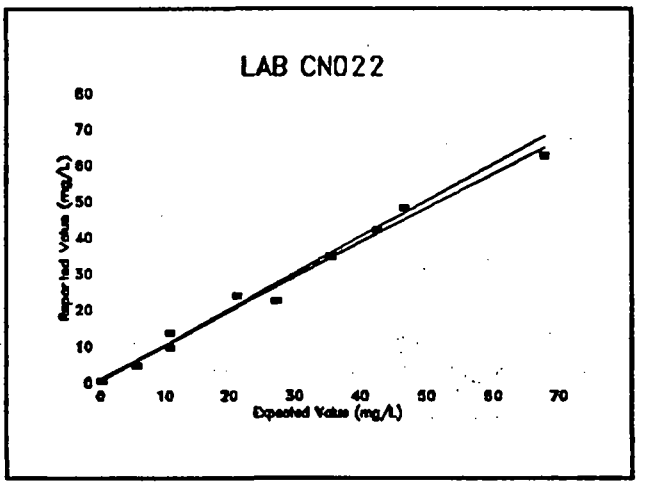
The flagging procedure indicated that no samples fell outside 3 standard deviations of the mean expected value. Sample H10 fell outside 1 standard deviation of the mean expected values.

The regression coefficient (R^2=0.986) indicated satisfactory precision.

The slope of the regression line (m=0.945, see figure) indicates no bias. The rank sum test also indicates no bias.

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed satisfactory precision with no bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

REPORT FOR LABORATORY CN024

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN024 Value (mg/L)	35.91	9.93	0.02	10.36	63.81	42.56	21.16	41.31	25.83	5.07

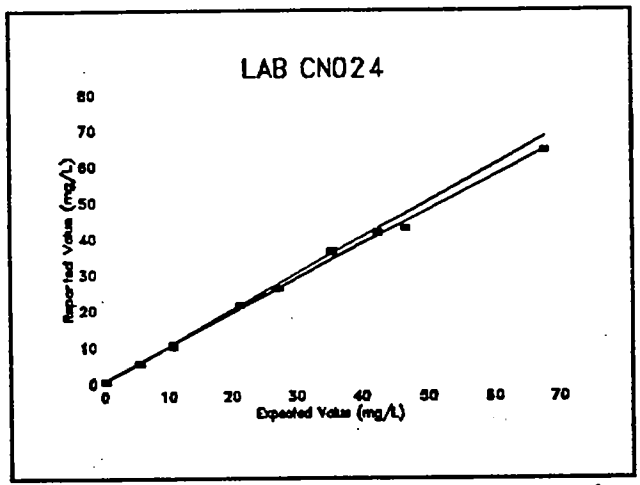
STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 1 standard deviation of the mean expected values. This observation and the regression coefficient (R^2=0.997) indicated good precision.

The slope of the regression line (m=0.945, see figure) indicates no bias. The rank sum test also indicates no bias.

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed good precision with no bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

REPORT FOR LABORATORY CN020

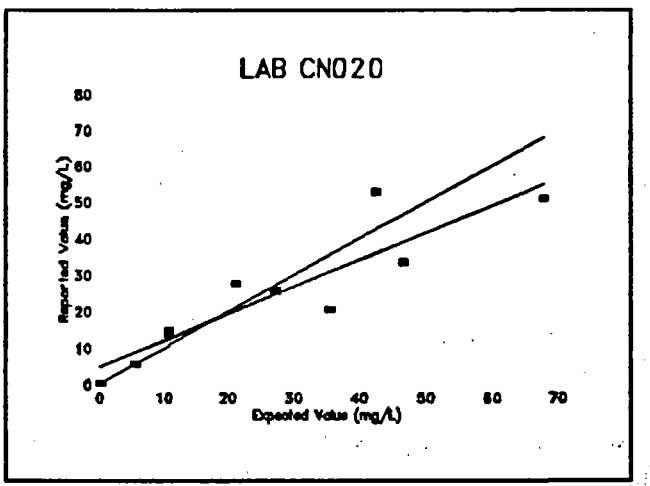
RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN020 Value (mg/L)	20.41	13.76	0.06	14.52	50.65	33.39	27.50	52.49	25.62	5.59

STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 3 standard deviations of the mean expected value. Samples H2, H3, H4, H7 and H8 fell outside 1 standard deviation of the mean expected values. This observation and the low regression coefficient (R^2=0.812) indicate poor precision.

The slope of the regression line (m=0.7367, see figure) indicates a low bias. The rank sum test detected no bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed poor precision. Although the regression slope indicates a low bias, an examination of the results indicates that the cyanide concentrations in the biox effluents were underestimated but the water-based standards were overestimated. The low regression slope (and also the high intercept) is, therefore probably the result of the large scatter in the results rather than any consistent tendency to underestimate the concentrations. The rank sum test did not detect any bias, but it is a recognized limitation of this approach that it has difficulty recognizing bias in imprecise data.

REPORT FOR LABORATORY CN021

RESULTS:

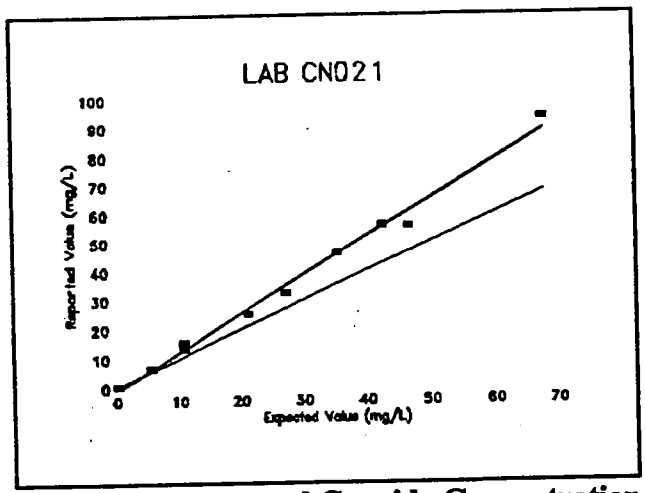
Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN021 Value (mg/L)	45.90	13.10	0.03	15.30	92.70	55.50	25.10	55.60	32.30	6.40

STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 3 standard deviations of the mean expected value. Samples H2, H4 and H8 fell outside 1 standard deviation of the mean expected values.

The regression coefficient (R^2=0.991) indicated satisfactory precision.

The slope of the regression line (m=1.328, see figure) indicates a high bias. The rank sum test also indicates a high bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed satisfactory precision but with a high bias. This bias was detected by both the regression slope and rank sum tests. It is also clearly evident in the above figure. The bias is most likely due to a calibration error.

REPORT FOR LABORATORY CN027

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN027 Value (mg/L)	34.20	4.74	0.02	10.40	66.20	44.00	20.70	37.20	25.30	19.40

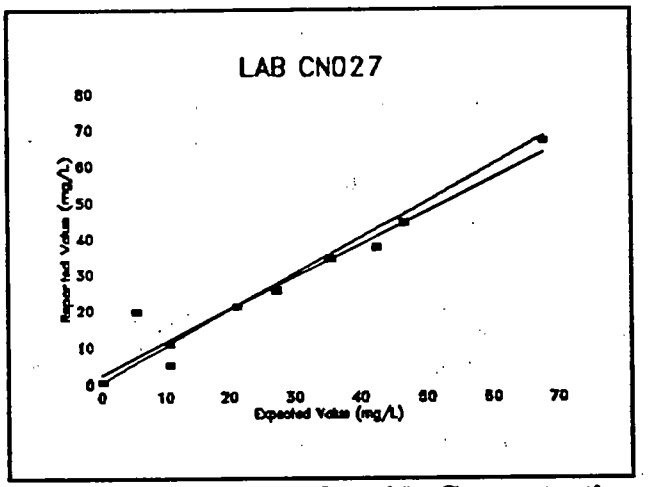
STATISTICAL SUMMARY:

The flagging procedure indicated that sample H10 was outside 3 standard deviations of the mean expected value. Sample H8 fell outside 1 standard deviation of the mean expected values. These observations and the regression coefficient (R^2=0.9354) indicated poor precision.

