THE WASTEWATER TECHNOLOGY CENTRE INTERLABORATORY STUDY FOR TOTAL CYANIDE:

PHASE 1: LOW LEVEL TOTAL CYANIDE

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Abbreviations and Key Terms ii.

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.

Effluent:

Final effluent from a gold mine. Taken from the outfall of the tailings

system.

Standard Solutions: The nine solutions or samples (labelled L1 through L9) sent to each

participating laboratory.

Target Values:

The theoretical cyanide concentrations of the Standard Solution as

calculated by weights and measures.

Expected Values:

The accepted or "correct" cyanide concentrations of the Standard

Solutions statistically determined using data from the most precise

participating laboratories.

mg/L:

Milligrams per litre, equal to Parts per million (ppm).

SCN:

Thiocyanate

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, 33 laboratories across Canada 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 influent 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 low 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 five techniques used to evaluate the data in this study include;

- Frequency analysis to check the distribution of results to confirm that parametric statistics (example: standard deviation, t-test) can be used.
- Comparison of the reported results to the Expected Values using a paired t-test.
- 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.

Examination of the distribution of the submitted results showed that the results were normally distributed. The use of normal statistics was found to be justified.

The key findings of this study are:

- 2.8% of results fell outside 3 standard deviations of the mean expected value and were flagged as Grubbs outliers. These results were contributed by 5 laboratories.
- 23% of results fell outside 1 standard deviation of the mean expected value. 61% of labs had at least 1 result flagged in this manner.
- 30% of labs submitted results which were identified as significantly different from the expected by the t-test.
- 75% of labs displayed good or satisfactory precision as judged by the regression correlation coefficient. 25% displayed poor precision.
- 72% of labs displayed no bias in the regression slope test. 85% displayed no bias in the Youden Rank Sum test.
- 14% of labs were judged to be biased high and 14% biased low by the regression slope test. 6% were biased high and 6% biased low by the Rank Sum test.
- 83% of labs displayed regression Y-intercepts which were judged to be good or satisfactory. 17% were judged to be poor, indicating problems with precision, method failure at high concentrations or inappropriate blank correction.
- 2 of 36 participating labs displayed serious method failure with these samples.
- There was no evidence of a difference between methods with respect to accuracy or precision. However, 4 of the 36 laboratories showed a possible positive interference from thiocyanate in sample L5. These laboratories all reported using autoanalyzer methods.
- There was no evidence of a general matrix effect although some labs did appear to have difficulty with the effluent matrix.

In summary, between 23% and 25% of the participants in this study displayed poor precision as judged by the outlier flagging test and regression correlation coefficient test, respectively. Between 12% and 28% of the participants were judged to be biased, or inaccurate, by the Youden Rank Sum test and regression slope test, respectively. In view of the fact that the Rank Sum test does not detect bias in labs displaying imprecision, the 28% assessment is expected to more closely reflect the actual situation.

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. As a result, 33 laboratories across Canada 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

Current and proposed environmental guidelines for acceptable cyanide concentrations in aqueous effluent are regulating the levels to the one mg/L range. Many laboratories now perform this analysis on various aqueous matrices and the relative precision and accuracy of these laboratories in producing analytical data in the low concentration range in effluents is not well defined.

The study was designed to test the laboratory's 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. In addition, one of the pure water samples was spiked with thiocyanate to provide a positive control on proper sample digestion and distillation procedures. Thiocyanate would be detected by methods employing UV digestion if proper corrections are not made.

A total of nine samples were sent to each laboratory using ferricyanide (Fe(CN)₆) as the spike. Four samples having target concentrations of 0.1 to 3.0 mg/L CN⁻ in pure water, four samples covering the range of 0.2 to 3.1 mg/L CN⁻ in gold mine effluent, and one sample containing 0.5 mg/L CN⁻ in pure water with an additional 1.0 mg/L CN⁻ (as thiocyanate) were prepared. The effluent matrix samples were 0.1 mg/L greater in concentration as the gold mine effluent used contained this background level of detectable cyanide.

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). These code numbers were used in all subsequent correspondence to ensure the confidentiality of the results.

The samples were initially sent to the participants on November 24, 1991 by overnight courier. Unfortunately the courier failed to make delivery and returned the samples. They were then re-sent by overnight courier on December 5, 1991. The nine samples were numbered randomly (as in table 3.1). The results were requested by December 31, 1991. A sample of the correspondence and results request form are included in Appendix 1.

On January 6, 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. One laboratory requested corrections and these were made.

3.2 PREPARATION OF STANDARDS AND SAMPLES

3.2.1 OVERVIEW

A set of nine 30 litre standard cyanide solutions was prepared in 50 litre carboys for the study. Of these, four were prepared in an effluent matrix and five 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 nine 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_4 Fe(CN)₆ · 3H₂O) 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.

The thiocyanate used for the positive digestion/distillation check was prepared in a stock solution using potassium thiocyanate (KSCN) provided by Fisher (Certified ACS potassium thiocyanate, Cat. No. P-317, Lot 781716).

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 effluent was final effluent from the tailings system outfall of an undisclosed gold mine.

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, CYANIDE, AND THIOCYANATE 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 density of the stock water was measured at 0.9962 g/mL.

The stock cyanide concentrate containing 1000 mg/L CN was prepared as follows: Into a 2 litre volumetric flask, 1 litre of water and 20 ml of 1 N NaOH were added and the pH tested with pH paper (pH 12.5). To this, 5.4126 g of $K_4Fe(CN)_6 \cdot 3H_2O$ was added and the volume brought up to below the 2 litre line. The pH was checked again and was stable at 12.5. The solution was made up to volume.

The target stock thiocyanate concentration was 1000 mg/L as CN. Into a 100 ml volumetric flask containing 50 ml of water, 0.1673 g of KSCN was added. The solution was made up to volume.

3.2.4 PREPARATION OF STANDARD SOLUTIONS

A set of nine 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, cyanide, and thiocyanate solutions discussed in section 3.2.3.

The standards were prepared in new clean 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 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.
- The required amount of 1000 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.
- Each addition, weight or volume, was checked by a second analyst and the record initialled.

- 7) The target concentration (determined from recorded weights and measures) was calculated using the exact stock water weight and stock solution volume added.
- 8) The solutions were bottled immediately and stored at room temperature until shipping.

Table 3.1

TARGET CONCENTRATIONS AND REAGENT QUANTITIES USED

| Sample Number | Matrix | Target Concentration (mg/L) | | Cyanide Stock [†] | Thiocyanate Stock [‡] | Stock Water |
|------------------|----------|-----------------------------|-----|-------------------------------|-----------------------------------|----------------|
| (random) | | Cyanide | SCN | (ml) | (ml) | (kg) |
| L1 | Water | 0.297 | | 9.0 | 0 | 30.094 |
| L2 | Effluent | 1.097 | | 30.0 | 0 | 29.971 |
| L3 | Water | 2.979 | | 0.0 | 0 | 30.094 |
| L4 | Effluent | 0.1997 | | 3.0 | 0 | 29.971 |
| L5 | Water | 0.499 | 1.0 | 15.0 | 30 | 29.971 |
| L6 | Effluent | 0.397 | | 9.0 | 0 | 30.094 |
| L7 | Water | 0.0997 | | 3.0 | 0 | 29.971 |
| L8 . | Water | 0.997 | | 30.0 | 0 | 29.971 |
| L9 | Effluent | 3.079 | | 90.0 | 0 | 30.094 |

^{†: 1000} 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 samples were not shipped until December 5, 1991 due to a mistake by the courier. The filling sequence was recorded and three samples per sequence (starting, middle, and end) were retained for internal analysis.

^{‡: 1000} mg/L Stock Thiocyanate Solution

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). Duplicate analysis of the Stock Effluent (Gold mine effluent with NaOH to pH 12) showed a cyanide concentration of 0.102 ±0.007 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 26), and one at the end of the series (bottle 54, 55, or 56). Each of these samples was analyzed for cyanide concentration. The purpose of this was to determine if the standard solutions were homogenous in the carboys so that there was no systematic difference between the first and last bottles dispensed.

There were no systematic differences in cyanide concentration between the first and last samples bottled in each Standard Solution. This means the standard solutions in the carboys were homogenous and there is no bias between the first and last bottles dispensed. The

analysis data is shown in Appendix 2.

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 six (6) times between the start of the project (November 25, 1991) and the date results were due from the participating laboratories (December 31, 1991).

There were no trends in cyanide concentration among the six samples analyzed for each Standard Solution. This means the cyanide concentration in the bottled standard samples did not change over the duration of the study. The analysis data and graphs for the sample stability are in Appendix 3.

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 3.4.5 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 five 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; Comparison of the reported results to the Expected Values using a paired t-test; 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; Ranking analysis to determine if any of the laboratories are consistently biased. Each technique is described below,

3.4.2 FREQUENCY DISTRIBUTION OF DATA

Round robin analytical data is usually 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. Calculations are done after Chapman and Schaufele, 1970.

3.4.3 COMPARISON WITH EXPECTED VALUES

The reported values for each standard solution from each laboratory are compared to the Expected Values using a paired t-test. The paired t-test is a statistical test used for normally distributed data where the two groups of data being compared are dependent on each other. In the case of the round robin data we are comparing $L1_{expected}$ to $L1_{measured}$ and $L2_{expected}$ to $L2_{measured}$ and so on.

The t statistic then is used to determine if the data submitted by the participating laboratory is significantly different from the Expected Values (ie. the values deemed "correct"). Calculations were done after Malik and Mullen, 1973.

To compare measured and expected values using the paired t-test, the authors arbitrarily adopted a probability of 10 percent (α =0.10) for this study. This means that laboratories whose data are shown to be significantly different from the Expected Values would likely be so nine times out of ten. Only one time out of ten would this difference be attributable to random variation. In the experience of the authors the 10 percent criteria is acceptable for the purposes of this study.

This test determines which laboratories submit data which is different than the expected results by a test which weighs the data's variability against it's deviation from the Expected Values. The advantage of this is it is an objective test which determines if a given laboratory's measured results are different from the Expected Values. The disadvantage is that a laboratory with a lot of variability in its data (ie. data which is not precise) will not tend to be detected whereas a laboratory with very precise data which is marginally different from the expected will be detected. These characteristics of the paired t-test are considered when the results are interpreted.

3.4.4 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)

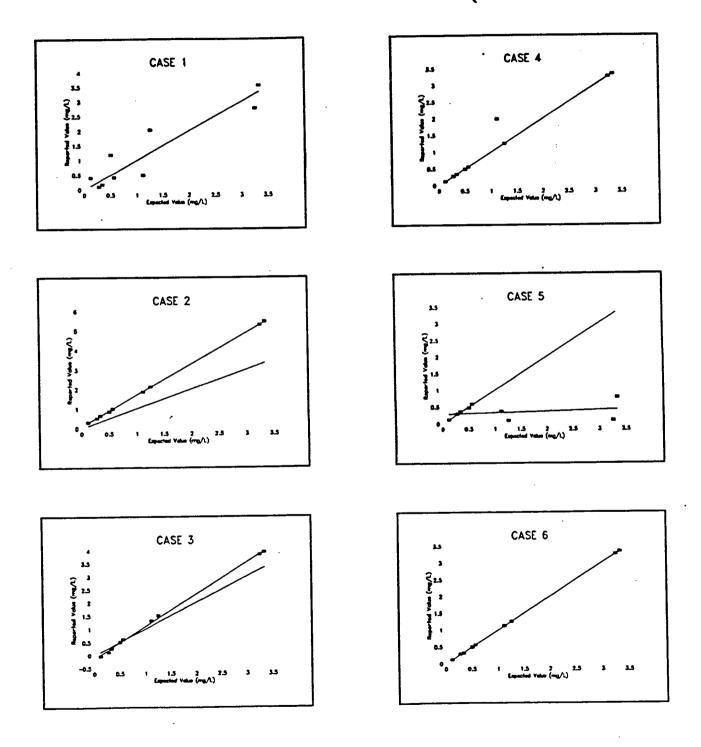
• Single sample outlier problems (case 4)

• 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 R². For the purposes of this study the authors have arbitrarily chosen the following criteria: A regression coefficient (R²) of greater than 0.995 to indicate good precision; An R² between 0.995 and 0.990 to indicate satisfactory precision; An R² 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 0.01 of the origin (10 percent of the lowest measured concentration) is considered good; A $Y_{intercept}$ within 0.10 is considered satisfactory; A $Y_{intercept}$ greater than 0.10 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 3.2

TABLE 3.2

SUMMARY OF DATA EVALUATION METHODS

| Method | Peatures | Weaknesses | Requires Normal Data? |
|---------------------|---|---|-----------------------|
| Paired t-Test | -looks at pooled sample set -tests differences from expected values -detects small consistent differences in precise data missed by regression slope or rank sum bias assessments | -tends to flag minor biases in very precise data -doesn't detect large bias in imprecise data | yes |
| 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 | 80 |

4.0 RESULTS AND DISCUSSION

4.1 SUMMARY OF PARTICIPATING LABORATORIES \

Thirty six laboratories participated in the study providing a total of 324 data for analysis. The geographical breakdown of the laboratory locations are in Table 4.1.

Table 4.1

INTERLABORATORY STUDY FOR LOW LEVEL TOTAL CYANIDE PARTICIPATING LABORATORY LOCATIONS

| LOCATION | NUMBER OF PARTICIPANTS |
|-----------------------|------------------------|
| Southern Ontario | 14 |
| Northern Ontario | 7 |
| Quebec | 4 |
| United States | 3 |
| British Columbia | 2 |
| Manitoba | 1 |
| Northwest Territories | 1 |

A list of the participating laboratories is in Appendix 4. 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 performance of each participating laboratory was assessed by considering the results of the statistical analyses. Although the various procedures used estimate the variability differently, they all tend to reflect the overall accuracy of a laboratory.

The purpose of the tests are to both determine the accuracy of each laboratory and to provide information as to why any specific laboratory had difficulty. This permits constructive comments as to potentially correctable problems such as calibration error, inappropriate blank correction, or method failure.

The laboratory performance is discussed by subject (for example: distribution, flags, regression, ranking) in the following subsections. These discussions provide an overview of the study results. In addition, laboratory specific performance information is given in section 6.0. A complete table of the raw results is in Appendix 5.