The slope of the regression line (m=0.903, see figure) indicates no bias. The rank sum test also indicates no bias.

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed no bias but poor precision.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

REPORT FOR LABORATORY CN028

RESULTS:

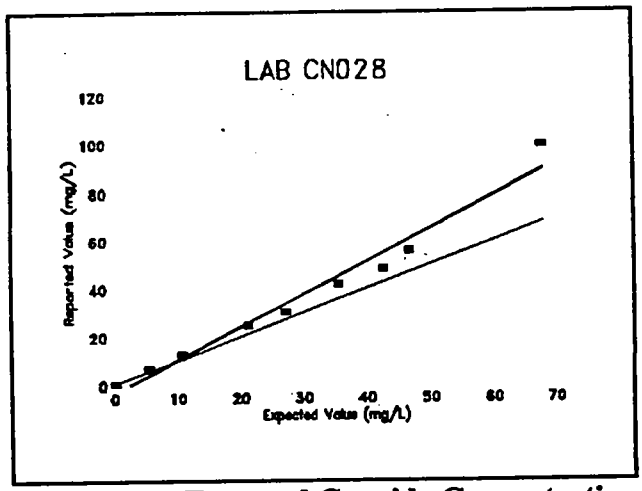
Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN028 Value (mg/L)	41.56	12.37	0.03	12.33	98.93	55.62	24.54	47.92	30.15	6.16

STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 3 standard deviations of the mean expected value. Sample H8 fell outside 1 standard deviation of the mean expected values.

The regression coefficient (R^2=0.974) indicated poor precision.

The slope of the regression line (m=1.37, see figure) indicates a high bias. The rank sum test also indicates a high bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed poor precision with a high bias.

The poor precision estimate is largely the result of an overestimation of the cyanide concentration in sample H5. This samples was not flagged as an outlier because so many other labs has difficulty with it. However, because this point lies so far off the line defined by the remaining points, the regression correlation coefficient is lowered. This also accounts for the negative y-intercept.

The precision evident from the results of the 9 lower concentration standards (H5 possesses the highest cyanide concentration) appears to be good. The high bias remains, however. This is likely the result of a calibration standard error.

REPORT FOR LABORATORY CN007

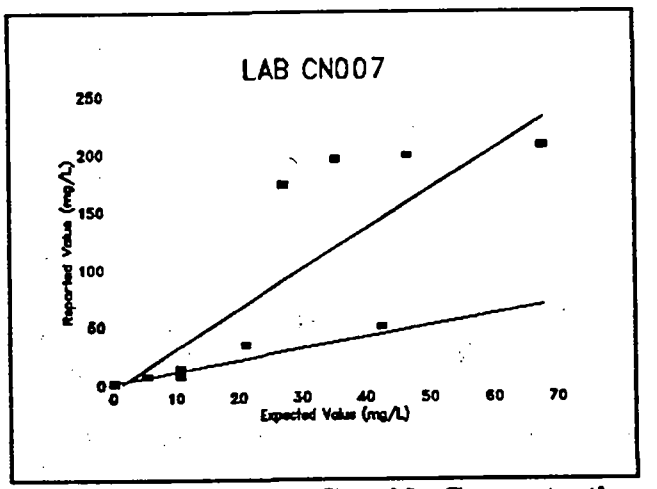
RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN007 Value (mg/L)	194.00	12.4	0.06	6.07	205.00	197.00	33.00	48.80	172.00	6.38

STATISTICAL SUMMARY:

The flagging procedure indicated that samples H1, H6 and H9 fell outside 3 standard deviations of the mean expected value. All samples except H2 and H10 fell outside 1 standard deviation of the mean expected values. This observation and the low regression coefficient (R^2=0.653) indicate poor precision.

The slope of the regression line (m=3.461, see figure) indicates a high bias. The rank sum test also indicates a high bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed poor precision and a high bias.
Further inspection of the results indicates that the high bias occurs primarily in the anaysis of the Biox effluent samples.

REPORT FOR LABORATORY CN008

RESULTS:

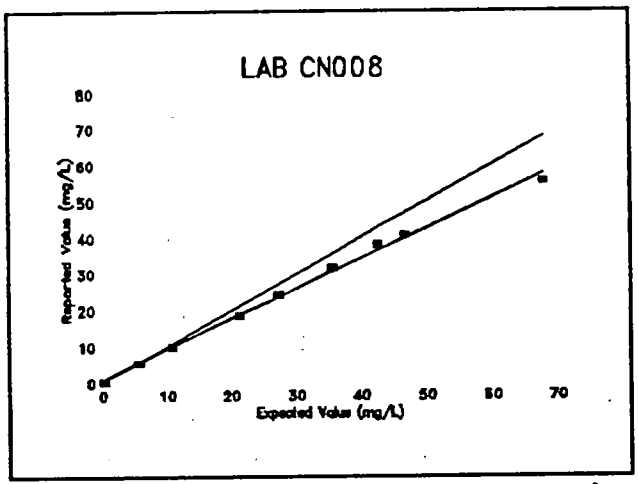
Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN008 Value (mg/L)	31.40	9.90	0.06	9.60	55.10	40.60	18.20	38.00	23.90	5.20

STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 3 standard deviations of the mean expected value. Samples H3 and H8 fell outside 1 standard deviation of the mean expected values.

The regression coefficient (R^2=0.996) indicates good precision.

The slope of the regression line (m=0.832, see figure) indicates a low bias. The rank sum test did not flag your results as biased low, but did indicate a tendency to low values.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed good precision and a low bias. The bias is probably the result of a calibration problem.

REPORT FOR LABORATORY CN004B

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN004B Value (mg/L)	35.93	9.83	0.02	9.59	66.96	44.17	19.60	39.07	26.42	4.74

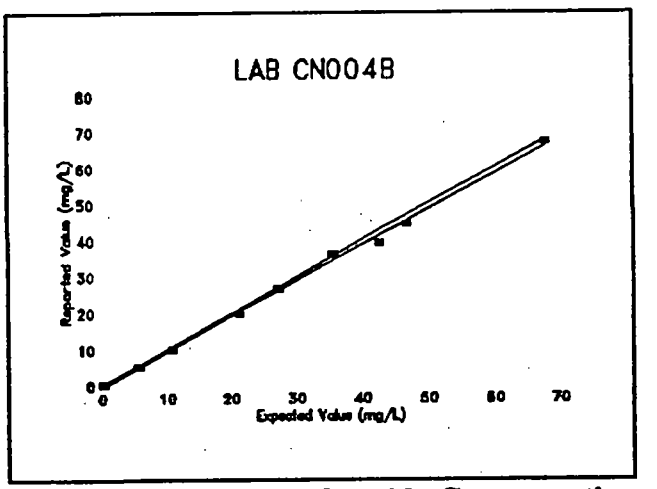
STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 1 standard deviation of the mean expected values. This observation and the high regression coefficient (R^2=0.997) indicate good precision.

The slope of the regression line (m=0.998, see figure) indicates no bias. The rank sum test also indicates no bias.

INFERENCE:

The statistical analysis of your data indicates that your laboratory displays good precision with no bias in high level cyanide analysis.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

REPORT FOR LABORATORY CN005

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN005 Value (mg/L)	180.00	16.00		16.00	236.00	206.00	38.00	79.00	170.00	9.00

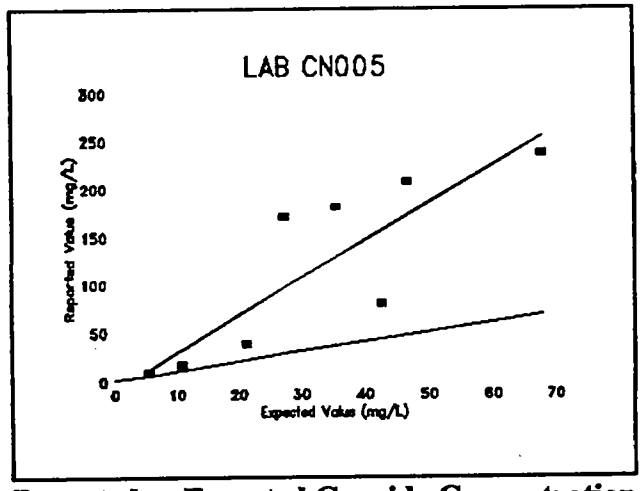
STATISTICAL SUMMARY:

The flagging procedure indicated that samples H1, H5, H6, H8 and H9 fell outside 3 standard deviations of the mean expected value. All samples except H3 fell outside 1 standard deviation of the mean expected values.