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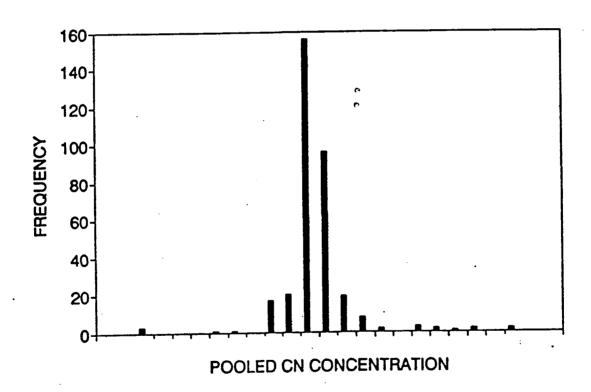
4.2.2 DATA DISTRIBUTION

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 the paired t-test and standard deviation statistics.

The frequency analysis is shown in Figure 4.1. The shape of the distribution indicates the data is normally distributed. There are small peaks at the low and high ends of the distribution but these are accounted for by five outlying results from laboratories CN001, CN005, CN007, and CN011. There is no indication of a skewed or bi-modal distribution. No general method failure is suspected and the use of normal statistics is justified.

DISTRIBUTION OF STUDY RESULTS

Interlaboratory Low Level Cyanide Study Frequency Analysis



4.2.3 COMPARISON WITH EXPECTED VALUES

In this study the Expected cyanide 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 Expected values and Target Values (values calculated from weights and measures) are in 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 |
|------------------|---------------------------|-----------------------------|
| L1 | 0.297 | 0.3283 |
| 1.2 | 1.097 | 1.2485 |
| L3 | 2.979 | 3.2488 |
| L4 | 0.1997 | 0.2676 |
| L5 | 0.499 | 0.5530 |
| L6 | 0.397 | 0.4948 |
| L7 | 0.0997 | 0.1111 |
| L8 | 0.997 | 1.1094 |
| L9 | 3.079 | 3.3314 |

The reported values for each standard solution from each laboratory were compared to the Expected Values using a paired t-test. This test shows which of the laboratories results varied significantly from the Expected Values. Laboratories were considered to be significantly different from the Expected Values at the ten percent level ($\alpha = 0.10$). An alpha value of 0.10 represents 5% chance of concluding that the reported lab results are significantly greater than, or significantly less than the expected when in fact they are not.

Thirty percent, or 11 of the 36, participating laboratories reported results which were

significantly different than the expected results. Table 4.3 shows the laboratories whose results differed significantly from the expected values. The percentages listed are the probabilities that the measured results are different from the expected values.

Table 4.3

INTERLABORATORY STUDY FOR LOW LEVEL TOTAL CYANIDE LABORATORIES WITH RESULTS SIGNIFICANTLY DIFFERENT THAN THE EXPECTED VALUES (Limit α =0.10)

| LABORATORY CODE | PROBABILITY OF BEING DIFFERENT FROM THE EXPECTED |
|--------------------|--|
| CN001 | 98% |
| CN004a | 95% |
| CN004b | 95% |
| CN005 | 95% |
| CN006 | 95% |
| CN012 | 90% |
| CN015 · | 90% |
| CN035a | 95% |
| CN035b | 95% |
| CN036a | 98% |
| CN036b | 95% |

NSD: Not Significantly different from Expected Values at $\alpha = 0.10$

4.2.4 ASSIGNING FLAGS

Assigning flags was done 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 nine of the 324 results or 2.8 percent of the total. Table 4.4 shows the sample results classified as Grubbs outliers.

Table 4.4

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

| LABORATORY CODE | SAMPLE NUMBERS OUTSIDE OF 3 Std. Dev. OF THE MEAN |
|--------------------|--|
| CN001 | L8 |
| CN005 | L2, L5, L9 |
| CN007 | L4, L6 |
| CN011 | L1, L2, L3, L7 |
| CN029 | L7 |

All of the sample numbers (ie. L1 to L9) are 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 6.

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 75 of the remaining 313 data or 23 percent of the total being identified as outliers. Table 4.5 shows the laboratories and sample numbers which are outside 1 standard deviation of the mean.

Table 4.5

SUMMARY OF RESULTS LYING OUTSIDE 1 STANDARD DEVIATION
OF THE MEAN

| LABORATORY CODE | SAMPLE NUMBERS FALLING OUTSIDE 1 STD. DEV. OF THE MEAN |
|--------------------|---|
| CN001 | L1-L9 |
| CN003 | L8 |
| CN005 | L1, L2, L3, L4, L5, L6, L8, L9 |
| CN006 | 1.2 |
| CN007 | L1, L2, L3, L4, L6, L7, L8, L9 |
| CN009 | L5, L7, L8 |
| CN010 | L7, L8 |
| CN011 | ALL |
| CN013 | L7 |
| CN014 | L1, L2, L3, L4, L8, L9 |
| CN015 | L7 |
| CN017 | L1, L5, L8 |
| CN018 | 1.2 |
| CN019 . | L5, L7 |
| CN021 | L1, L3, L4, L9 |
| CN025 | 13, 18 |
| CN026 | L7 |
| CN027 | L6 |
| CN029 | L1, L2, L7 |
| CN031 | L1, L2, L3, L7, L8 |
| CN032 | L1, L5, L7 |
| CN033 | L3 |

A total of 22 of the 36 labs earned at least one flagged result. The sample numbers (ie. L1 to L9) are evenly represented in the outlier data pool therefore no particular sample seemed to cause analytical difficulty. A table of the full data set with the outliers marked is in Appendix 7.

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.

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 R². In this study we have assumed that a regression coefficient (R²) of greater than 0.995 indicates good precision and an R² between 0.995 and 0.990 indicates satisfactory precision. An R² of less than 0.990 indicates poor precision.

Table 4.6 shows the participating laboratories with regression coefficients in descending order of R².

Table 4.6

REGRESSION COEFFICIENTS OF PARTICIPATING LABORATORIES

| LABORATORY CODE | REGRESSION COEFFICIENT | INFERENCE |
|--------------------|---------------------------|------------------------|
| CN008 | 0.9996 | Good Precision |
| CN002 | 0.9994 | . " |
| CN015 | 0.9994 | 99 |
| CN035a | 0.9993 | 11 |
| CN024 | 0.9992 | ** |
| CN036b | 0.9991 | н |
| CN036a | 0.9990 | н |
| CN035b | 0.9989 | n |
| CN026 | 0.9985 | |
| CN004a | 0.9985 | н |
| CN010 | 0.9984 | н |
| CN004b | 0.9982 | н |
| CN006 | 0.9981 | н |
| CN014 | 0.9981 | н |
| CN028 | 0.9980 | 11 |
| CN012 | 0.9979 | н |
| CN001 | 0.9976 | 11 |
| CN027 | .09968 | н |
| CN022 | 0.9959 | * |
| CN032 | 0.9956 | н |
| CN021 | 0.9945 | Satisfactory Precision |
| CN003 | 0.9939 | " |
| CN019 | 0.9914 | н |
| CN023 | 0.9912 | ŧı |
| CN031 | 0.9911 | Ħ |

| LABORATORY CODE | REGRESSION COEFFICIENT | INFERENCE |
|--------------------|---------------------------|----------------|
| CN025 | 0.9905 | . " |
| CN016 | 0.9905 | 4 |
| CN018 | 0.9826 | Poor Precision |
| CN017 | 0.9829 | ** |
| CN033 | 0.9822 | " |
| CN009 | 0.9781 | W |
| CN013 | 0.9702 | # |
| CN029 | 0.9463 | n |
| CN005 | 0.9241 | Ħ |
| CN011 | 0.1073 | н. |
| CN007 | 0.0037 | • |

Twenty seven of the 36 laboratories (75%) displayed good or satisfactory precision according to these criteria. Nine of 63 labs displayed poor precision. Of the latter group, 2 labs displayed serious method failure, as characterized by R² values of less than 0.2.

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 4.7 lists the laboratories, regression slopes and bias assessments.

Table 4.7

REGRESSION SLOPES AND BIAS ASSESSMENTS OF PARTICIPATING LABORATORIES

| LABORATORY CODE | REGRESSION SLOPE | INFERENCE |
|--------------------|---------------------|------------------|
| CN002 | 1.0000 | No Bias Detected |
| CN022 | 0.9923 | 99 |
| CN016 | 1.0080 | N |
| CN008 | 0.9884 | * |
| CN029 | 0.9651 | н |
| CN009 | 0.9630 | H |
| CN024 | 0.9563 | # |
| CN035b | 1.0440 | H |
| CN026 | 1.0490 | * |
| CN036a | 1.0530 | * |
| CN004b | 1.0610 | # |
| CN036b | 1.0650 | H |
| CN028 | 1.0660 | н . |
| CN035a | 1.0670 | 11 |
| CN018 | 1.0720 | 11 |
| CN015 | 1.0780 | * |
| CN004a | 1.0796 | н |
| CN023 | 1.0800 | н |
| CN003 | 0.8954 | ** |
| CN033 | 0.8894 | N |
| CN027 | 1.1110 | # |
| CN019 | 0.8870 | н |
| CN013 | 0.8815 | н |
| CN017 | 0.8726 | н |

| LABORATORY CODE | REGRESSION SLOPE | INFERENCE |
|--------------------|---------------------|-------------|
| CN012 | 1.1288 | |
| CN032 | 0.8626 | |
| CN025 | 0.8285 | Biased Low |
| CN031 | 0.8259 | Biased Low |
| CN010 | 0.8248 | Biased Low |
| CN006 | 1.1890 | Biased High |
| CN014 | 1.3730 | Biased High |
| CN021 | 1.4760 | Biased High |
| CN001 | 1.4779 | Biased High |
| CN005 | 1.6870 | Biased High |
| CN011 | 0.1170 | Biased Low |
| CN007 | 0.0621 | Biased Low |

No bias was detected in 26 of 36 laboratories (72 percent of the participants) listed in Table 4.7. Bias was detected in 10 laboratories. There were an equal number of high and low biases in the flagged group. In 2 laboratories, major difficulties were noted.

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 \pm 0.01 mg/L is considered good and those within \pm 0.10 mg/L are considered satisfactory. A $Y_{intercept}$ greater than 0.10 mg/L is designated as poor.

Table 4.8 lists the laboratories and regression Y intercepts sorted from the best (ie. closest to the origin) to the most deviant.

Table 4.8

REGRESSION Y INTERCEPTS OF PARTICIPATING LABORATORIES LISTED IN DESCENDING ORDER

| LABORATORY CODE | REGRESSION Y-INTERCEPT | INFERENCE |
|--------------------|------------------------|--------------|
| CN004b | 0.0013 | Good |
| CN036b | 0.0031 | и |
| CN004a | 0.0032 | н |
| CN035a | 0.0055 | n . |
| CN002 | -0.0081 | н |
| CN033 | 0.0093 | н |
| CN008 | -0.0097 | н |
| CN035b | 0.0113 | Satisfactory |
| CN016 | -0.0117 | Ħ |
| CN032 | 0.0129 | н |
| CN015 | -0.0147 | н |
| CN031 | 0.0154 | Ħ |
| CN036a | 0.0155 | н |
| CN006 | -0.0185 | н |
| CN010 | 0.0189 | н |
| CN029 | 0.0207 | n |
| CN028 | -0.0304 | H |
| CN009 | 0.0324 | 11 |
| CN012 | -0.0367 | н |
| CN024 | -0.0402 | н |
| CN022 | -0.0424 | n |
| CN026 | -0.0431 | n |
| CN023 | 0503 | н |

| LABORATORY CODE | REGRESSION Y- INTERCEPT | INFERENCE |
|--------------------|----------------------------|-----------|
| CN001 | 0.0536 | * |
| CN019 | 0.0551 | |
| CN025 | 0.0585 | • |
| CN027 | -0.0688 | * |
| CN017 | 0.0696 | •• |
| CN003 | 0.0750 | • |
| CN013 | 0.0760 | • |
| CN018 | -0.1165 | Poor |
| CN011 | 0.1471 | n |
| CN014 | -0.1596 | ** |
| CN005 | 0.1837 | " |
| CN021 | -0.2644 | • |
| CN007 | 1.1780 | 9 |

Thirty or the 36 participants (83%) displayed good or satisfactory intercept values. Six labs fell into the poor category. 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 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 4.9 with the Laboratory code, the Rank Sum, and inference.

Table 4.9

RANK SUM TEST RESULTS FOR PARTICIPATING LABORATORIES

| LABORATORY CODE | RANK SUM | INFERENCE |
|--------------------|----------|------------------|
| CN011 | 41 | Biased Low |
| CN010 | 69 | N |
| CN033 | 80 | No Bias Detected |
| CN024 | 86 | н |
| CN032 | 88 | |
| CN031 | 103 | * |
| CN025 | 110 | # |
| CN018 | 111 | п |
| CN017 | 112 | |
| CN019 | 115 | н |
| CN022 | 121 | n |
| CN008 | 134 | п |
| CN009 | 139 | ** |
| CN016 | 139 | н |

| LABORATORY CODE | RANK SUM | INFERENCE |
|--------------------|----------|-------------|
| CN026 | 141 | |
| CN023 | 148 | |
| CN002 | 149 | * |
| CN013 | 170 | * |
| CN007 | 171 | |
| CN003 | 171 . | я |
| CN021 | 174 | H |
| CN027 | 185 | н |
| CN029 | 192 | PI |
| CN028 | 196 | . • |
| CN035b | 199 | 11 |
| CN004b | 210 | , |
| CN014 | 215 | " |
| CN036a | 215 | " |
| CN015 | 216 | и |
| CN036b | 219 | n |
| CN035a | 223 | " |
| CN012 | 238 | " |
| CN004a | 238 | н |
| CN006 | 252 | " |
| CN005 | 310 | Biased High |
| CN001 | 314 | |

No bias was detected by the rank sum test in 32 (89 percent of the total) of the participating laboratories. Laboratories CN011 and CN010 were assessed as biased low, meaning they consistently underestimated the concentration of the standard solutions and would do so more that 95 times out of 100. Laboratories CN005 and CN001 were assessed as biased high, meaning that they consistently overestimated the concentration of the standard solutions and would do so more than 95 times out of 100.

4.3 PERFORMANCE vs METHOD OF ANALYSIS

The participating laboratories were requested to submit the method of cyanide analysis used in their laboratories. The two general methods used were 1) manual determination, and 2) autoanalyzer. For each of these general methods one of four specific methods was used. These are:

- Colourimetric determination using isonicotinic/barbituric acid
- Colourimetric determination using pyridine/barbituric acid
- Colourimetric determination of tetracyano-nickelate complex
- Ion specific electrode

Table 4.10 summarizes the methods used by each of the participating laboratories.