The regression coefficient (R^2=0.744) indicates poor precision. The slope of the regression line (m=3.890, see figure) indicates a high bias. The rank sum test was not conducted for your laboratory because an incomplete set of results were submitted.

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed poor precision with a high bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

REPORT FOR LABORATORY CN003

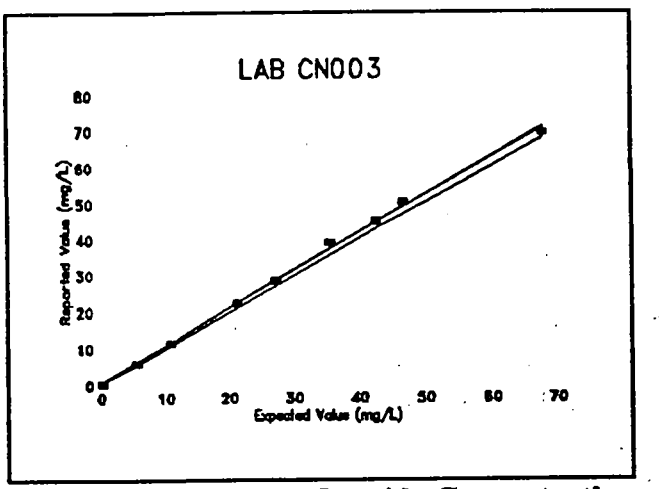
RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN003 Value (mg/L)	38.80	11.20	0.02	11.20	69.10	50.00	22.10	44.60	28.20	5.61

STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 1 standard deviation of the mean expected values. This observation and the high regression coefficient (R^2=0.998) indicate good precision.

The slope of the regression line (m=1.040, see figure) indicates no bias. The rank sum test also indicates no bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

INFERENCE:

The statistical analysis of your data indicates that your laboratory displays satisfactory precision in high level cyanide analysis. No bias was detected by the two methods used in this study.

REPORT FOR LABORATORY CN004A

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN004A Value (mg/L)	37.11	9.69	0.01	9.81	68.75	46.05	19.81	39.97	27.51	4.93

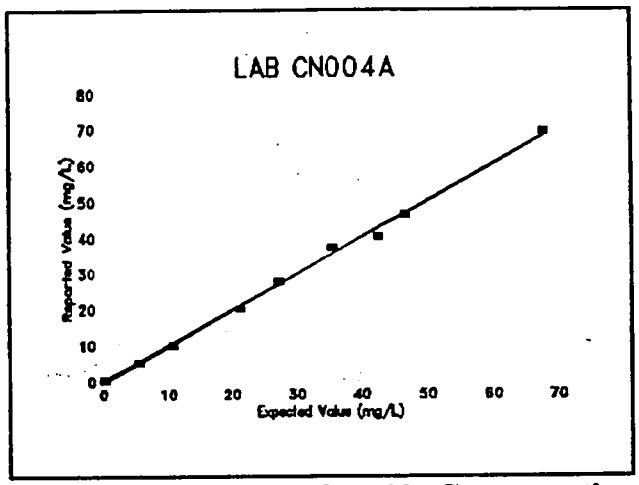
STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 1 standard deviation of the mean expected values. This observation and the high regression coefficient (R^2=0.997) indicate good precision.

The slope of the regression line (m=1.014, see figure) indicates no bias. The rank sum test also indicates no bias.

INFERENCE:

The statistical analysis of your data indicates that your laboratory displays good precision with no bias in high level cyanide analysis.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

REPORT FOR LABORATORY CN009

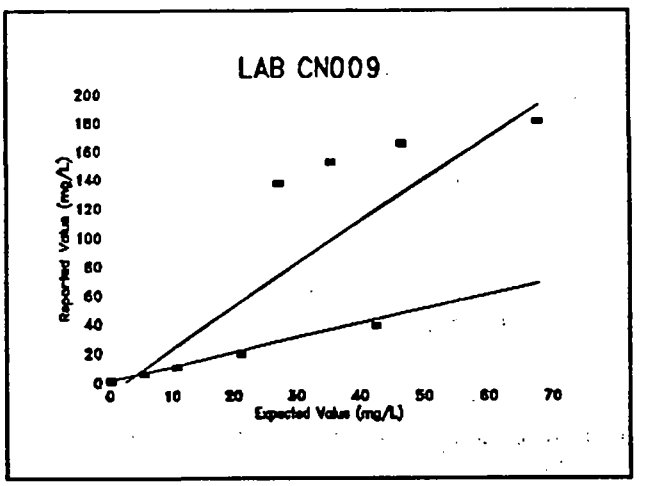
RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN009 Value (mg/L)	151.00	9.65	0.03	9.85	179.50	164.00	19.00	38.20	136.00	5.05

STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 3 standard deviations of the mean expected value. Samples H1, H5, H6, H8, and H9 fell outside 1 standard deviation of the mean expected values. These observations and the low regression coefficient (R^2=0.683) would normally indicate poor precision.

In this case, however, this is caused by an overestimate of the concentrations present in the biox effluent samples. The slope of the regression line (m=2.934, see figure) indicates a high bias as a result. The rank sum test did not detect bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed a high bias for all of the biox effluent samples. The assessment of poor precision was the result of the overestimate of the concentrations present in these samples. A visual examination of the above figure indicates that the level of precision in your analysis of water-based standards is acceptable.

REPORT FOR LABORATORY CN010

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN010 Value (mg/L)	41.07	12.57	0.04	12.32	66.07	50.71	24.64	46.43	28.57	6.43

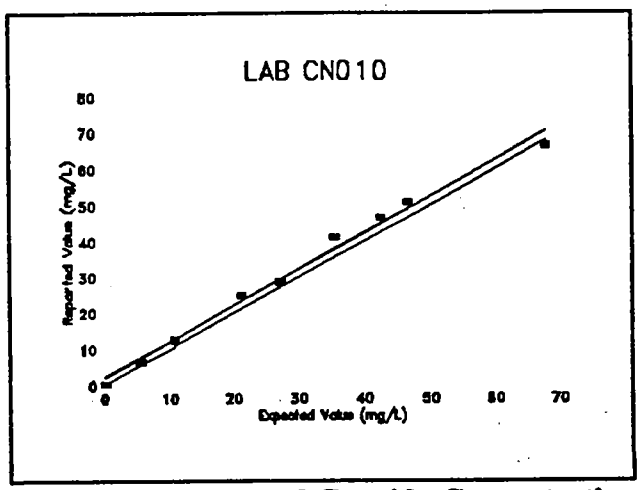
STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 1 standard deviation of the mean expected values.

The regression coefficient (R^2=0.990) indicated satisfactory precision.

The slope of the regression line (m=1.008, see figure) indicates no bias. The rank sum test also indicates no bias.

The Y-intercept of the regression line (1.99) is higher than normal and may reflect an improper blank correction.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed satisfactory precision and no bias. A high regression line intercept and the parallel slope may indicate in improper blank correction.