Table 4.10

ANALYTICAL METHODS USED BY PARTICIPATING LABORATORIES

| LABORATORY CODE | MANUAL OR AUTOANALYZER | DETAILS OF METHOD |
|--------------------|---------------------------|----------------------|
| CN001 | Autoanalyzer | None given |
| CN002 | Manual | Pyr/barb |
| CN003 | Autoanalyzer | Isonic/barb |
| CN004a | Autoanalyzer | Pyr/barb . |
| CN004b | Autoanalyzer | Pyr/barb |
| CN005 | Autoanalyzer | Pyr/barb |
| CN006 | Autoanalyzer | None given |
| CN007 | Autoanalyzer | None given |
| CN008 | Autoanalyzer | None given |
| CN009 | Autoanalyzer | None given |
| CN010 | Manual | Isonic/barb |
| CN011 | Manual | Pyr/barb |
| CN012 | Manual | Isonic/barb |
| CN013 | Manual | Isonic/barb |
| CN014 | Manual | Isonic/barb |

| LABORATORY CODE | MANUAL OR AUTOANALYZER | DETAILS OF METHOD |
|--------------------|---------------------------|----------------------|
| CN015 | Manual | Ion spec. elect. |
| CN016 | Manual | Pyr/barb |
| CN017 | Autoanalyzer | Pyr/barb |
| CN018 | Autoanalyzer | None given |
| CN019 | Autoanalyzer | None given |
| CN021 | Manual | None given |
| CN022 | Manual | None given |
| CN023 | Manual | Ion spec. elect. |
| CN024 | Manual | Pyr/barb |
| CN025 | Manual | Isonic/barb |
| CN026 | Manual | Isonic/barb |
| CN027 | Manual | Tetra-nickel |
| CN028 | Manual | Isonic/barb . |
| CN029 | Manual | Pyr/barb |
| CN031 | Manual | Ion spec. elect. |
| CN032 | Manual | Tetra-Nickel |
| CN033 | Manual | Pyr/barb |
| CN035a | Autoanalyzer | Pyr/barb |
| CN035b | Autoanalyzer | Pyr/barb |
| CN036a | Autoanalyzer | Pyr/barb |
| CN036b | Autoanalyzer | Pyr/barb |

Isonic/barb:
Pyr/barb:
Tetra-nickel:
Ion spec elect:

Colourimetric determination using isonicotinic/barbituric acid Colourimetric determination using pyridine/barbituric acid Colourimetric determination of tetracyano-nickelate complex

Ion specific electrode

Paired t-tests were performed to compare the following methods:

Autoanalyzer vs Manual Methods
Ion Specific Electrode vs Other Methods
Tetracyano-nickelate vs Other Methods

Isonicotinic/barbituric acid vs Pyridine/barbituric acid

The tests showed no significant difference between any of the pairs indicating that there was no detectable difference in the performance of the various methods used in the study..

4.4 PERFORMANCE vs PRESENCE OF THIOCYANATE

Sample L5 contained 1 mg/L thiocyanate (SCN) combined with a 0.5 mg/L CN⁻ (as ferricyanide) in pure water. This was done to determine if any of the laboratories suffered from a positive interference as the result of the presence of thiocyanate.

If the thiocyanate had been read as cyanide, it would have resulted in a measured value of greater than the expected value of 0.553 mg/L. The data indicate that 4 of the participating laboratories (CN001, CN009, CN017 and CN019) exhibited behaviour consistent with a positive thiocyanate interference. This was judged by comparing the results for sample L5 against the 95% confidence interval for that sample calculated from the raw results with all outliers removed (see Appendix 7). These laboratories all reported using autoanalyzer methods.

4.5 PERFORMANCE WITH EFFLUENTS vs WATER MATRIX

The standard samples analyzed by the participating laboratories were provided in both effluent and pure water matrices. The water matrix samples (L1, L3, L5, L7, L8) were a matrix of Milli-Q water at pH 12. The effluent matrix samples (L2, L4, L6, L9) were a matrix of final gold mine effluent from the outfall of the tailings system 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 (CN001, CN005, CN007, CN011, CN029) removed were calculated to determine if there was a trend towards more variability in effluent samples. These calculations are summarized in the Table 4.11 below.

Table 4.11

WATER vs EFFLUENT MATRIX EFFECTS

| | | | RAW D | ATA | GRUBBS REMOVED | | | |
|------------------|----------|-------------|-------|----------------|-------------------|------|----------------|--|
| SAMPLE NUMBER | MATRIX | MEAN | SD | COEFF. VAR. | MEAN | SD | COEFF. VAR. | |
| L1 | Water | 0.34 | 0.07 | 21 | 0.32 | 0.03 | 11 | |
| L2 | Effluent | 1.22 | 0.36 | 29 | 1.24 | 0.15 | 12 | |
| L3 | Water | 3.22 | 0.80 | 25 | 3.28 | 0.45 | 14 | |
| L4 | Effluent | 0.38 | 0.67 | 174 | 0.26 | 0.05 | 18 | |
| L5 | Water | 0.59 | 0.19 | 31 | 0.57 | 0.10 | 17 | |
| L6 | Effluent | 0.52 | 0.19 | 36 | 0.49 | 0.07 | 14 | |
| L7 | Water | 0.11 | 0.03 | 24 | 0.11 | 0.01 | 13 | |
| L8 | Water | 1.12 | 0.18 | 16 | 1.08 | 0.11 | 10 | |
| L9 | Effluent | 3.41 | 0.90 | 27 | 3.40 | 0.45 | 13.2 | |

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 Grubbs outlying labs removed shows a substantial difference between effluent and water matrices. The coefficient of variation for effluent matrices was 66% while that for water was 24%. Once the Grubbs outlying laboratories were removed from the data set, however, the difference between the matrices disappeared. The coefficient of variation for effluent matrices became 14 while that for water became 13. The effect of removing the most imprecise laboratories from the data set indicates that there is no general matrix effect on low level cyanide analysis in this study. As is evident from an examination of the laboratory specific summaries given in Section 6.0, some labs did appear to have trouble determining cyanide accurately in the effluent matrix. This effect will be explored in more detail in the following phase of this study.

5.0 SUMMARY AND CONCLUSIONS

The key findings of this study are:

- 2.8% of results fell outside 3 standard deviations of the mean expected value and were flagged as Grubbs outliers. These results were contributed by 5 laboratories.
- 23% of results fell outside 1 standard deviation of the mean expected value. 61% of labs had at least 1 result flagged in this manner.
- 30% of labs submitted results which were identified as significantly different from the expected by the t-test.
- 75% of labs displayed good or satisfactory precision as judged by the regression correlation coefficient. 25% displayed poor precision.
- 72% of labs displayed no bias in the regression slope test. 85% displayed no bias in the Youden Rank Sum test.
- 14% of labs were judged to be biased high and 14% biased low by the regression slope test. 6% were biased high and 6% biased low by the Rank Sum test.
- 83% of labs displayed regression Y-intercepts which were judged to be good or satisfactory. 17% were judged to be poor, indicating problems with precision, method failure at high concentrations or inappropriate blank correction.
- 2 of 36 participating labs displayed serious method failure with these samples.
- There was no evidence of a difference between methods with respect to accuracy or precision.
- 4 of the 36 laboratories showed a possible positive interference from thiocyanate in sample L5. These laboratories all reported using autoanalyzer methods.
- There was no evidence of a general matrix effect although some labs did appear to have difficulty with the effluent matrix.

 the big message is calibration. High end failure shown by a slope problem

In summary, 25% of the participants in this study displayed poor precision as judged by the regression correlation coefficient test. Between 12% and 28% of the participants were judged to be biased, or inaccurate, by the Youden Rank Sum test and regression slope test, respectively. In view of the fact that the Rank Sum test does not detect bias in labs displaying imprecision, the 28% assessment is expected to more closely reflect the actual situation.

Precision generally depends on several factors including the method itself, general

laboratory practice and the skill of the analyst. As a results, it is sometimes difficult to improve the overall level of precision of any given method.

Problems in accuracy are usually the result of inaccurate standards and are often correctable by simply purchasing or preparing better standards. It is therefore expected that the majority of laboratories assessed as biased in this study should be able to cure the problem relatively easily. Laboratories with serious precision problems will have considerably more work to do to rectify the situation.

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.

RESULTS:

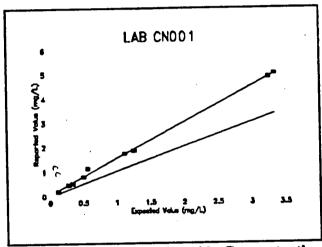
| Sample Number | 1.1 | 12 | 1.3 | 1.4 | 1.5 | 16、 | L7 | 1.8 | L9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN001 Value (mg/L) | 0.49 | 1.82 | 4.84 | 0.43 | 1.10 | 0.77 | 0.16 | 1.70 | 5.00 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were statistically different from the expected results with a probability of 98 percent (ie. 98 times out of 100 your laboratory would not produce the expected results).

The flagging procedure indicated that sample L8 was outside 3 standard deviations of the mean expected value. All samples were outside 1 standard deviation of the mean expected values.

The regression coefficient $(R^2=0.9976)$ indicated good precision and a satisfactory Y-intercept $(Y_{ini}=0.0536)$. The slope of the regression line (m=1.4779, 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. Line passing through the boxes is the best regression fit. The second line represents the expected values.)

The analytical method used worked equally well with samples in water and effluent matrices. The method may have been influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has good precision in low level cyanide analysis but appears to be biased high probably as a result of a calibration problem. This is indicated by the good regression coefficient combined with the major difference in regression slopes between your results and the expected values.

RESULTS:

| Sample Number | L1 | 1.2 | 1.3 | 1.4 | 1.5 | 1.6 | 1.7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN002 Value (mg/L) | 0.29 | 1.23 | 3.23 | 0.30 | 0.55 | 0.52 | 0.10 | 1.05 | 3.35 |

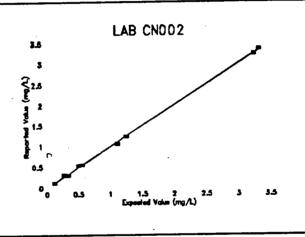
STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. No samples were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated good precision (R^2 =0.9994) and a good Y-intercept (Y_{int} =-0.0081). The slope of the regression line (m=1.000) indicated no bias.

The analytical method used worked equally values.)
well with samples in water and effluent
matrices. The method was not influenced by the presence of thiocyanate in sample L5.



Reported vs Expected Cyanide Concentration

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

INFERENCE:

The statistical analysis of your data indicates that your laboratory has both good precision and good accuracy in low level cyanide analysis.

RESULTS:

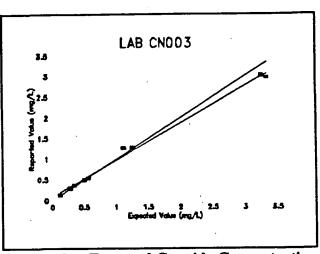
| Sample Number | Li | 1.2 | 1.3 | 1.4 | 1.5 | 16 | 1.7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN003 Value (mg/L) | 0.35 | 1.27 | 3.01 | 0.28 | 0.52 | 0.48 | 0.12 | 1.26 | 2.96 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. Sample L8 was outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated satisfactory precision (R²=0.9939) and a satisfactory Y-intercept (Y_{int}=0.0750). No bias was detected by either the slope of the regression line (m=0.8954) or the rank sum test.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has satisfactory precision in low level cyanide analysis. Sample L8 is the only result classified as an outlier. Although the slope of the regression line does not detect any bias, it does indicate that your laboratory may have a problem underestimating cyanide concentrations above 3 mg/L. In this study, the underestimation of the high concentrations causes the y intercept to be greater than zero.

RESULTS:

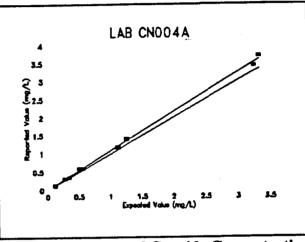
| Sample Number | Li | 1.2 | 1.3 | 1.4 | 1.5 | 16 | L7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN004A Value (mg/L) | 0.34 | 1.40 | 3.42 | 0.30 | 0.59 | 0.58 | 0.11 | 1.16 | 3.68 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were statistically different from the expected results with a probability of 95 percent (ie. 95 times out of 100 your laboratory would not produce the expected results).

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. No samples were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated good precision (R^2 =0.9985) and a good Y-intercept (Y_{int} =0.0032). The slope of the regression line (m=1.0796) indicated no bias.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has good precision in low level cyanide analysis as indicated by the regression coefficient. Although no bias was detected by either the regression slope or the rank sum test, the t-test results and a visual examination of the figure, suggest that a slight high bias exists in your results. This is most likely the result of a calibration standard problem.

RESULTS:

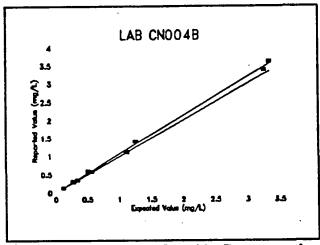
| Sample Number | Li | 1.2 | 1.3 | 1.4 | 1.5 | 16 | 1.7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN004B Value (mg/L) | 0.34 | 1.40 | 3.37 | 0.29 | 0.56 | 0.57 | 0.12 | 1.11 | 3.61 |

STATISTICAL SUMMARY:

Your laboratory's results were statistically different from the expected results with a probability of 95 percent (ie. 95 times out of 100 your laboratory would not produce the expected results).

No samples were outside 3 standard deviations of the mean expected values. No samples were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) showed a good linear regression coefficient (R^2 =0.9982), good $Y_{intercept}$ (Y_{int} =0.0013), and a good slope of the regression line (m=1.0610).



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has good precision in low level cyanide analysis but may have a minor calibration problem. This is evident by the difference in regression slopes between yourself and the expected values.

RESULTS:

| Sample Number | Li | 1.2 | 1.3 | LA | 1.5 | 1.6 | 1.7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN005 Value (mg/L) | 0.43 | 3.43 | 4.74 | 0.67 | 1.25 | 0.99 | 0.13 | 1.63 | 6.44 |

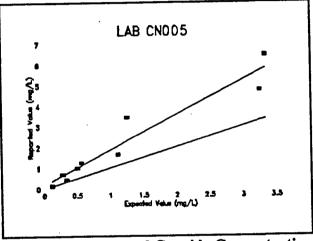
STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were statistically different from the expected results with a probability of 95 percent (ie. 95 times out of 100 your laboratory would not produce the expected results).

The flagging procedure indicated that samples L2, L5 and L8 were outside 3 standard deviations of the mean expected value. All samples except L7 were outside 1 standard deviation of the mean expected values.

The regression coefficient (R²=0.9241) indicated poor precision and a poor Y-intercept (Y_{int}=0.1837). The slope of the regression line (m=1.687, see figure) indicates a high bias. The rank sum test also

indicates a high bias. The rank sum test also indicates a high bias.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method does not appear to have been influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has poor precision in low level cyanide analysis and appears to be biased high. This is indicated by the low regression coefficient combined with the major difference in regression slopes between your results and the expected values.

RESULTS:

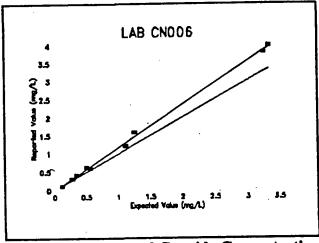
| Sample Number | Li | 12 | 1.3 | 1.4 | LS | 16 、 | 1.7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN006 Value (mg/L) | 0.40 | 1.58 | 3.80 | 0.30 | 0.58 | 0.61 | 0.10 | 1.20 | 3.98 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were statistically different from the expected results with a probability of 95 percent (ie. 95 times out of 100 your laboratory would not produce the expected results).

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. Sample L2 was outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated pagood precision (R^2 =0.9981) and a satisfactory fit Y-intercept (Y_{int} =-0.0185). The slope of the regression line (m=1.1890) indicated a high bias. No bias was detected by the rank sum test.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has good precision in low level cyanide analysis as indicated by the regression coefficient. A high bias was detected by the regression slope. This is confirmed by a visual examination of the figure. This is most likely the result of a calibration standard problem.

RESULTS:

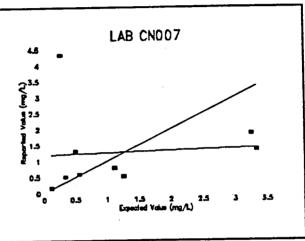
| Sample Number | Li | 12 | 1.3 | I.A | 1.5 | 1.6 | 1.7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN007 Value (mg/L) | 0.50 | 0.51 | 1.83 | 4,31 | 0.58 | 1.30 | 0.14 | 0.77 | 1.33 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure indicated that samples L4 and L6 were outside 3 standard deviations of the mean expected value. All samples except L5 were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated poor precision and very little relationship between the measured results and the expected values (R²=0.0037). A poor Y-intercept (Y_{int}=1.1780) is also indicated. The slope of the regression line (m=0.0621) indicated a low bias. No bias was detected by the rank sum test.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method did not appear to have been influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has a serious problem with the analysis of low level cyanide. The regression results and the attached figure indicate a high degree of imprecision. The failure of the paired t-test to establish a significant difference between your results and the expected values may be attributed to the recognized weakness of this test in recognizing differences in data sets with large standard deviations. This should not be taken to indicate that the reported results are correct. The regression slope suggests a low bias in your results. It is more likely, however, that the observed slope is the result of imprecision rather than a consistent low bias.

RESULTS:

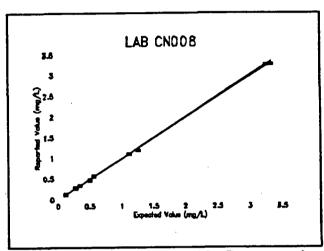
| Sampl: Number | Li | 1.2 | 13 | 1.4 | LS | 1.6 | 1.7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN008 Value (mg/L) | 0.33 | 1.18 | 3.24 | 0.27 | 0.55 | 0.45 | 0.11 | 1.09 | 3.26 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. No samples were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated good precision (R^2 =0.9996) and a good Y-intercept (Y_{int} =-0.0097). The slope of the regression line (m=0.9984) indicated no bias.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has both good precision and good accuracy in low level cyanide analysis.

RESULTS:

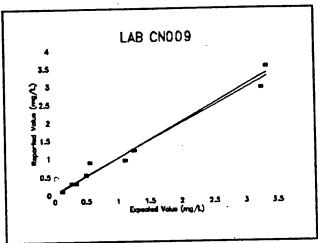
| Sample Number | Li | 1.2 | 1.3 | 1.4 | 1.5 | 1.6 | 1.7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN009 Value (mg/L) | 0.29 | 1.19 | 2.92 | 0.29 | 0.86 | 0.52 | 0.09 | 0.92 | 3.51 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. Samples L5, L7 and L8 were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated poor precision (R^2 =0.9781) and a satisfactory Y-intercept (Y_{int} =0.0324). The slope of the regression line (m=0.9630) indicated no bias.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method may have been influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has no detectable biases but exhibited poor precision in this study. This is indicated by the low regression coefficient and the three values falling outside the 1 standard deviation limit. This is confirmed by a visual inspection of the above figure.

RESULTS:

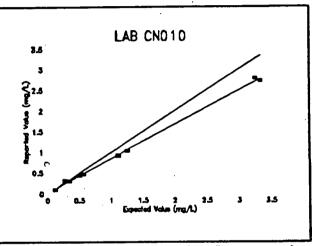
| Sample Number | Li | 12 | L3 | 1.4 | 1.5 | 16` | 1.7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN010 Value (mg/L) | 0.29 | 1.03 | 2.77 | 0.30 | 0.46 | 0.43 | 0.09 | 0.91 | 2.71 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. Samples L7 and L8 were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated good precision (R^2 =0.9984) and a satisfactory Y-intercept (Y_{int} =0.0189). The slope of the regression line (m=0.8248) indicates a low bias. A low bias was also detected by the rank sum test.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has good precision in low level cyanide analysis as indicated by the regression coefficient. A low bias was, however, detected by both the regression slope and the rank sum test. This is most likely the result of a calibration standard problem.

RESULTS:

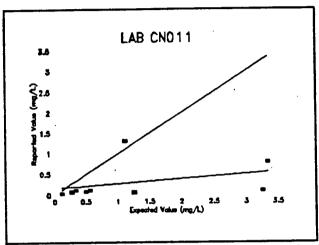
| Sample Number | L1 | 1.2 | 1.3 | 1.4 | 1.5 | 16 | L7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN011 Value (mg/L) | 0.10 | 0.05 | 0.09 | 0.06 | 0.10 | 0.08 | 0.02 | 1.30 | 0.77 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure indicated that samples L1, L2, L3 and L7 were outside 3 standard deviations of the mean expected value. All samples were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicates poor precision and very little relationship between the measured results and the expected values (R²=0.1073). A poor Y-intercept (Y_{int}=0.1471) is also indicated. The slope of the regression line (m=0.1170) indicated severe low bias. Low bias was also detected by the rank sum test.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method did not appear to have been influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has a serious problem with the analysis of low level cyanide. The regression slope and rank sum tests, as well as a visual inspection of the above figure, suggest a low bias in your results. This may be the results of a calibration standard problem, however, the high degree of imprecision evident in the results confounds diagnosis of the problem. The failure of the paired t-test to establish a significant difference between your results and the expected values may be attributed to the recognized weakness of this test in recognizing differences in data sets with large standard deviations. This should not be taken to indicate that the reported results are correct.

RESULTS:

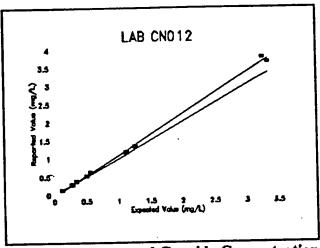
| Sample Number | Li | 1.2 | 13 | 1.4 | 1.5 | 1.6 ` | 1.7. | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN012 Value (mg/L) | 0.36 | 1.32 | 3.76 | 0.27 | 0.61 | 0.51 | 0.12 | 1.16 | 3.63 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were statistically different from the expected results with a probability of 90 percent (ie. 90 times out of 100 your laboratory would not produce the expected results).

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. No samples were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated good precision (R^2 =0.9979) and a satisfactory Y-intercept (Y_{ini} =-0.0367). The slope of the regression line (m=1.1288) indicated no bias.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has good precision in low level cyanide analysis as indicated by the regression coefficient. Although no bias was detected by either the regression slope or the rank sum test, the t-test results and a visual examination of the figure, suggest that a slight high bias exists in your results. This is most likely the result of a calibration standard problem.

RESULTS:

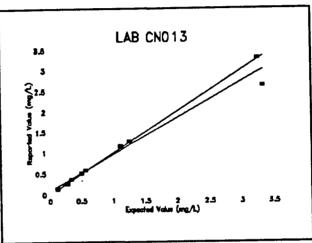
| Sample Number | Li | 12 | 1.3 | 1.4 | 1.5 | 1.6 | 1.7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN013 Value (mg/L) | 0.35 | 1.26 | 3.29 | 0.25 | 0.57 | 0.50 | 0.13 | 1.14 | 2.62 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. Sample L7 was outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated poor precision (R^2 =0.9702) and a satisfactory Y-intercept (Y_{int} =0.0760). No bias was detected by either the slope of the regression line (m=0.8815) or the rank sum test.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

Statistical analysis of your data indicates that your laboratory may have a precision problem in low level cyanide analysis. This imprecision is evident from the low regression correlation coefficient and the deviation in the regression slope from the expected. The results do not indicate any systematic bias in your results.

RESULTS:

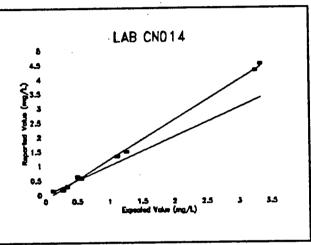
| Sample Number | Li | 1.2 | 1.3 | 1.4 | LS | 16、 | L7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN014 Value (mg/L) | 0.27 | 1.46 | 4.27 | 0.15 | 0.57 | 0.60 | 0.12 | 1.31 | 4.49 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value, however, samples L1, L2, L3, L4, L8 and L9 were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated good precision (R^2 =0.9981) but a poor Y-intercept (Y_{int} =-0.1596). The slope of the regression line (m=1.3730) indicated a high bias. No bias was detected by the rank sum test.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has good precision in low level cyanide analysis as indicated by the regression coefficient. A high bias was detected by the regression slope. This is confirmed by a visual examination of the figure. This is most likely the result of a calibration standard problem. The crossing of the regression line over the expected line and the resulting large negative Y-intercept evident in the above figure may indicate an inappropriate blank correction.

RESULTS:

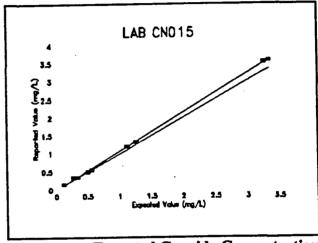
| Sample Number | Li | 1.2 | 1.3 | 1.4 | 1.5 | 16 ` | 1.7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN015 Value (mg/L) | 0.33 | 1.31 | 3.52 | 0.33 | 0.54 | 0.49 | 0.14 | 1.19 | 3.56 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were statistically different from the expected results with a probability of 90 percent (ie. 90 times out of 100 your laboratory would not produce the expected results).

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. Sample L7 was outside 1 standard deviation of the mean expected value.

Regression analysis (see figure) indicated good precision (R^2 =0.9994) and a satisfactory Y-intercept (Y_{int} =-0.0147). The slope of the regression line (m=1.0780) indicated no bias.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has good precision in low level cyanide analysis as indicated by the regression coefficient. Although no bias was detected by either the regression slope or the rank sum test, the t-test results and a visual examination of the figure, suggest that a slight high bias exists in your results. This is most likely the result of a calibration standard problem.

RESULTS:

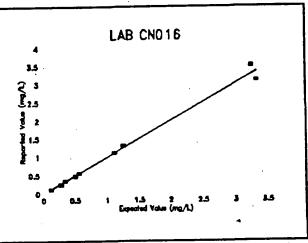
| Sample Number | u | 12 | 1.3 | 1.4 | 1.5 | 1.6 | 1.7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN016 Value (mg/L) | 0.33 | 1.30 | 3.50 | 0.23 | 0.54 | 0.47 | 0.10 | 1.10 | 3.10 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. No samples were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated satisfactory precision (R^2 =0.9905) and a satisfactory Y-intercept (Y_{int} =-0.0117). The slope of the regression line (m=1.0080) indicated no bias.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has good accuracy in low level cyanide analysis. The results also indicate that your laboratory may have a problem with precision in samples containing the higher levels of cyanide, such as in samples L3 and L9 in this study. This can be seen in the above figure and is reflected in the correlation coefficient and Y-intercept.

RESULTS:

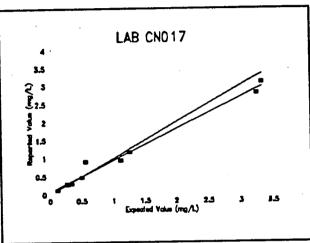
| Sample Number | L1 | 1.2 | 1.3 | 1.4 | 1.5 | 1.6 | 1.7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN017 Value (mg/L) | 0.28 | 1.15 | 2.79 | 0.27 | 0.89 | 0.46 | 0.10 | 0.93 | 3.09 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. Samples L1, L5 and L8 were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated poor precision (R^2 =0.9829) and a satisfactory Y-intercept (Y_{int} =0.0696). No bias was detected by either the slope of the regression line (m=0.8726) or the rank sum test.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method may have been influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory may have a precision problem in low level cyanide analysis. This is indicated by the three samples falling outside 1 standard deviation, the low correlation coefficient and a visual inspection of the above graph. Although no biases were detected by either the regression slope of the rank sum tests, the slope of the regression line indicates a tendency to underestimate cyanide concentrations.

RESULTS:

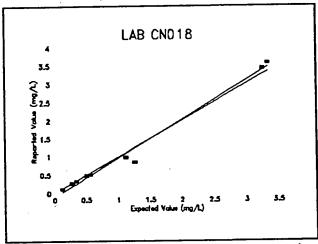
| Sample Number | L1 | 1.2 | 1.3 | L4 | LS | 1.6 | L7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN018 Value (mg/L) | 0.32 | 0.84 | 3.41 | 0.26 | 0.50 | 0.47 | 0.10 | 0.97 | 3.56 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. Sample L2 was outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated poor precision (R^2 =0.9862) and a poor Y-intercept (Y_{int} =-0.1165). No bias was detected by either the slope of the regression line (m=1.0720) or the rank sum test.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that the accuracy of your laboratory is good but there may be a precision problem in the analysis. This is indicated by the sample result falling outside 1 standard deviation and by the low regression correlation coefficient.

RESULTS:

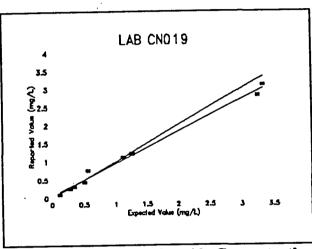
| Sample Number | Li | 1.2 | L3 | L4 | L5 | L6 | L7 | L8 | L9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN019 Value (mg/L) | 0.29 | 1.20 | 2.80 | 0.24 | 0.74 | 0.42 | 0.09 | 1.10 | 3.10 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. Samples L5 and L7 were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated satisfactory precision (R²=0.9914) and a satisfactory Y-intercept (Y_{int}=0.0551). No bias was detected by either the slope of the regression line (m=0.8870) or the rank sum test.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method may have been influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has satisfactory precision in low level cyanide analysis as indicated by the regression coefficient. The precision indicators would likely have been better but for a possible overestimation of sample L5; the sample spiked with both cyanide and thiocyanate. The L5 result was flagged as a outlier and may indicate a positive interference from thiocyanate. The slope of the regression line and a visual inspection of the figure may indicate a tendency to underestimate cyanide concentrations.