REPORT FOR LABORATORY CN011

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN011 Value (mg/L)	71.00	21.00	0.03	22.00	130.00	100.00	89.00	86.00	42.00	9.80

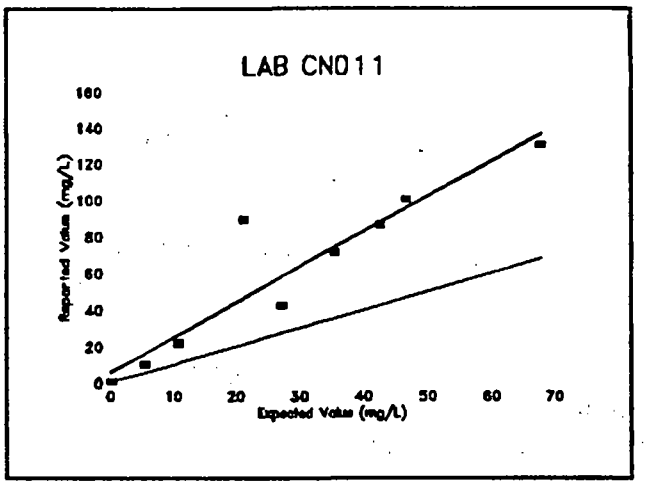
STATISTICAL SUMMARY:

The flagging procedure indicated that samples H2, H6 and H8 fell outside 3 standard deviations of the mean expected value. All samples except H3 and H9 fell outside 1 standard deviation of the mean expected values. These observations and the low regression coefficient (R^2=0.871) indicate poor precision.

The slope of the regression line (m=1.925, see figure) indicates a high bias. The rank sum test also indicates a high bias.

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed poor precision and a high bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

REPORT FOR LABORATORY CN012A

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN012A Value (mg/L)	31	9.74	0.02	10.80	69.40	43.70	20.90	43.90	22.40	5.03

STATISTICAL SUMMARY:

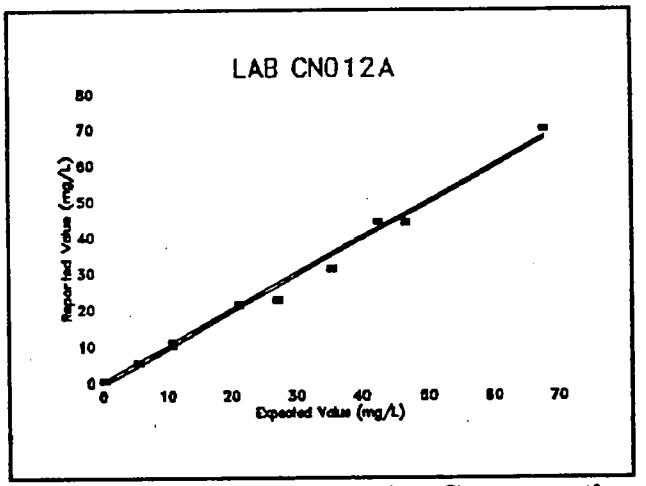
The flagging procedure indicated that no samples fell outside 1 standard deviation of the mean expected values.

The regression coefficient (R^2=0.989) indicated satisfactory precision.

The slope of the regression line (m=1.005, see figure) indicates no bias. The rank sum test also indicates no bias.

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed satisfactory precision and no bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

REPORT FOR LABORATORY CN012B

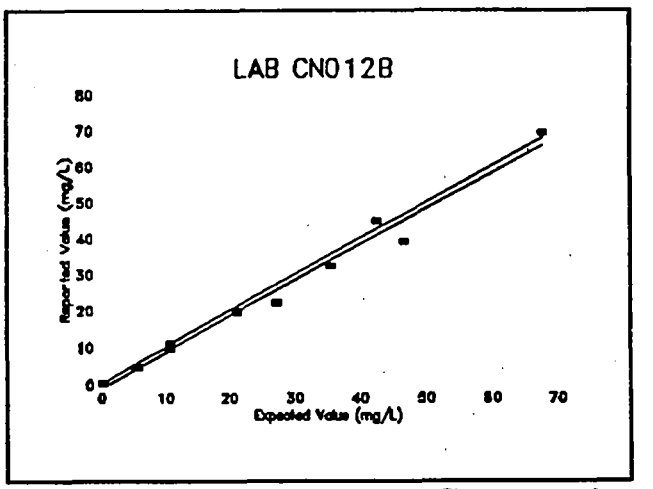
RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN012B Value (mg/L)	32.20	9.60	0.03	10.90	69.20	38.80	19.60	44.70	22.00	4.54

STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 1 standard deviation of the mean expected values. This observation indicates satisfactory precision. The regression coefficient (R^2=0.980), however, indicates satisfactory to poor precision.

The slope of the regression line (m=0.989, see figure) indicates no bias. The rank sum test also indicates no bias.



Reported vs Expected Cyanide Concentration

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displays satisfactory precision, but with more scatter in the results than most labs in the satisfactory category. No bias was detected.

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

REPORT FOR LABORATORY CN013

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN013 Value (mg/L)	34.60	10.70	0.05	10.40	69.40	44.90	21.00	41.70	25.80	6.97

STATISTICAL SUMMARY:

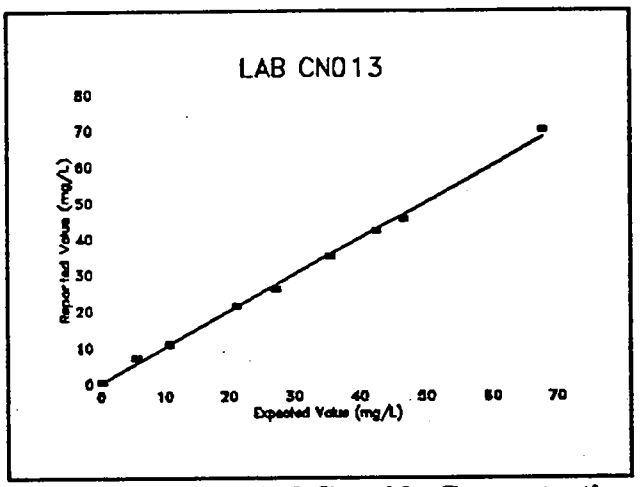
The flagging procedure indicated that no samples fell outside 3 standard deviations of the mean expected value. Sample H10 fell outside 1 standard deviation of the mean expected value.

The regression coefficient (R^2=0.997) indicated good precision.

The slope of the regression line (m=0.998, see figure) indicates no bias. The rank sum test also indicates no bias.

INFERENCE:

The statistical analysis of your data indicates that, in this study your laboratory displayed good precision with no bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

REPORT FOR LABORATORY CN016

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN016 Value (mg/L)	34.80	11.70	0.02	10.00	68.20	45.40	23.10	46.20	23.00	4.80

STATISTICAL SUMMARY:

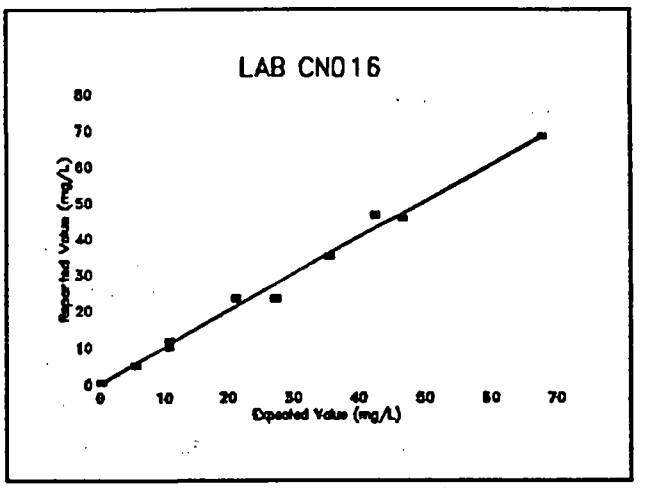
The flagging procedure indicated that no samples fell outside 1 standard deviation of the mean expected values.

The regression coefficient (R^2=0.991) indicated satisfactory precision.

The slope of the regression line (m=1.012, see figure) indicates no bias. The rank sum test also indicates no bias.