RESULTS:

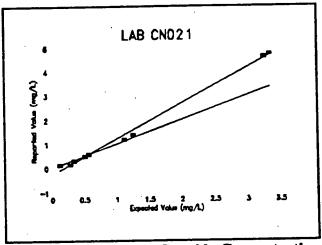
| Sample Number | Li | 12 | 1.3 | 1.4 | 1.5 | 1.6 | 1.7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN021 Value (mg/L) | 0.28 | 1.35 | 4.60 | 0.13 | 0.56 | 0.48 | 0.11 | 1.17 | 4.72 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value, however, samples L1, L3, L4 and L9 were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated satisfactory precision (R^2 =0.9945) but a poor Y-intercept (Y_{int} =-0.2644). The slope of the regression line (m=1.4760) indicated a high bias. No bias was detected by the rank sum test.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has good precision in low level cyanide analysis as indicated by the regression coefficient. A high bias was detected by the regression slope. This is confirmed by a visual examination of the figure and is most likely the result of a calibration standard problem. The crossing of the regression line over the expected line and the resulting large negative Y-intercept evident in the above figure may indicate an inappropriate blank correction.

RESULTS:

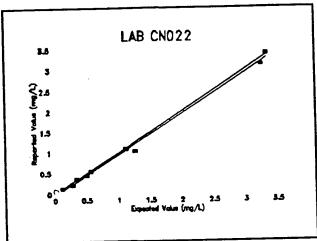
| Sample Number | Li | 1.2 | 1.3 | 1.4 | 1.5 | 1.6 | 1.7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN022 Value (mg/L) | 0.34 | 1.03 | 3.12 | 0.20 | 0.53 | 0.44 | 0.11 | 1.08 | 3,37 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. No samples were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated good precision (R^2 =0.9959) and a satisfactory Y-intercept (Y_{int} =-0.0424). The slope of the regression line (m=0.9923) indicated no bias.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has good accuracy and good precision in low level cyanide analysis.

RESULTS:

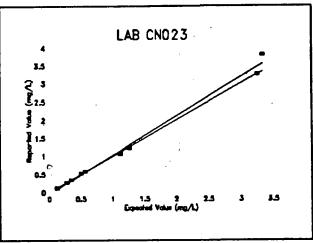
| Sample Number | Li | 1.2 | 1.3 | 1.4 | LS | 1.6 | L7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN023 Value (mg/L) | 0.34 | 1.21 | 3.25 | 0.26 | 0.56 | 0.51 | 0.11 | 1.05 | 3.80 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. No samples were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated satisfactory precision (R^2 =0.9912) and a satisfactory Y-intercept (Y_{ini} =-0.0503). The slope of the regression line (m=1.0800) indicated no bias.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory displays good accuracy and satisfactory precision in low level cyanide analysis.

RESULTS:

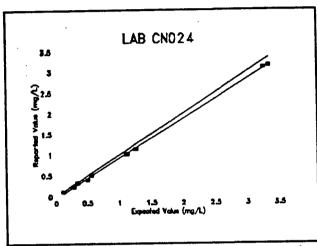
| Sample Number | u | 1.2 | 1.3 | Ĭ.A | 1.5 | 1.6 | L7 | L8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN024 Value (mg/L) | 0.32 | 1.11 | 3.10 | 0.21 | 0.50 | 0.38 | 0.10 | 1.00 | 3.14 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. No samples were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated good precision (R^2 =0.9992) and a satisfactory Y-intercept (Y_{int} =-0.0402). The slope of the regression line (m=0.9563) indicated no bias.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has good accuracy and good precision in low level cyanide analysis. Although no bias was detected by either the regression slope or the rank sum test, a visual inspection of the above graph may indicate a slight tendency to underestimate cyanide concentrations.

RESULTS:

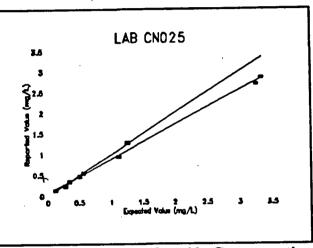
| Sample Number | Li | 1.2 | 1.3 | I.A | 1.5 | 1.6 | L7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN025 Value (mg/L) | 0.33 | 1.27 | 2.68 | 0.23 | 0.53 | 0.46 | 0.12 | 0.93 | 2.84 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. Samples L3 and L8 were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated satisfactory precision (R^2 =0.9905) and a satisfactory Y-intercept (Y_{int} =0.0585). The slope of the regression line (m=0.8285) indicates a low bias. No bias was detected by the rank sum test.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has satisfactory precision in low level cyanide analysis as indicated by the regression coefficient. A low bias was detected by the regression slope. This may be the result of a calibration standard problem or may reflect an underestimation of the higher cyanide concentrations.

RESULTS:

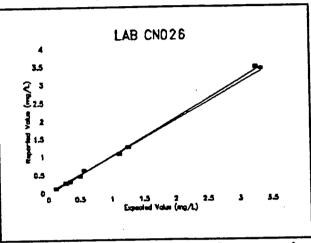
| Sample Number | Li | 1.2 | 1.3 | 1.4 | 1.5 | 1.6 | L7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN026 Value (mg/L) | 0.29 | 1.24 | 3.44 | 0.26 | 0.61 | 0.45 | 0.09 | 1.06 | 3.40 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. Sample L7 was outside 1 standard deviation of the mean expected value.

Regression analysis (see figure) indicated good precision (R^2 =0.9985) and a satisfactory Y-intercept (Y_{int} =-0.0431). The slope of the regression line (m=1.0490) indicated no bias.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has both good precision and good accuracy in low level cyanide analysis.

RESULTS:

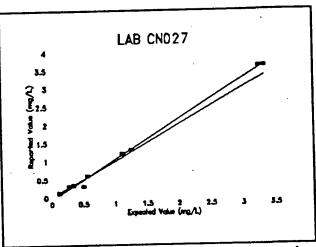
| Course Number | 1.1 | 12 | ıз | 14 | 1.5 | 1.6 | 1.7 | 1.8 | 1.9 |
|--------------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Sample Number Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN027 Value (mg/L) | 0.32 | 1.30 | 3.60 | 0.29 | 0.58 | 0.29 | 0.11 | 1.18 | 3.59 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. Sample L6 was outside 1 standard deviation of the mean expected value.

Regression analysis (see figure) indicated good precision (R^2 =0.9968) and a satisfactory Y-intercept (Y_{int} =-0.0688). The slope of the regression line (m=1.1110) indicated no bias.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory displays good precision in low level cyanide analysis. Although no bias was detected by either the regression slope or the rank sum test, a visual inspection of the above graph indicates a slight tendency to overestimate cyanide concentrations.

RESULTS:

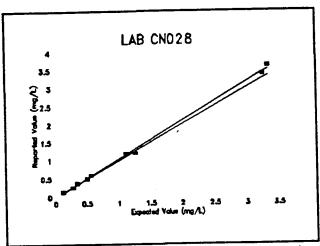
| Sample Number | Li | 1.2 | 1.3 | 1.4 | 1.5 | 1.6 | 1.7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN028 Value (mg/L) | 0.36 | 1.19 | 3.37 | 0.24 | 0.58 | 0.48 | 0.12 | 1.17 | 3.61 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. No samples were outside 1 standard deviation of the mean expected value.

Regression analysis (see figure) indicated good precision (R^2 =0.9980) and a satisfactory Y-intercept (Y_{int} =-0.0304). The slope of the regression line (m=1.0660) indicated no bias.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory displays both good precision and good accuracy in low level cyanide analysis.

RESULTS:

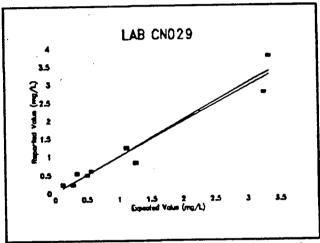
| Sample Number | Li | 12 | 1.3 | 14 | 1.5 | 1.6 | 1.7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN029 Value (mg/L) | 0.52 | 0.81 | 2.74 | 0.21 | 0.58 | 0.48 | 0.21 | 1.21 | 3.74 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected one sample (L7) outside 3 standard deviations of the mean expected value. Samples L1, L2 and L7 were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated poor precision (R^2 =0.9463) and a satisfactory Y-intercept (Y_{int} =0.0207). The slope of the regression line (m=0.9651) indicated no bias.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has no detectable biases but exhibited poor precision in this study. This is indicated by the low regression coefficient and the three values falling outside the 1 standard deviation limit. This is confirmed by a visual inspection of the above figure.

REPORT FOR LABORATORY CN031

RESULTS:

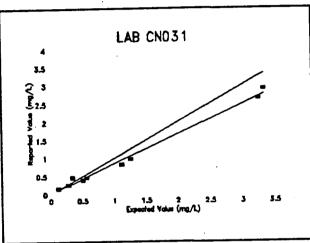
| Sample Number | Li | 1.2 | 1.3 | 1.4 | 1.5 | 1.6 | L7 | L8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN031 Value (mg/L) | 0.45 | 0.96 | 2.63 | 0.25 | 0.44 | 0.38 | 0.15 | 0.81 | 2.90 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. Samples L1, L2, L3, L7 and L8 were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated satisfactory precision (R^2 =0.9911) and a satisfactory Y-intercept (Y_{int} =0.0154). The slope of the regression line (m=0.8259) indicates a low bias. No bias was detected by the rank sum test.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has satisfactory precision in low level cyanide analysis as indicated by the regression coefficient. A low bias was, however, detected by the regression slope. This is most likely the result of a calibration standard problem.

REPORT FOR LABORATORY CN032

RESULTS:

| Sample Number | L1 | 12 | 13 | 1.4 | 1.5 | 1.6 | 1.7 | 1.8 | L9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN032 Value (mg/L) | 0.27 | 1.10 | 2.70 | 0.30 | 0.41 | 0.51 | 0.09 | 0.96 | 3.00 |

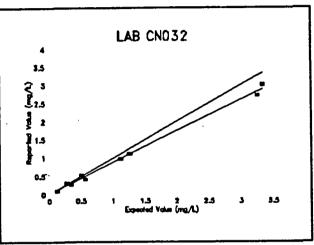
STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. Samples L1, L5 and L7 were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated good precision (R^2 =0.9956) and a satisfactory Y-intercept (Y_{ini} =0.0129). No bias was detected by either the slope of the regression line (m=0.8626) or the rank sum test.

The analytical method used worked equally values.)
well with samples in water and effluent
matrices. The method was not influenced by the presence of thiocyanate in sample L5.



Reported vs Expected Cyanide Concentration

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

INFERENCE:

The statistical analysis of your data indicates that your laboratory has good precision in low level cyanide analysis as indicated by the regression coefficient. Although no bias was detected by either the regression slope or the rank sum test, a visual inspection of the above figure indicates a tendency to underestimate cyanide concentrations. This is most likely the result of a calibration standard problem.

REPORT FOR LABORATORY CN033

RESULTS:

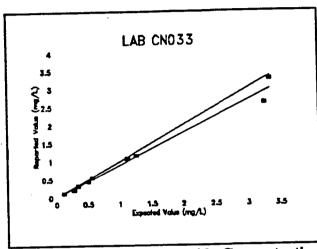
| Sample Number | 1.1 | 1.2 | 1.3 | 1.4 | 1.5 | 1.6 | L7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN033 Value (mg/L) | 0.31 | 1.14 | 2.59 | 0.20 | 0.53 | 0.43 | 0.10 | 1.05 | 3.25 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were not statistically different from the expected results.

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. Sample L3 was outside 1 standard deviation of the mean expected value.

Regression analysis (see figure) indicated poor precision (R²=0.9822) but a good Y-intercept (Y_{int}=0.0093). The slope of the regression line (m=0.8894) indicated no bias.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory displayed poor precision in this study. This is indicated by the low regression coefficient. A visual inspection of the above figure, however, suggests that this is largely the result of the one outlying value detected (sample L3).

REPORT FOR LABORATORY CN035A

RESULTS:

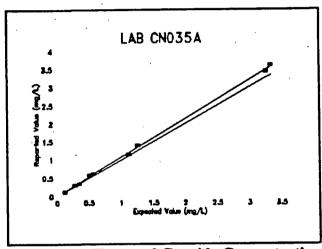
| Sample Number | u | 1.2 | 1.3 | 1.4 | 1.5 | 1.6 | L7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN035A Value (mg/L) | 0.34 | 1.38 | 3.43 | 0.30 | 0.60 | 0.56 | 0.11 | 1.14 | 3.60 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were statistically different from the expected results with a probability of 95 percent (ie. 95 times out of 100 your laboratory would not produce the expected results).

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. No samples were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated good precision (R^2 =0.9993) and a good Y-intercept (Y_{int} =0.0055). The slope of the regression line (m=1.0670) indicated no bias.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has good precision in low level cyanide analysis as indicated by the regression coefficient. Although no bias was detected by either the regression slope or the rank sum test, the t-test results and a visual examination of the figure, suggest that a slight high bias exists in your results. This is most likely the result of a calibration standard problem.

REPORT FOR LABORATORY CN035B

RESULTS:

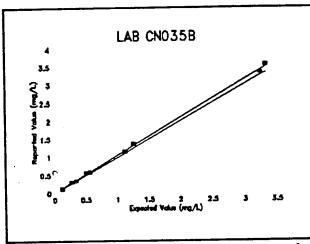
| Sample Number | Li | 1.2 | 1.3 | 1A | 1.5 | 1.6 . | 1.7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN035B Value (mg/L) | 0.33 | 1.36 | 3.33 | 0.30 | 0.57 | 0.57 | 0.11 | 1.14 | 3.55 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were statistically different from the expected results with a probability of 95 percent (ie. 95 times out of 100 your laboratory would not produce the expected results).

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. No samples were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated good precision (R^2 =0.9989) and a satisfactory Y-intercept (Y_{int} =0.0113). The slope of the regression line (m=1.0440) indicated no bias.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has good precision in low level cyanide analysis as indicated by the regression coefficient. Although no bias was detected by either the regression slope or the rank sum test, the t-test results and a visual examination of the figure, suggest that a very slight high bias exists in your results. This is most likely the result of a calibration standard problem.