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed satisfactory precision with no bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

REPORT FOR LABORATORY CN017

RESULTS:

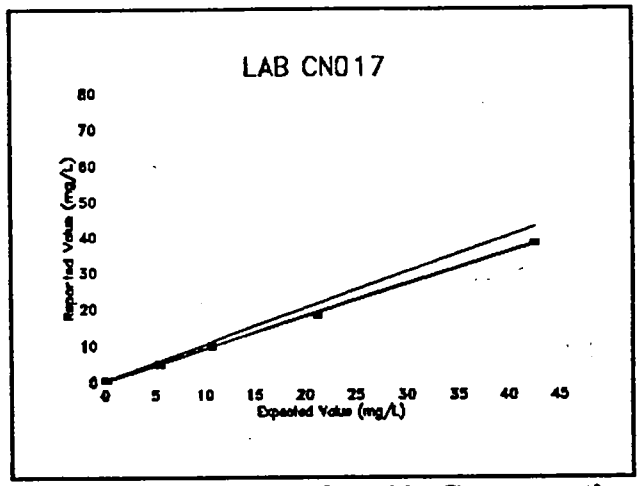
Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN017 Value (mg/L)		9.60	0.02	9.60			18.00	38.00		4.60

STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 3 standard deviations of the mean expected value. Samples H7 and H8 fell outside 1 standard deviation of the mean expected values. Results for the biox samples were not received from your laboratory.

The regression coefficient (R^2=0.999) indicated good precision on the sample results submitted.

The slope of the regression line (m=0.891, see figure) indicates no bias. The rank sum test was not conducted.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed good precision on water-based standards and spiked municipal STP effluents.The regression slope detected no bias but a visual inspection of the above figure indicates a tendency to consistently underestimate the concentrations of cyanide.

REPORT FOR LABORATORY CN018

RESULTS:

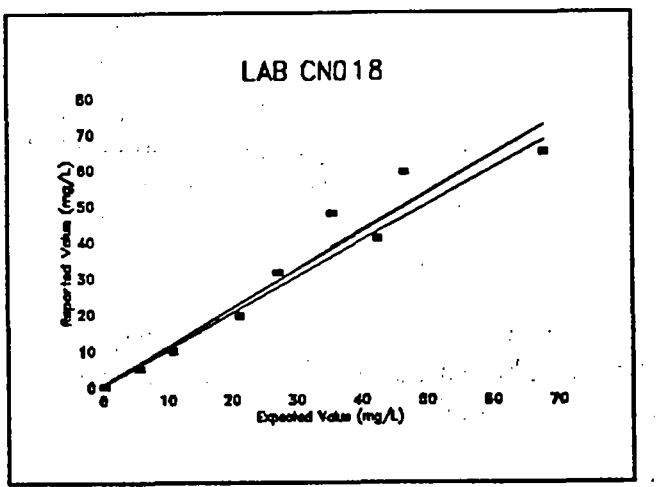
Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN018 Value (mg/L)	47.40	9.35	0.00	9.73	64.40	58.80	19.30	40.60	31.10	4.76

STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 3 standard deviations of the mean expected value. Sample H3 fell outside 1 standard deviation of the mean expected values.

The regression coefficient (R^2=0.942) indicated poor precision.

The slope of the regression line (m=1.0603, see figure) indicates no bias. The rank sum test also indicates no bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed poor precision but no bias. The poor precision assesment was largely the result of an overestimate of the cyanide concentrations on two of the biox samples. The result flagged as a Grubbs outlier was the result of a reporting deficiency (0.00 was reported) rather than an analytical one.

REPORT FOR LABORATORY CN019

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN019 Value (mg/L)	41.20	11.60	0.04	11.40	71.40	50.60	22.40	44.70	28.60	5.80

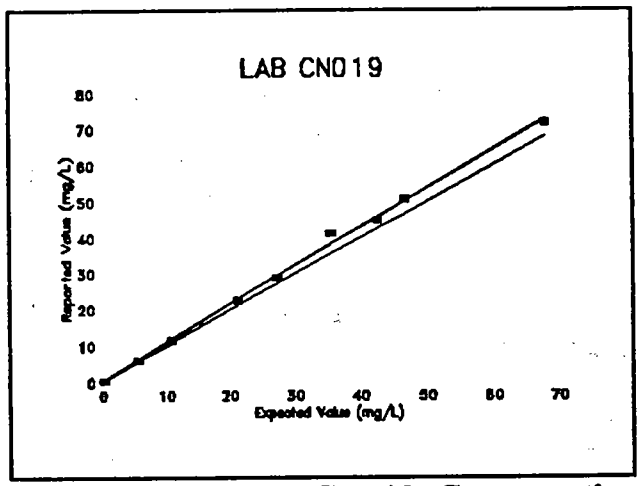
STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 1 standard deviation of the mean expected values, This observation and the regression coefficient (R^2=0.997) indicate good precision.

The slope of the regression line (m=1.068, see figure) indicates no bias. The rank sum test also indicates no bias.

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed good precision and no bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

REPORT FOR LABORATORY CN029

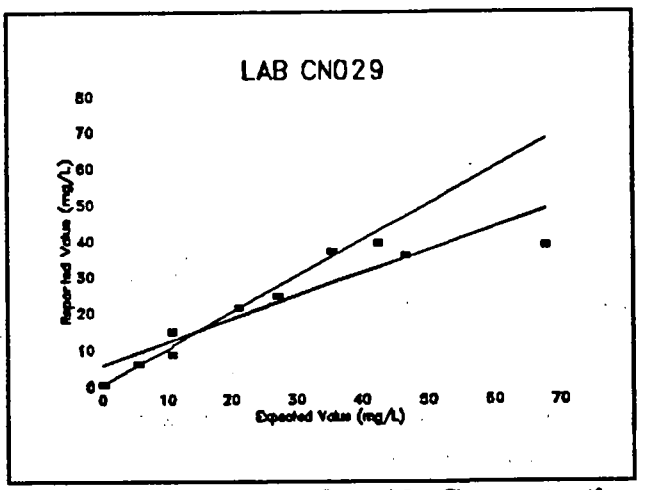
RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN029 Value (mg/L)	36.75	14.50	0.15	8.50	38.33	35.83	21.25	39.16	24.38	5.80

STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 3 standard deviations of the mean expected value. Samples H2, H3 and H4 fell outside 1 standard deviation of the mean expected values. These observations and the regression coefficient (R^2=0.851) suggest poor precision.

The slope of the regression line (m=0.636, see figure) indicates a low bias. The rank sum test did not detect any bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed poor precision with a possible low bias. Visual inspection of the above graph, however, suggests that the poor precision and low bias assessments are largely the result of a serious underestimation of concentrations above about 40 mg/L.

REPORT FOR LABORATORY CN030

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN030 Value (mg/L)	33.30	10.80	0.03	11.30	63.00	40.50	21.30	42.50	23.50	5.50

STATISTICAL SUMMARY:

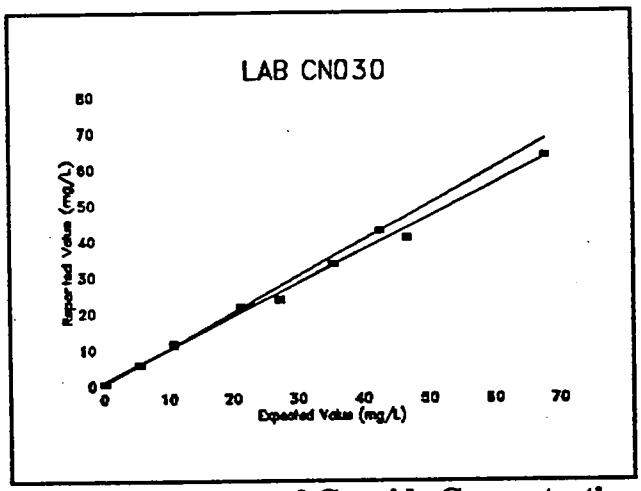
The flagging procedure indicated that no samples fell outside 1 standard deviation of the mean expected values.

The regression coefficient (R^2=0.993) indicated satisfactory precision.

The slope of the regression line (m=0.916, see figure) indicates no bias. The rank sum test also indicates no bias.

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed satisfactory precision with no bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

REPORT FOR LABORATORY CN031

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN031 Value (mg/L)	33.00	11.00	<1	12.00	70.00	55.00	30.00	53.00	34.00	6.00

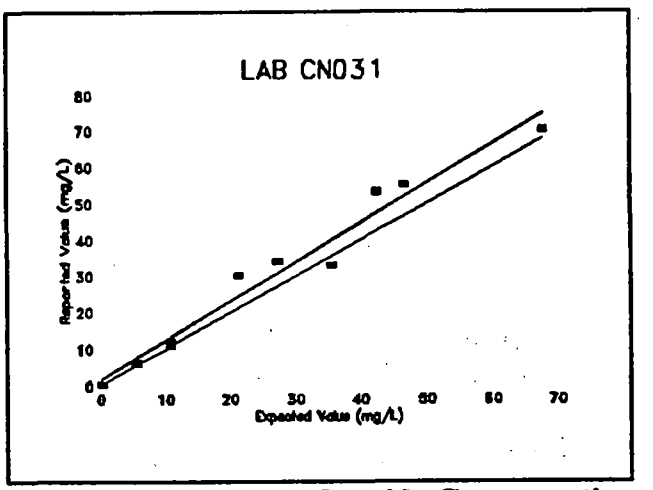
STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 3 standard deviations of the mean expected value. Samples H7 and H8 fell outside 1 standard deviation of the mean expected values. These observation and the regression coefficient (R^2=0.967) indicated poor precision.

The slope of the regression line (m=1.079, see figure) indicates no bias. The rank sum test also indicates no bias.

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed no bias but poor precision.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

REPORT FOR LABORATORY CN032

RESULTS:

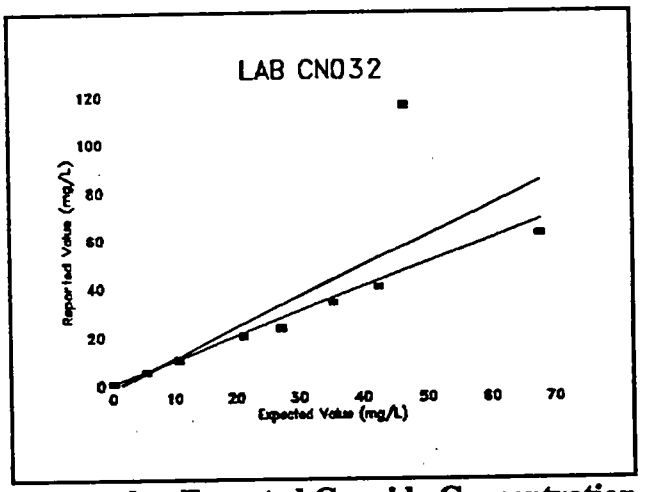
Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN032 Value (mg/L)	33.20	10.10	0.05	10.30	61.70	115.40	19.80	39.80	23.00	5.20

STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 3 standard deviations of the mean expected value. Sample H6 fell outside 1 standard deviation of the mean expected values.

The regression coefficient (R^2=0.606) indicated poor precision.

The slope of the regression line (m=1.264, see figure) indicates a high bias (see INFERENCE below). The rank sum test indicates no bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

INFERENCE:

In this study, one result submitted by your laboratory (sample H6) was seriously overestimated. As a result, the regression analysis assessed your lab as displaying poor precision and a high bias. Visual inspection of the above graph indicates, however, that a more appropriate assessment would be that your laboratory displayed satisfactory precision with no bias, but with one out of control point. The overestimated result is a sample of steel industry biox effluent and the error is likely either due to a positive interference from the sample itself to which your method is sensitive (several labs showed this) or a method control problem. The absence of a similar overestimation in sample H5, which is also biox
effluent, suggests that the latter may be the case.

REPORT FOR LABORATORY CN035A

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN035A Value (mg/L)	40.08	10.15	0.02	10.01	68.26	49.92	20.19	41.05	28.82	5.18

STATISTICAL SUMMARY:

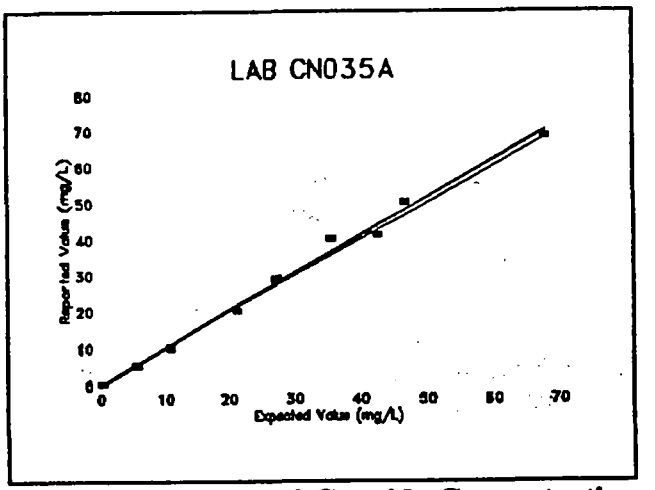
The flagging procedure indicated that no samples fell outside 1 standard deviation of the mean expected values.

The regression coefficient (R^2=0.993) indicated satisfactory precision.

The slope of the regression line (m=1.034, see figure) indicates no bias. The rank sum test also indicates no bias.

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed satisfactory precision and no bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

REPORT FOR LABORATORY CN035B

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN035B Value (mg/L)	35.84	10.26	0.02	10.19	69.24	46.70	20.53	40.64	28.04	5.28

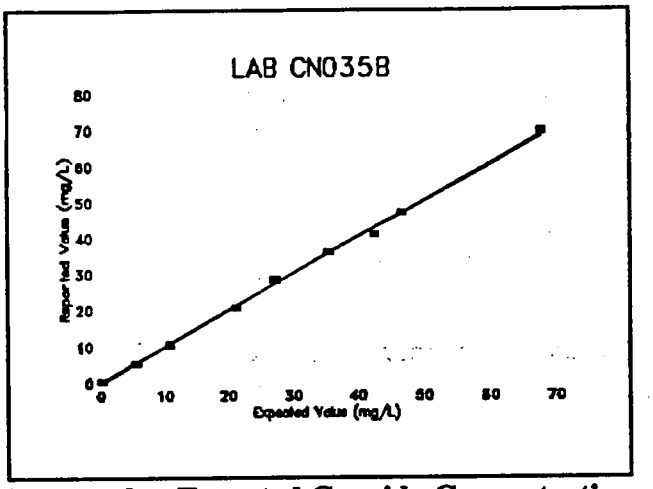
STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell outside 1 standard deviation of the mean expected values. This observation and the regression coefficient (R^2=0.998) indicated good precision.

The slope of the regression line (m=1.015, see figure) indicates no bias. The rank sum test also indicates no bias.

INFERENCE:

The statistical analysis of your data indicates that your laboratory displays good precision with no bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

REPORT FOR LABORATORY CN036A

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN036A Value (mg/L)	40.17	10.56	0.01	10.41	69.78	54.24	20.87	41.87	26.80	5.07

STATISTICAL SUMMARY:

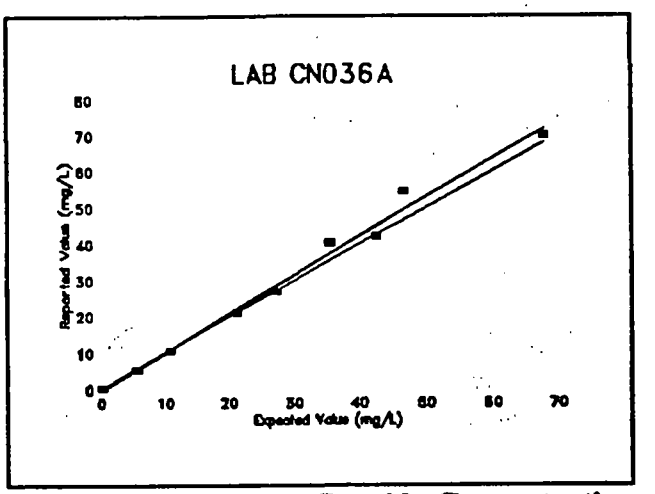
The flagging procedure indicated that no samples fell outside 1 standard deviation of the mean expected values.