REPORT FOR LABORATORY CN036A

RESULTS:

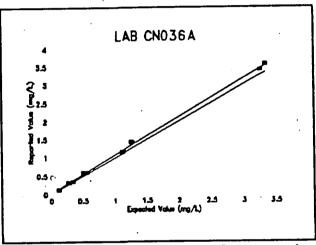
| Sample Number | u | 1.2 | 1.3 | 1.4 | 1.5 | 1.6 | 1.7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN036A Value (mg/L) | 0.33 | 1.41 | 3.39 | 0.31 | 0.58 | 0.58 | 0.11 | 1.14 | 3.55 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were statistically different from the expected results with a probability of 98 percent (ie. 98 times out of 100 your laboratory would not produce the expected results).

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. No samples were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated good precision (R^2 =0.9990) and a satisfactory Y-intercept (Y_{ini} =0.0155). The slope of the regression line (m=1.0530) indicated no bias.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has good precision in low level cyanide analysis as indicated by the regression coefficient. Although no bias was detected by either the regression slope or the rank sum test, the t-test results and a visual examination of the figure, suggest that a very slight high bias exists in your results. This is most likely the result of a calibration standard problem.

REPORT FOR LABORATORY CN036B

RESULTS:

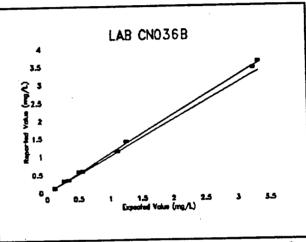
| Sample Number | Li | 1.2 | 1.3 | 1.4 | 1.5 | 1.6 | 1.7 | 1.8 | 1.9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Expected Value (mg/L) | 0.3283 | 1.2485 | 3.2488 | 0.2676 | 0.5530 | 0.4948 | 0.1111 | 1.1094 | 3.3314 |
| CN036B Value (mg/L) | 0.33 | 1.38 | 3.42 | 0.32 | 0.58 | 0.56 | 0.11 | 1.12 | 3.60 |

STATISTICAL SUMMARY:

The paired t-test showed that your laboratory's results were statistically different from the expected results with a probability of 95 percent (ie. 95 times out of 100 your laboratory would not produce the expected results).

The flagging procedure detected no samples outside 3 standard deviations of the mean expected value. No samples were outside 1 standard deviation of the mean expected values.

Regression analysis (see figure) indicated good precision (R^2 =0.9991) and a good Y-intercept (Y_{int} =0.0031). The slope of the regression line (m=1.0650) indicated no bias.



Reported vs Expected Cyanide Concentration

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

The analytical method used worked equally well with samples in water and effluent matrices. The method was not influenced by the presence of thiocyanate in sample L5.

INFERENCE:

The statistical analysis of your data indicates that your laboratory has good precision in low level cyanide analysis as indicated by the regression coefficient. Although no bias was detected by either the regression slope or the rank sum test, the t-test results and a visual examination of the figure, suggest that a very slight high bias exists in your results. This is most likely the result of a calibration standard problem.

7.0 REFERENCES

Chapman, D.G. and R.A. Schaufele, 1970 <u>Elementary Probability Models and Statistical Inference</u>. 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
Initial Correspondence and Results Reporting Form

Date

Participant Address

Dear:

The Wastewater Technology Centre invites you to participate in an interlaboratory comparison study for total cyanide scheduled to begin in November 1991. The samples will be prepared from spiked reagent water and industrial effluents from the gold mining and iron and steel sectors.

We anticipate that the program will be operated in two phases, the first; a study of cyanide levels in the 0 to 100 ppm range, and the second; a study involving low levels in the 0 to 1 ppm range. Each phase will be comprised of 10 to 15 samples. We expect that the first phase samples will be distributed in November 1991, while the second phase will likely take place in January 1992.

The aim of the study is to assist laboratories in assessing their analytical performance on real industrial effluents. As such, all analyses should be carried out according to the normal routine in your laboratory. We will, however, request details of the method of analysis used. The results will be evaluated both statistically and graphically in a manner that will be informative to the analyst.

Should you wish to participate in this program, please return the attached form to Mr. Peter Fowlie by telefax at (416) 336 4765 before October 20, 1992.

Thank you for your consideration and we look forward to your participation in this program.

Yours truly, WASTEWATER TECHNOLOGY CENTRE,

Peter Fowlie, Laboratory Manager

Wastewater Technology Centre operated by RockCliffe Research Management Inc.

Centre Technique des Eaux Usées dirigé par Gestion de Recherche RockCliffe Inc.

867, chemin Lakeshore Road P.O. Box / C.P. 5068, Burlington Ontario, Canada, L7R 4L7 (416) 336-4855 Fax/Fac (416) 336-4765



November 24, 1991

LAB CODE: CNOO1

Dear

Enclosed please find samples for determination of Total Cyanide as part of an interlaboratory comparison study carried out by the Wastewater Technology Centre (WTC).

The samples are based on industrial effluent or laboratory water and contain cyanide in concentrations ranging from 0 to 3 ppm. Each bottle is labelled with a sample number ranging from 1 to 9. Please refer to this sample number when recording your results.

On each bottle label you will also find a bottle number which may range from 1 to 60. This indicates the order in which the bottles were filled. You do not need to refer to this number when recording your results.

Your results should be recorded on the attached sheets. Please include a brief description of the methods used including the date of analysis.

Your laboratory has been assigned a unique code number to ensure the confidentiality of your results. This code will be used in all future correspondence with your laboratory and in the subsequent reports.

Your results should be faxed or mailed to the address indicated on the results sheets by Tuesday, December 31, 1991. A summary of the results from all participating labs, identified only by their code numbers, will be mailed to you shortly afterwards. At this time you will have an opportunity to check any data entry errors that may have occurred at our end. We regret that we will not be able to change the results submitted to us from your laboratory at this time. A final report of the entire interlaboratory comparison will be mailed to you on completion of the study.

Should you require any assistance please contact Dr. Peter Child at (416)336-6428 or Mr. Jim Fraser at (416)336-

Yours sincerely,

Peter Child, Ph.D., C.Chem.



RESULTS REPORT FORM

LAB CODE:CNOO1

TOTAL CYANIDE:

Results:

| Units | | Sample N | lumber | | | | | | |
|-------|----|----------|--------|-----|-----|-----|----|-----|----|
| | L1 | 1.2 | L3 | 1.4 | 1.5 | 1.6 | L7 | 1.8 | L9 |
| mg/L | | | | | | | | | |

Date Analysis Completed:

Methods:

Please provide a short description of the methods used.

Please return this form before <u>Tuesday, December 31, 1991</u> to Dr. Peter Child by Fax at (416) 336-4765 or by mail to: Wastewater Technology Centre, 867 Lakeshore Road, Burlington, Ontario, L7R 4A6

APPENDIX 2

Analysis of Cyanide in Test Samples Collected During the Bottling Run

WTC3 LOW LEVEL CYANIDE STUDY ANALYSIS OF CYANIDE IN TEST SAMPLES COLLECTED DURING THE BOTTLING RUN

| | | | | | | MEAN | STANDARD | IBOTTL | E /-MEAN | -1SD | IBOTTL | e#-MEAN | -2SD |
|------------------|------------------------|----------|--------|-----------|--------|---------|-----------|---------|----------|---------|---------|---------|---------|
| SAMPLE NUMBER | TARGET CONC. (mg/L) | MATRIX | Start | TTLE NUMB | End | M.C.A.V | DEVIATION | Start | Middle | End | Start | Middle | End |
| L3 | | Water | 3.3550 | 3.0150 | 3.0700 | 3.1487 | 0.1490 | 0.0593 | -0.0173 | -0.0723 | -0.0897 | -0.1664 | -0.2214 |
| LO. | | Effluent | 3.3050 | 2.9700 | 3.3800 | 3.2183 | 0.1782 | -0.0916 | 0.0701 | -0.0166 | -0.2698 | -0.1082 | -0.1948 |
| | | Water | 1.0950 | 1.0750 | 1.0400 | 1.0700 | 0.0227 | 0.0023 | -0.0177 | 0.0073 | -0.0205 | -0.0405 | -0.0155 |
| L8 (| | Effluent | 1.1800 | 1.0450 | 1.3100 | 1.1783 | 0.1082 | -0.1065 | 0.0251 | 0.0235 | -0.2147 | -0.0831 | -0.084 |
| L2 L5 | 0.5 | Water | 0.4900 | 0.5815 | 0.5260 | 0.5258 | 0.0292 | 0.0068 | 0.0065 | -0.0290 | -0.0225 | -0.0227 | -0.058. |
| | 0.5 | Effluent | 0.4010 | 0.4340 | o5010 | 0.4453 | 0.0416 | 0.0027 | -0.0303 | 0.0141 | -0.0389 | -0.0719 | -0.027 |
| . 1.6 | 0.2 | Water | 0.2995 | 0.3330 | 0.3130 | 0.3152 | 0.0138 | 0.0010 | 0.0041 | -0.0116 | -0.0119 | -0.0097 | -0.025 |
| 4. | | Effluent | 0.1960 | | 0.2400 | 0.2170 | 0.0180 | 0.0030 | -0.0160 | 0.0050 | -0.0150 | -0.0340 | -0.013 |
| L4 L7 | 0.2 | Water | 0.1165 | 1 | 0.1220 | 0.1247 | 0.0080 | 0.0002 | 0.0029 | -0.0053 | -0.0078 | -0.0051 | -0.013 |

APPENDIX 3
Analysis of Bottled Standards for Cyanide over the Six Week Period of the Study

WTC3 LOW LEVEL CYANIDE STUDY ANALYSIS OF BOTTLED STANDARDS FOR CYANIDE OVER THE SIX WEEK PERIOD OF THE STUDY

| | | MATRIX | | TIME SERIES | ANALYSIS OF | [CN] | | 1 34 2 34 | | MEAN | STANDARD |
|------------------|--------------|-------------------|------------------|------------------|------------------|--------------------|------------------|------------------|------------------|--------|------------------|
| SAMPLE NUMBER | CONC. (mg/L) | | Week 0 | Week 1 | Wook 2 | Week 3 | Week 4 | Week 5 | Week 6 | | DEVIATION |
| | | | | 3.1900 | 2.8900 | 2,9300 | 3.7500 | 3.0800 | 3.4700 | 3.2183 | 0.2821 |
| L9 | 3.1 | Effluent Water | 3.2180 3.1470 | 3.0720 | 3.1050 | 2.7100 | 3.4000 | 3.1800 | 3.1300 | 3.1063 | 0.1898 0.0543 |
| L3 L2 | 1.1 | Effluent | 1.1780 | 1.0950 | 1.0300 | 1.0650 | 1.1900 | 1.0800 1.0250 | 1.1200 | 1.1083 | 0.0549 |
| LB | 1 | Water | 1.0700 | 1.0370 0.5580 | 0.9650 0.5610 | 0.9850 0.5290 | 1.1600 0.5830 | 0.5660 | 0.4345 | 0.5368 | 0.0458 |
| L5 | 0.5 | Water Effluent | 0.5260 0.4450 | 0.4270 | 0.4235 | 0.4080 | 0.4480 | 0.4820 | 0.3590 | 0.4246 | 0.0315 |
| 16 | 0.4 | Water | 0.3150 | 0.3430 | 0.3385 | 0.3160 | 0.3740 | 0.3240 0.2115 | 0.3335 0.2010 | 0.3349 | 0.0166 |
| 14 | 0.2 | Effluent | 0.2170 | 0.2360 | 0.2350 0.1115 | 0.1840 0.1200 | 0.2900 | 0.2115 | 0.1005 | 0.1106 | 0.0103 |
| LT | 0.1 | Water | 0.1250 | 0.1080 | 0.1118 | 5.7200 | 3.000 | | | | |

| SAMPLE | TARGET | MATRIX | F | TIME SERIES | ANALYSIS O | PICKI. (IICK) | | | 101.04 |
|----------|--------------|----------|---------|-------------|------------|---------------|---|---------|--------|
| NUMBER | CONC. (mg/L) | | Week 0 | Week 1 | Week 2 | Week 3 | Wook 4 | Week 5 | Wook 6 |
| | | Effluent | -0.2818 | -0.2538 | 0.0462 | 0.0062 | 0.2497 | -0.1438 | -0.030 |
| L9 | 3.1 | - | -0.1491 | -0.1555 | -0.1885 | 0.2065 | 0.1039 | -0.1161 | -0.166 |
| L3 | 3 | Water | 1 1 | -0.0410 | 0.0240 | -0.0110 | 0.0274 | -0.0260 | -0.042 |
| L2 | 1.1 | Effluent | 0.0154 | | 0.0150 | -0.0050 | 0.0623 | -0.0450 | -0.050 |
| LB . | 1 | Water | -0.0277 | -0.0570 | | -0.0380 | 0.0004 | -0.0166 | 0.056 |
| L5 | 0.5 | Water | -0.0350 | -0.0246 | -0.0216 | -0.0149 | - · · · · · · · · · · · · · · · · · · · | 0.0059 | 0.034 |
| L6 | 0.4 | Effluent | -0.0111 | -0.0291 | -0.0304 | | | -0.0080 | -0.017 |
| <u></u> | 0.3 | Water | 0.0010 | -0.0107 | -0.0152 | 0.0000 | 0.0203 | | _ |
| | 0.2 | Effluent | -0.0238 | -0.0204 | -0.0214 | 0.0094 | 0.0338 | -0.0181 | -0.00 |
| L4 L7 | 0.1 | Water | 0.0040 | -0.0077 | -0.0095 | -0.0010 | 0.0073 | -0.0045 | -0.000 |

| SAMPLE | TARGET | MATRIX | | TIME SERIES | ANALYSIS OF | F [CN], (CN)- | | | 144 |
|--------------|--------------|----------|---------|-------------|-------------|-----------------|---------|---------|---------|
| NUMBER | CONC. (mg/L) | | Week Q | Week 1 | Week 2 | Week 3 | Week 4 | Week 5 | Week 6 |
| | | Effluent | -0.5638 | -0.5358 | -0.2358 | -0.2758 | -0.0324 | -0.4258 | -0.3124 |
| LO | 3.1 | Water | -0.3389 | -0.3453 | -0.3783 | 0.0167 | -0.0859 | -0.3059 | -0.3556 |
| L3 | 3 | Effluent | -0.0389 | -0.0954 | -0.0304 | -0.0654 | -0.0269 | -0.0804 | -0.0969 |
| . <i>L</i> 2 | 1.1 | Water | -0.0866 | -0.1159 | -0.0439 | -0.0639 | 0.0034 | -0.1039 | -0.1086 |
| L8 | , | Water | -0.0808 | -0.0703 | -0.0673 | -0.0838 | -0.0453 | -0.0623 | 0.0107 |
| L5 | 0.5 | Effluent | -0.0427 | -0.0607 | -0.0619 | -0.0464 | -0.0397 | -0.0257 | 0.0026 |
| LB | 0.4 | Water | -0.0178 | -0.0295 | -0.0340 | -0.0188 | 0.0015 | -0.0268 | -0.0363 |
| L1 | 0.3 | Effluent | -0.0551 | -0.0519 | -0.0529 | -0.0221 | 0.0021 | -0.0496 | -0.039 |
| L4 L7 | 0.2 | Water | -0.0063 | -0.0181 | -0.0198 | -0.0113 | -0.0031 | -0.0148 | -0.0106 |

APPENDIX 4
List of Participating Laboratories

Mr. Ken Little Supervisor Analytical Services Research and Development Dow Chemical Canada Inc Vidal Street, P.O. Box 3030 Sarnia, Ontario, N7T 7M1

Mr. George Slaney Cyanamid Canada Ltd. Welland Plant Gardner Rd., P.O. Box 240 Niagara Falls, Ontario L2E 6T4

Mr. Andrew Murray
Barringer Laboratories Limited
5735 McAdam Rd.
Mississauga, Ontario
LAZ 1N9

Mr. Jeffrey Pike Canviro Analytical Laboratories Ltd. 50 Bathurst Dr., Unit 12 Waterloo, Ontario N2V 2C5

Mr. John Fenwick Novalab Ltd. 9420 Cote de Liesse Lachine, Quebec H8T 1A1

Mr. George Crawford
Ontario Ministry of Environment
Laboratory Services Branch
125 Resources Rd., P.O. Box 213
Rexdale, Ontario
M9W 5L1

Dr. Barry R. Loescher Zenon Environmental Laboratories Inc. 5555 North Service Road Burlington, Ontario L7N 5H7 Mr. Nabih Kelada Methodology & Toxic Substances Section Egan WRP Research & Development Laboratory 550 S. Meacham Rd. Schaumburg, Illinois USA 60193

Ms. Jane Lindsay Ortech International 2395 Speakman Drive Mississauga, Ontario L5K 1B3

Mr. John Robertson Beak Consultants Ltd. 14 Abacus Rd. Brampton, Ontario L6T 5B7

Dr. Murray Fisher
Environment Protection Laboratories Inc.
6850 Goreway Drive
Toronto, Ontario
L4V 1P1

Mr. Michael Booth Ontario Hydro Research Division 800 Kipling Ave., KR 310 Toronto, Ontario M8Z 5S4

Mr. Ronald M. Connell Placer Dome Inc., Dome Mine P.O. Box 70 South Porcupine, Ontario PON 1H0

Dr. Eric Devuyst Inco Research 2060 Flavelle Blvd. Sheridan Park Mississauga, Ontario L5K 1Z9 Mr. Harold Laser Walker Industries Ltd. P.O. Box 100 Thorold, Ontario L2V 3Y8

Mr. Sing Ha
Dofasco Inc.
Industrial Drive Chem. Lab.
1330 Burlington St. E.
P.O. Box 2460
Hamilton, Ontario, L8N 3J5

Mile. Dominique Duval Laboratoire C.S.L. Environnement Canada 1001 Pierre Dupuy Longueuil, PQ L4K 1A1

M. Amr Rouchdy Technitrol-Eco 121 boul. Hymus Pointe-Claire, PQ H9R 1E6

Mr. Victor Rafuse Chief Chemist Williams Operating Corp. P.O. Bag 500 Marathon, Ontario POT 2E0

Doug Johnson Chief Chemist Royal Oak Mines Inc. P.O. Bag 2010 Timmins, Ontario P4N 7X7 Mr. S. Wade Stogran
Lakefield Research
P.O. Bag 4300, 185 Concession Street.
Lakefield, Ontario
KOL 2H0

Mr. Tony Robles American Barrick Inc. P.O. Box 278 Kirkland Lake, Ontario P2N 3H7

Mme Anick Tremblay Laboratoire C.N.F.S. 1325 Newton Boucherville, PQ J2B 5H2

Mr. William Coedy Chemist-in-Charge Water Resources Laboratory Dept. of Indian and Northern Affairs Box 1500 Yellowknife, NWT X1A 2R3

Mr. Dave Maskery Inco Limited Copper Cliff, Ontario P0M 1N0

T. Onggowodjaja Detour Mines P.O. 2016 Timmins, Ontario P4N 2S9

Ernie Goodwin Hemlo Goldmines Inc. Golden Giant Mine P.O. Box 40 Marathon, Ontario POT 2E3 Terry Webber
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P2N 3J7

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8577 Commerce Court
Burnaby, BC
V5A 4N5

Mr. P. Kluckner
Director, Laboratories
C&P, Pacific and Yukon Region
4195 Marine Dr.
West Vancouver, BC
Canada, V7V 1N8

Anver Najak Stelco Hilton Works Metallurgy QA Section 100 King St. W. L8N 3T1

Mr. Fred Doern AECL Research Whiteshell Laboratories Pinawa, Manitoba Canada, ROE 1LO

APPENDIX 5
Complete Table of Results (Raw Data)

WTC3 ROUND ROBIN STUDY FOR TOTAL CYANIDE: RAW DATA

| BAMPLE | TARGET | CN001 | CN003 | CHOOS | CNOOLA | CN0048 | CN005 | CNDOS | CN007 | CNOOS | CN000 | CN010 | CN011 | CN012 | CNOIS | CN014 | CN015 | CN016 | CN017 |
|--------|--------|-------|-------|-------|--------|--------|--------|------------|-------|-------|-------|--------|--------|-------|-------|-------|-------|-------|-------|
| NUMBER | | | 9888 | | | | 11 Y Y | | | | 0.29 | 0.20 | 0.103 | 0.36 | 0.36 | 0.27 | 0.33 | 0.33 | 0.26 |
| LI | 0.297 | 0.49 | 0.291 | 0.36 | 0.336 | 0.337 | 0.426 | 0.4 | 0.496 | 0.326 | 0.25 | | | | | | | l | |
| L2 | 1.097 | 1.82 | i.23 | 1.27 | 1.396 | 1.4 | 243 | 1.58 | 0.513 | 1,18 | 1.19 | 1.03 | 0.0467 | 1.32 | 1.26 | 1.46 | 1.31 | 1.3 | 1.1. |
| | 2.979 | 4.84 | 3.23 | 3.01 | 3.422 | 3.371 | 4.74 | 3.0 | 1.43 | 124 | 2.92 | 2.77 | 0.0911 | 3.76 | 3.29 | 4.27 | 3.62 | 3.6 | 2.7 |
| is | 0.1997 | 0.43 | as | 0.26 | 0.200 | 0.268 | 0.667 | 0.3 | 4.31 | 0.268 | 0.29 | 0.0 | 0.0811 | 0.27 | 0.26 | 0.16 | 0.326 | 0.23 | 0.2 |
| | | 1.1 | 0.545 | 0.62 | 0.686 | 0.659 | 1.26 | 0.58 | 0.58 | 0.562 | 0.88 | 0.46 | 41 | 0.01 | 0.67 | 0.67 | 0.638 | 0.64 | 0.6 |
| . 16 | 0.490 | | 0.621 | 24 | 0.682 | 0.571 | 0.966 | 0.61 | 1.3 | 0.454 | 0.52 | 0.43 | 0.077 | 0.61 | 0.5 | 0.6 | 0.486 | 0.47 | 0. |
| LB | .0.397 | 0.77 | | | | 0.110 | 0.126 | 0.1 | 0.14 | 0.113 | 0.09 | 0.09 | 0.0226 | 0.12 | 0.13 | 0.12 | 0.14 | 0.1 | 0.0 |
| L7 | 0.0997 | a.ie | 0.104 | 0.119 | 0.113 | | İ | 1.2 | 0.768 | 1.09 | 0.02 | 0.91 | 1.3 | 1.18 | 1.14 | 1.31 | 1.10 | 1.1 | 0. |
| u | 0.997 | 1.7 | 1.05 | 1.26 | 1.158 | 1.100 | 1.63 | <u>[</u> . | | | l | 2.71 | 0.744 | 162 | 2.62 | 4.49 | 3.58 | 2.1 | 3 |
| LO | 3.079 | | 3.36 | 2.96 | 3.682 | 3.611 | 0.44 | 3.98 | 1.33 | 3.26 | 3.51 | 1 2.71 | 3.744 | | | | | | |

| SAMPLE | TARGET | CN016 | CN019 | CN021 | CN022 | CN023 | CN024 | CN026 | CN026 | CN027 | CN028 | CN029 | CNO31 | CW035 | CMODS | CN036A | CN0368 | CN036A | CN0368 |
|--------|--------|-------|-------|-------|-------|-------|-------|---------|-------|-------|-------|---------|--------------|-------|-------|--------|--------|----------|--------|
| NUMBER | | | | · (1) | 0.341 | 0.34 | 0.310 | 0.332 | 0.207 | 0.321 | 0.36 | 0.621 | 0.45 | 0.27 | 0.300 | 0.3361 | 0.3316 | 0.331 | 0.332 |
| LI | 0.297 | 0.316 | 0.20 | 0.20 | u.s=1 | | 5.5.0 | | 1 | | | | 0.96 | 1.1 | 1.14 | 1.38 | 1.361 | 1.41 | 1.3 |
| 12 | 1.097 | 0.835 | 1.2 | 1.35 | 1.03 | 1.21 | 1.113 | 1.27 | 1.243 | 1.296 | 1.19 | 0.812 | <i>0.9</i> 6 | | 1.14 | | ,,,,,, | | |
| | 2.979 | 341 | 2.8 | 4.6 | 3.12 | 3.26 | 3.096 | 2.68 | 3.443 | 3.6 | 3.37 | 2.74 | 2.63 | 2.7 | 2.59 | 3.426 | 3.33 | 3,302 | 3.41 |
| L3 | 2.9/9 | | | | | | | 2 222 | 0.257 | 0.29 | 0.237 | 0.208 | 0.26 | 0.3 | 0.202 | 0.2968 | 0.2972 | 0.309 | 0.3 |
| L4 | 0.1997 | 0.260 | 0.24 | 0.13 | 0.202 | 0.26 | 0.211 | 0.226 | 0.287 | 0.25 | " | | | | | | | 0.578 | 0.5 |
| 1.6 | 0.499 | 0.498 | 0.74 | 0.56 | 0.633 | 0.66 | 0.501 | 0.534 | 0.607 | 0.56 | 0.58 | 0.683 | 0.44 | 0.41 | 0.626 | 0.8012 | 0.674 | 0.070 | |
| LS | | l . | | | | 0.51 | 0.383 | 0.458 | 0.447 | 0.293 | 0.40 | 0.479 | 0.38 | 0.61 | 0.426 | 0.564 | 0.5676 | 0.575 | 0.6 |
| LB | 0.397 | 0.467 | 0.42 | 0.48 | 0.439 | 0.61 | 0.363 | """ | 0.500 | | į | | | | 4 100 | 0.1129 | 0.1109 | 0.111 | 0.1 |
| L7 | 0.0997 | aı | 0.001 | 211 | 0.114 | 0.11 | 0.102 | 0.116 | 0.093 | 0.11 | 0.124 | 0.213 | 0.15 | 0.00 | 0.102 | 4,12 | 0.7700 | V | " |
| • | | l . | | | | 1,05 | 1.001 | . 0.003 | 1.055 | 1.18 | 1.17 | 1.21 | 0.81 | 0.96 | 1.05 | 1.136 | 1.144 | 1.142 | 1.7 |
| L | 0.997 | 0.971 | 1.7 | 1.17 | 1.08 | 1 " | | | | | 1 | | ٠., | ١, | 3.26 | 3.698 | 3.654 | 3.651 | 3.5 |
| LO | 1079 | 3.56 | 3.1 | 4.72 | 3.37 | 3.08 | 3.14 | 2.84 | 34 | 3.59 | 3.61 | 3.74 | 2.9 | 1 | 0.20 | | | | |

APPENDIX 6
Table of Results with Invalid Data (Grubbs outliers) Removed

RAW DATA WITH GRUBBS OUTLIERS REMOVED (+/- 3 Std. Dev.) AND MEANS AND +/- 1 STD. DEV. CALCULATED

| | ATA WITH | GRUB | BS OUT | LIERS R | ONOOHA | CN0048 | CN006 | CNDOS | CH007 | CNOOS | CN000 | CN010 | CN011 | CN012 | CN013 | CN014 | CN015 | CN018 | CN017 | CN018 | CN019 | CNO |
|--------------|----------|------|--------|---------|--------|--------|----------|-------|-------|-------|-------|-------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-----|
| mple mber | (mg/L) | ا | | | | | | | | | | | | | | 2.00 | 0.33 | 0.33 | 0.20 | 0,315 | 0,20 | 0. |
| L1 | 0.297 | 0.49 | 0.201 | 0.36 | 0.336 | 0.337 | 0.426 | 0.4 | 0.496 | 0.325 | 0.29 | 0.20 | | 0.36 | 0.36 | 0.27 | 0.33 | | •:-• | | | ı |
| | 1.097 | 1.82 | 1.20 | 1.27 | 1,396 | 1.4 | | 1.58 | 0.513 | 1.18 | 1.19 | 1.03 | | 1.32 | 1.26 | 1.46 | 1.31 | 1.3 | 1.15 | 0.836 | 1.2 | } |
| L2 | , 1 | | | 3.01 | 1.422 | 3.371 | 4.74 | 3.6 | 1.83 | 3.24 | 2.92 | 2.77 | | 3.76 | 1.29 | 4.27 | 3.62 | 3.6 | 2.79 | 3.41 | 2.8 | 1 |
| LJ | 2.979 | 4.84 | 1.20 | | | 0.268 | 0.067 | 0.3 | | 0.268 | 0.29 | 0.3 | 0.0811 | 0.27 | 0.25 | 0.16 | 0.326 | 0.23 | 0.27 | 0.268 | 0.24 | |
| L | 0.1997 | 0.43 | a.s | 0.26 | 0.299 | | J | 0.58 | 0.68 | 0.662 | 0.88 | 0.46 | 0.1 | 0.61 | 0.67 | 0.57 | 0.630 | 0.54 | 0.89 | 0.498 | 0.74 | |
| .6 | 0.490 | 1.1 | 0.545 | 0.52 | 0.565 | 0.550 | | Ì | | | 0.62 | 0.43 | 0.077 | 0.51 | 0.5 | 0.0 | 0.485 | 0.47 | 0.48 | 0.487 | 0.42 | |
| . a. | 0.397 | 0.77 | 0.621 | 0.48 | 0.562 | 0.671 | 0.966 | 0.61 | | 0.454 | 0.52 | " | | "" | | 1 | 1 | | | ٠. | 0.001 | |
| .7 | 0.0907 | 0.18 | 0.104 | 0.110 | 0.113 | 0.118 | 0.126 | 0.1 | 0.14 | 0.113 | 0.00 | 0.00 | | 0.12 | 0.13 | 0.12 | 0.14 | a i | 0.097 | 0.1 | | |
| 7 jun. | 0.997 | | 1.06 | 1.26 | 1.156 | 1.100 | 1.63 | 1.2 | 2.768 | 1.09 | 0.92 | 0.01 | 1.3 | 1.16 | 1.14 | 1.31 | 1.19 | 1.1 | 0.93 | 0.971 | 1.1 | |
| L | 1079 | | 3.36 | | 1 | 1 | | 3.96 | 1.33 | 3.26 | 3.51 | 2.71 | 0.744 | 3.63 | 2.62 | 4.40 | 3.56 | 3.1 | 3.09 | 3.66 | 3.1 | L |