The regression coefficient (R^2=0.989) indicated satisfactory precision.

The slope of the regression line (m=1.069, see figure) indicates no bias. The rank sum test also indicates no bias.

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed satisfactory precision with no bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

REPORT FOR LABORATORY CN036B

RESULTS:

Sample Number	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
Expected Value (mg/L)	35.366	10.629	0.025	10.658	67.634	45.510	21.131	42.458	27.102	5.386
CN036B Value (mg/L)	37.22	10.41	0.02	10.32	70.87	49.07	21.14	43.05	27.24	5.19

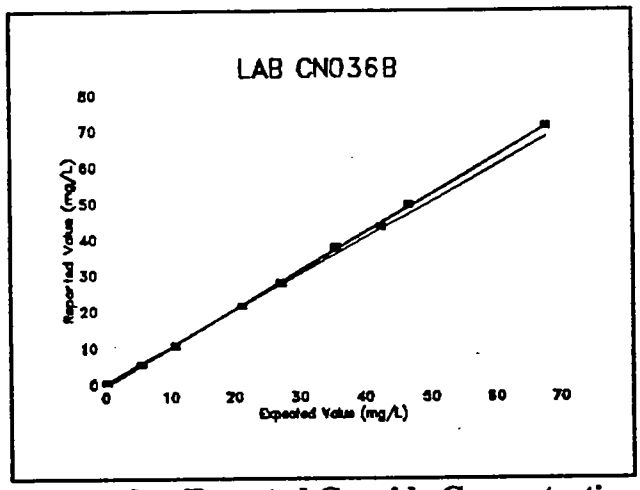
STATISTICAL SUMMARY:

The flagging procedure indicated that no samples fell were outside 1 standard deviation of the mean expected values.
This observation and the regression coefficient (R^2=0.999) indicated excellent precision.

The slope of the regression line (m=1.054, see figure) indicates no bias. The rank sum test also indicates no bias.

INFERENCE:

The statistical analysis of your data indicates that, in this study, your laboratory displayed excellent precision with no bias.



Reported vs Expected Cyanide Concentration

(Note: Dark boxes indicate reported results. Heavy line passing through the boxes is the best regression fit. The thin line represents the expected values.)

7.0 REFERENCES

Chapman, D.G. and R.A. Schaufele, 1970 Elementary Probability Models and Statistical Inference. Xerox College Publishing Company, Mass. U.S.A.

Grubbs, F.E., 1969 Procedures for Detecting Outlying Observations in Samples. Technometrics 11: 1–21

Malik, H.J. and K. Mullen, 1973 A First Course in Probability and Statistics. Addison–Wesley Pub. Co., Mass. U.S.A.

Ostle, B. and R.W. Mensing, 1975 Statistics in Research. 3rd ed. Iowa state University Press, Iowa, U.S.A.

Youden, W.J. and E.H. Steiner, 1975 Statistical Manual of the Association of Official Analytical Chemists. AOAC, Va., U.S.A.

8.0 APPENDICES

APPENDIX 1
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APPENDIX 2
Complete Table of Results (Raw Data)

WTC4 HIGH LEVEL CYANIDE STUDY: RAW DATA (As of May 21, 1992)

Lab Code / Sample Number	CN001	CN002	CN003	CN004A	CN004B	CN005	CN006	CN007	CN008	CN009	CN010	CN011	CN012A	CN012B	CN013	CN014	CN015	CN016	CN017	CN018	CN019
H1		40.10	38.80	37.11	35.93	180.00		194.00	31.40	181.00	41.07	71.00	31.00	32.20	34.60	30.20	37.50	34.80		47.40	41.20
H2		10.60	11.20	9.69	9.83	16.00		12.40	8.90	9.65	12.57	21.00	8.74	9.60	10.70	12.30	10.50	11.70	9.60	9.35	11.60
H3		0.01	0.02	0.01	0.02			0.06	0.06	0.03	0.04	0.03	0.02	0.03	0.05	0.03	0.20	0.02	0.02	0.00	0.04
H4		10.40	11.20	9.61	9.59	16.00		6.07	9.60	9.65	12.32	22.00	10.60	10.60	10.40	10.60	10.60	10.00	9.60	9.73	11.40
H5		71.60	69.10	68.75	68.96	236.00		205.00	55.10	179.50	68.07	130.00	68.40	69.20	69.40	64.70	69.00	68.20		64.40	71.40
H6		51.60	50.00	46.05	44.17	208.00		197.00	40.60	184.00	50.71	100.00	43.70	38.80	44.90	39.10	45.90	45.40		58.80	50.60
H7		21.30	22.10	19.81	19.60	38.00		33.00	18.20	19.00	24.64	89.00	20.80	19.60	21.00	20.00	21.30	23.10	18.00	19.30	22.40
H8		43.00	44.60	39.97	39.07	79.00		48.80	38.00	38.20	46.43	86.00	43.60	44.70	41.70	41.60	45.70	46.20	38.00	40.60	44.70
H9		29.30	28.20	27.51	26.42	170.00		172.00	23.90	136.00	28.57	42.00	22.40	22.00	25.60	25.70	26.60	23.00		31.10	28.60
H10		5.27	5.61	4.83	4.74	9.00		6.38	5.20	5.05	6.43	9.60	5.03	4.54	6.97	6.46	5.58	4.80	4.60	4.76	5.80

Lab Code / Sample Number	CN020	CN021	CN022	CN023	CN024	CN025	CN026	CN027	CN028	CN029	CN030	CN031	CN032	CN033	CN034	CN035A	CN035B	CN036A	CN036B
H1	20.41	46.80	34.50		35.91	36.80	39.84	34.20	41.56	36.75	33.30	33.00	33.20			40.08	35.84	40.17	37.22
H2	13.76	13.10	9.29		9.93	10.60	11.63	4.74	12.37	14.50	10.80	11.00	10.10			10.15	10.28	10.58	10.41
H3	0.06	0.03	0.02		0.02	0.04	0.03	0.02	0.03	0.15	0.03	<1	0.05			0.02	0.02	0.01	0.02
H4	14.52	15.30	13.30		10.36	9.91	11.44	10.40	12.33	8.50	11.30	12.00	10.30			10.01	10.19	10.41	10.32
H5	50.65	62.70	62.30		63.81	61.80	78.18	66.20	66.63	38.33	63.00	70.00	61.70			68.28	69.24	69.78	70.67
H6	33.39	55.50	47.80		42.56	43.00	45.34	44.00	55.62	35.63	40.50	55.00	115.40			49.82	46.70	54.24	49.07
H7	27.50	25.10	23.60		21.16	19.60	20.68	20.70	24.54	21.25	21.30	30.00	19.60			20.19	20.53	20.67	21.14
H8	52.49	55.60	41.70		41.31	40.60	44.96	37.20	47.62	39.16	42.50	53.00	38.60			41.05	40.64	41.67	43.06
H9	25.62	32.30	22.30		25.63	23.70	27.89	25.30	30.15	24.38	23.50	34.00	23.00			28.62	28.04	28.60	27.24
H10	5.59	6.40	4.27		5.07	5.09	4.88	19.40	6.16	5.80	5.50	6.00	5.20			5.18	5.28	5.07	5.19

MEAN (AVERAGE)	STANDARD DEVIATION
49.647	40.669
11.161	2.439
0.036	0.039
11.185	2.584
61.751	42.041
62.662	42.588
24.237	11.638
43.520	10.083
38.769	38.017
6.029	2.550