RAW DATA WITH GRUBBS OUTLIERS REMOVED (+/- 3 Std. Dev.) AND MEANS AND +/- 1 STD. DEV. CALCULATED

| | | | | | | | ~~~ | CMD20 | CN031 | CN032 | CN033 | CN035A | CN0368 | CNOSSA | CNUSCO | NUMBER | | BTANDARD | | |
|-------------|--|--|---|--|---|---|--|--|--|--|--|--|--|--|--|--|--|--|--|--|
| Spike Level | CN022 | CNOSS | CNOS | CN036 | CN028 | CNUZI | CHUZO | - C | | | | | · | A 14 | | of | | DEVIATION | + | 150 |
| (mg/L) | | | | | | | | | ľ | | _ : | | · | | | | 0.0404 | 0.000 | | 0.20 |
| 0.007 | 0.341 | 0.34 | 0.314 | 0.332 | 0.267 | 0.321 | 0.30 | 0.521 | 0.45 | 0.27 | 0.300 | 0.3381 | 0.3316 | 0.331 | 0.332 | 36 | 0.3434 | 0.0020 | | J.20 |
| | | | ļ | 1 | 1,243 | 1.296 | 1.10 | 0.812 | 0.96 | 1.1 | 1.14 | 1.38 | 1.361 | 1.41 | 1.36 | . 34 | 1.2261 | 0.2279 | 1.4541 | 0.90 |
| | | | • | | | 3.6 | 3.37 | 2.74 | 2.63 | 2.7 | 2.69 | 3.428 | 3.33 | 3.392 | 3.416 | 36 | 3.3113 | 0.6114 | 3.9228 | 2.00 |
| - | | | | 1 | | 0.29 | 0.237 | 0.208 | 0.25 | 0.3 | 0.202 | 0,2968 | 0.2972 | 0.309 | 0.316 | 35 | 0.2711 | 0.0910 | 0.3621 | 0.1 |
| | | | | | | 1 | 0.58 | 0.683 | 0.44 | 0.41 | 0.526 | 0.6012 | 0.674 | 0.578 | 0.676 | 36 | 0.6763 | 0.1608 | 0.7262 | 0.4 |
| 0.499 | 0.633 | 0.50 | 1 | | | | | . ' | 0.38 | 0.61 | 0.426 | 0.564 | 0.5676 | 0.676 | 0.562 | 36 | 0.4990 | 0.1368 | 0.6347 | 0.3 |
| 0.397 | 0.439 | 0.51 | 0.363 | 0.458 | 0.447 | 0.200 | 0.48 | "" | | · | | | | | 0 114 | 34 | 0.1129 | 0.0166 | 0,1296 | 0.0 |
| 0.0997 | 0.114 | 211 | 0.102 | 0.115 | 0.093 | 0.11 | 0.124 | | 0.16 | 0.09 | 0.102 | 0.1129 | 0.7109 | 3.777 | | | ļ | | | ١., |
| 0.997 | 1.08 | 1.06 | 1.001 | 0.833 | 1.056 | 1.10 | 1.17 | 1.21 | 0.61 | 0.96 | 1.05 | 1.135 | 1.144 | 1.142 | 1.121 | 36 | 1.1001 | 0.1637 | 1.2638 | 0.6 |
| | | ,,, | و | 244 | 14 | 3.50 | 3.61 | 2.74 | 2.9 | 3 | 3.26 | 3.698 | 3.554 | | | | 3.3207 | 0.7659 | 4.0766 | 2.6 |
| | 0.297 1.097 2.979 0.1997 0.1997 0.499 | 0.207 0.341 1.097 1.03 2.979 1.12 0.1997 0.202 0.499 0.533 0.397 0.439 0.0907 0.114 0.907 1.00 | CM022 (mg/L) 0.207 0.341 0.34 1.097 1.03 1.21 2.979 3.12 3.25 0.1997 0.202 0.28 0.499 0.533 0.56 0.397 0.439 0.51 0.0907 0.114 0.11 0.697 1.08 1.06 | Que Level (mg/L) CN022 CN023 CN024 (mg/L) 0.341 0.34 0.318 1.097 1.03 1.21 1.113 2.979 3.12 3.26 3.096 0.1997 0.202 0.28 0.211 0.499 0.633 0.66 0.601 0.397 0.439 0.61 0.363 0.0997 0.114 0.11 0.102 0.897 1.06 1.05 1.001 | Que Level (mg/L) CN022 (CN023 (CN024 (CN026 (mg/L))) CN022 (CN026 (CN026 (CN026 (Mg/L))) 1.097 0.341 0.34 (0.34 (0.318 (0.332 (| Que Level (mg/L) CN022 CA023 CA024 CA028 CA028 1.097 0.341 0.34 0.316 0.332 0.267 1.097 1.03 1.21 1.113 1.27 1.243 2.979 3.12 3.26 3.996 2.68 3.443 0.1997 0.202 0.28 0.211 0.226 0.267 0.499 0.533 0.56 0.501 0.534 0.607 0.397 0.439 0.51 0.363 0.456 0.447 0.0907 0.114 0.11 0.102 0.115 0.093 0.897 1.08 1.06 1.001 0.933 1.055 | Que Level (mg/L) CN022 CA023 CA024 CA028 CA029 CA029 | Que Level (mg/L) CN022 CN023 CN024 CN026 CN028 CN027 CN028 1.097 0.341 0.34 0.316 0.332 0.267 0.321 0.30 1.097 1.03 1.21 1.113 1.27 1.243 1.296 1.19 2.679 3.12 3.26 3.096 2.68 3.443 3.6 3.37 0.1997 0.202 0.28 0.211 0.226 0.267 0.29 0.237 0.499 0.533 0.58 0.501 0.534 0.807 0.58 0.58 0.397 0.439 0.51 0.303 0.456 0.447 0.290 0.48 0.097 0.114 0.11 0.102 0.115 0.093 0.11 0.124 0.697 1.08 1.06 1.001 0.603 1.055 1.18 1.17 | Que Level (mg/L) CN022 CN023 CN024 CN028 CN028 CN028 CN028 CN028 CN028 CN027 CN028 CN027 CN028 CN027 CN028 CN028 | Character Char | CHO25 CHO25 CHO25 CHO26 CHO26 CHO26 CHO26 CHO27 CHO2 | CAUCHO C | Chicago Chic | Chicago Chic | CAUCHO C | CANGE CANG | CHO22 (MgA) CHO23 (CHO23 CHO24 CHO25 CHO26 CHO26 CHO26 CHO26 CHO26 CHO27 CHO27 CHO26 CHO26 CHO27 CHO27 CHO26 CHO27 CHO26 CHO26 CHO26 CHO27 CHO26 CHO2 | CM022 CM023 CM024 CM024 CM026 CM027 CM02 | CA022 CA023 CA023 CA024 CA02 | CANGE CANG |

APPENDIX 7
Table of Results with Outliers marked

| | ATA WITH | CNOOL | ERS (+/- | CN003 | CNDO4A | CHOOLE | CNOOS | | CN007 | CNOOS | CN009 | CN010 | CN011 | CN012 | CN013 | CN014 | CN016 | CN016 | CN017 | CN01 |
|--------|----------|-------|--|-------|--------|--------|-------|------|-------|-------|-------|-------|----------|-------|--------|----------|-------|-------|-------|----------|
| lumber | (mg/L) | | | | | | | | | 0.326 | 0.29 | 0.20 | | 0.36 | . 0.36 | | 0.33 | 0.33 | | 0.31 |
| LI. | 0.297 | | 0.291 | 0.36 | 0.334 | 0.337 | | 0.4 | | 0.325 | 0.20 | | } | | 1,26 | | 1.31 | 1.3 | 1.15 | |
| | 1.097 | ļ | 1.23 | 1.27 | 1.506 | 1.4 | | | | 1.18 | 1.19 | 1.03 | 1 | 1.32 | 1.20 | | | | | 3.4 |
| L2 | 1.007 | | \ \ \\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\ | | - 422 | 2.371 | | 3.0 | | 3.24 | 2.92 | 2.77 | ١٠ | 3.76 | 3.29 | | 3.62 | 3.6 | 2.70 | |
| w | 2.979 | | 3.29 | 3.01 | 1422 | 200 | | | | 0.268 | 0.29 | 0.3 | | 0.27 | 0.26 | | 0.326 | 0.23 | 0.27 | 0.2 |
| 44: | 0.1907 | | as | 0.26 | 0.299 | 0.266 | 1 | 0.3 | | 0.200 | | | ! | | 0.57 | 0.67 | 0.536 | 0.54 | | 0.4 |
| | 0.490 | · | 1 0.545 | 0.52 | 0.585 | 0.550 | | 0.58 | 0.58 | 0.552 | 1 | 0.46 | 1 | 0.61 | 0.07 | | | | 0,46 | 0.4 |
| LS | 0.44 | | l' l | | 0.642 | 0.671 | | 0.61 | | 0.464 | 0.62 | 0.43 | 1 | 0.51 | 0.6 | 0.0 | 0.485 | 0.47 | 0.40 |] " |
| 16 | 0.397 | ' | 0.621 | 0.48 | " | | | | 1 | 0.113 | 1 | 1 | | 0.12 | 1 | 0.12 | | 0.1 | 9.097 | ' |
| L7 | 0.0907 | | 0.104 | 0.110 | 0.113 | 0.116 | 0.126 | 0.1 | | | 1 | | | 1.16 | 1.14 | 1 | 1.19 | 1.1 | | 0.6 |
| LE | 0.907 | | 1.05 | | 1.156 | 1,109 | | 1.2 | | 1.09 | 1 | 1 | | "." | | | | ٠. | 3.09 | 3 |
| | | ĺ | 1.36 | 2.96 | 164 | 2611 | } | 3.96 | 1 | 3.20 | 3.61 | 2.71 | <u> </u> | 3.63 | 2.62 | <u> </u> | 3.56 | 3.1 | 3.00 | <u> </u> |

| aW D | ATA WITH | ιουτμ | ERS (+/- | - 1 Std. | Dev.) RE | MOVEL | ANDE | PECTE | DMEAN | IS CALC | CNOSE | CN031 | CN032 | CN033 | CNOSSA | CN0368 | CNOOSA | CN0368 | NUMBER | MEAN | STANDARI |
|-------|-------------|-----------|----------|----------|----------|-------|----------|-------|-------|---------|-------|-------|----------|-------|--------|----------|--------|---------|--------|--------|----------|
| emple | Spike Level | CNDID | CNOSI | CN022 | CND23 | CN034 | CN026 | CM038 | CN027 | CHIPA | | | | | | *** | | | DATA | | 35500 |
| umber | (mg/L) | | | | | 48 | | | 3 | | | | | 0.309 | 0.3361 | 0,3316 | 0.331 | 0.332 | 26 | 0.3263 | 0.026 |
| LI | 0.297 | 0.29 | <u> </u> | 0.341 | 0.34 | 0.310 | 0.332 | 0.267 | 0.321 | 0.36 | | ŀ | l | | | 1.361 | 1.41 | 1.36 | 27 | 1.2485 | 0.10 |
| | | | | 1.03 | 1.21 | 1.113 | 1.27 | 1.243 | 1.298 | 1.19 | , , | i | 1.1 | 1.14 | 1.36 | 7.501 | | | | | 1 |
| IJ | 1.007 | 1.2 | 1.36 | | 1 | | | 3.443 | 3.6 | 3.37 | 2.74 | | 2.7 | | 3.428 | 3.33 | 3.302 | 3.416 | 27 | 3.2468 | 0.30 |
| L3 | 2.979 | 2.6 | | 3.12 | 3.26 | 3.096 |] | | | l | 0.208 | 0.26 | 0.3 | 0.202 | 0.2968 | 0.2972 | 0.309 | 0.316 | 30 | 0.2676 | 0.03 |
| u | 0.1997 | 0.24 | | 0.202 | 0.26 | 0.211 | 0.226 | 0.267 | 0.29 | 0.237 | 0.20 | | . | | | 0.574 | 0.678 | 0.576 | 29 | 0.5530 | 0.03 |
| | | | 0.56 | 0.633 | 0.56 | 0.501 | 0.634 | 0.607 | 0.58 | 0.68 | 0.583 | 0.44 | | 0.625 | 0.6012 | | | | i ' | 1 | |
| L5 | 0.499 | | | 1 | | | 0.458 | 0.447 | ł | 0.46 | 0.479 | 0.38 | 0.61 | 0.425 | 0.564 | 0.6676 | 0.675 | 0.662 | 31 | 0.4944 | 0.00 |
| LO | 0.397 | 0.42 | 0.46 | 0.430 | 0.51 | 0.363 | 0.400 | | 1 | | 1 | | | 0.102 | 0.1120 | 0.1100 | 0.111 | 0.114 | 24 | 0.1111 | 1 0.0 |
| L7 | 0.0997 | | 211 | 0.114 | 0.11 | 0.102 | 0.115 | | 011 | 0.124 | | | | | | ! | 1.142 | 1,121 | 25 | 1.109 | 0.0 |
| • | | 1.1 | 1.17 | 1.08 | 1.05 | 1.001 | | 1.055 | 1.18 | 1.17 | 1.21 | } | 0.96 | 1.05 | 1.135 | 1,144 | 1 " | "" | | | |
| u | 0.997 | <i>""</i> | "" | " | \ | Į. | ! | 1 |] | مما | 3.74 | 20 | | 3.25 | 3.696 | 3.654 | | | | | 4 0.3 |
| Le | 1079 | 3.5 | l | 3.37 | 2.04 | 3.14 | 2.84 | 3.4 | 3.69 | 3.6 | 3.74 | | <u> </u> | | | | 101 | AL DATA | 248 | ני | |