APPENDIX 3
Table of Results with Invalid Data (Grubbs outliers) Removed

WTC4 HIGH LEVEL CYANIDE STUDY: RAW DATA WITH VALUES FALLING OUTSIDE 1 STANDARD DEVIATION REMOVED

Lab Code / Sample Number	CN001	CN002	CN003	CN004A	CN004B	CN005	CN006	CN007	CN008	CN009	CN010	CN011	CN012A	CN012B	CN013	CN014	CN015	CN016	CN017	CN018	CN019
H1		40.10	38.80	37.11	35.89				31.40		41.07		31.00	32.20	34.60	30.20	37.80	34.80		47.40	41.20
H2		10.60	11.20	9.69	9.83			12.40	9.90	9.65	12.57		9.74	9.60	10.70	12.30	10.50	11.70	9.60	9.35	11.60
H3		0.01	0.02	0.01	0.02					0.03	0.04	0.03	0.02	0.03	0.05	0.03		0.02	0.02		0.04
H4		10.40	11.20	9.81	9.59				9.60	9.85	12.32		10.80	10.80	10.40	10.60	10.60	10.00	9.60	9.73	11.40
H5		71.60	69.10	68.75	68.96				55.10		68.07		69.40	69.20	69.40	64.70	69.00	68.20		64.40	71.40
H6		51.60	50.00	46.05	44.17				40.60		50.71		43.70	38.60	44.80	38.10	45.80	45.40		58.80	50.60
H7		21.30	22.10	19.81	19.60				18.20	19.00	24.64		20.80	19.60	21.00	20.00	21.20	23.10		19.30	22.40
H8		43.00	44.60	39.97	39.07						46.43		43.80	44.70	41.70	41.80	45.70	46.20		40.80	44.70
H9		29.30	28.20	27.51	26.42				23.80		28.57	42.00	22.40	22.00	25.60	25.70	28.80	23.00		31.10	28.60
H10		5.27	5.61	4.93	4.74			6.38	5.20	5.05	6.43		5.03	4.54		6.46	5.58	4.80	4.60	4.76	5.80

Lab Code / Sample Number	CN020	CN021	CN022	CN023	CN024	CN025	CN026	CN027	CN028	CN029	CN030	CN031	CN032	CN033	CN034	CN035A	CN035B	CN036A	CN036B
H1	20.41	45.90	34.50		35.91	36.80	39.84	34.20	41.56	36.75	33.30	33.00	33.20			40.08	35.84	40.17	37.22
H2			9.29		9.93	10.60	11.83		12.37		10.80	11.00	10.10			10.15	10.28	10.56	10.41
H3		0.03	0.02		0.02	0.04	0.03	0.02	0.03		0.03	<1	0.05			0.02	0.02	0.01	0.02
H4			13.30		10.36	9.91	11.44	10.40	12.33		11.30	12.00	10.30			10.01	10.19	10.41	10.32
H5	50.65	82.70	62.30		63.81	61.80	78.18	66.20	66.93	38.33	63.00	70.00	61.70			66.29	69.24	69.78	70.67
H6	33.39	55.50	47.80		42.56	43.00	45.34	44.00	55.62	35.63	40.50	55.00				49.92	46.70	54.24	48.07
H7		25.10	23.60		21.16	19.60	20.69	20.70	24.64	21.35	21.30		19.80			20.19	20.53	20.67	21.14
H8			41.70		41.31	40.60	44.66			39.16	42.50		39.80			41.05	40.64	41.67	43.05
H9	25.62	32.30	22.30		25.83	33.70	27.69	25.30	30.15	24.39	23.50	34.00	23.00			28.62	28.04	28.60	27.24
H10	5.59	6.40			5.07	5.09	4.69		6.16	5.60	5.50	6.00	5.20			5.18	5.28	5.07	5.19

MEAN (AVERAGE)	STANDARD DEVIATION
36.400	5.108
10.629	0.970
0.025	0.012
10.658	0.912
67.634	10.407
46.510	6.057
21.131	1.694
42.456	2.189
27.102	3.997
5.366	0.559

APPENDIX 4
Table of Results with All Outliers Removed

WTC4 HIGH LEVEL CYANIDE STUDY: RAW DATA WITH GRUBBS OUTLIERS REMOVED

Lab Code / Sample Number	CN001	CN002	CN003	CN004A	CN004B	CN005	CN006	CN007	CN008	CN009	CN010	CN011	CN012A	CN012B	CN013	CN014	CN015	CN016	CN017	CN018	CN019
H1		40.10	36.80	37.11	35.83				31.40	151.00	41.07	71.00	31	32.20	34.80	30.20	37.80	34.80		47.40	41.20
H2		10.60	11.30	9.69	9.83	16.00		12.40	9.90	9.66	12.57		9.74	9.60	10.70	12.30	10.50	11.70	9.60	9.35	11.60
H3		0.01	0.02	0.01	0.02			0.06	0.06	0.03	0.04	0.03	0.02	0.03	0.05	0.03		0.02	0.02	0.00	0.04
H4		10.40	11.20	9.81	9.58	16.00		6.07	9.80	9.86	12.32	22.00	10.80	10.90	10.40	10.60	10.60	10.00	9.60	9.73	11.40
H5		71.60	69.10	68.79	66.96			205.00	65.10	179.90	66.07	130.00	69.40	69.20	68.40	64.70	69.00	68.20		64.40	71.40
H6		51.60	50.00	46.05	44.17				40.60	164.00	50.71	100.00	43.70	36.80	44.80	36.10	46.90	45.40		56.80	50.60
H7		21.30	22.10	19.81	19.80	36.00		33.00	18.20	19.00	24.64		20.90	19.60	21.00	20.00	21.30	23.10	18.00	18.30	22.40
H8		43.00	44.60	39.97	38.07			46.60	36.00	36.30	46.43		43.90	44.70	41.70	41.80	46.70	46.20	36.00	40.60	44.70
H9		29.30	28.20	27.51	26.42				23.90	136.00	26.57	42.00	22.40	22.00	25.80	25.70	26.90	23.00		31.10	28.60
H10		5.27	5.61	4.93	4.74	9.00		6.36	5.20	5.05	6.43	9.80	5.03	4.54	6.97	6.46	5.58	4.80	4.60	4.76	5.80

Lab Code / Sample Number	CN020	CN021	CN022	CN023	CN024	CN025	CN026	CN027	CN028	CN029	CN030	CN031	CN032	CN033	CN034	CN035A	CN035B	CN036A	CN036B
H1	20.41	45.90	34.50		35.91	36.80	39.84	34.20	41.56	36.76	33.30	33.00	33.20			40.08	35.84	40.17	37.22
H2	13.78	13.10	9.29		9.93	10.60	11.83	4.74	12.37	14.50	10.80	11.00	10.10			10.15	10.26	10.56	10.41
H3	0.06	0.03	0.02		0.02	0.04	0.03	0.02	0.03	0.15	0.03	<1	0.06			0.02	0.02	0.01	0.02
H4	14.52	15.30	13.30		10.36	9.91	11.44	10.40	12.33	8.80	11.30	12.00	10.30			10.01	10.19	10.41	10.32
H5	50.65	82.70	62.30		63.81	61.80	78.18	66.20	66.93	36.33	63.00	70.00	61.70			66.26	69.24	66.78	70.67
H6	33.39	55.50	47.80		42.56	43.00	45.34	44.00	55.62	35.83	40.50	55.00	115.40			46.92	46.70	54.24	49.07
H7	27.50	25.10	23.60		21.16	19.60	20.88	20.70	24.54	21.25	21.30	30.00	19.80			20.19	20.53	20.87	21.14
H8	52.49	55.60	41.70		41.31	40.60	44.96	37.20	47.82	36.16	42.50	53.00	36.80			41.06	40.64	41.87	43.06
H9	25.62	32.30	22.30		25.83	23.70	27.89	25.30	30.15	24.38	23.50	34.00	23.00			26.82	26.04	26.80	27.24
H10	5.59	6.40	4.27		5.07	5.09	4.86		6.16	5.80	5.50	6.00	5.30			5.19	5.38	5.07	5.19

MEAN (AVERAGE)	STANDARD DEVIATION
41.062	21.548
10.862	1.874
0.031	0.026
11.185	2.584
77.077	32.835
54.006	25.419
22.333	4.157
43.279	4.379
30.505	18.352
5.636	1.132

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