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UPPER GREAT LAKES CONNECTING CHANNELS INTERLABORATORY PERFORMANCE EVALUATION STUDY QM-5: TRACE METALS IN SURFACE WATERS FINAL REPORT

by
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Burlington, Ontario, Canada, L7R 4A6

and the Quality Management Work Group

August 1987

UPPER GREAT LAKES CONNECTING CHANNELS

INTERLABORATORY PERFORMANCE EVALUATION STUDY

QM-5: TRACE METALS IN SURFACE WATERS

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sent to the QMWG for review and approval

MANAGEMENT PERSPECTIVE

The Upper Great Lakes Connecting Channels (UGLCC) have been designated as "Areas of Concern" by the International Joint Commission. A Canada-U.S. binational study, involving the identification and assessment of the environmental impacts of toxic substances, in those areas, was initiated in 1984. In order to assist analytical laboratories, which are contributing data to the UGLCC study, to generate reliable and accurate data during the study, a Quality Management Work Group was formed and thirteen interlaboratory performance evaluation studies were implemented. This report describes the results from the fifth interlaboratory performance evaluation study, QM-5, which consisted of the analysis of seven trace metals in water samples. Results were received from 11 out of 14 participating laboratories (six Canadian, five U.S.). Overall, most of the data received from the participants were satisfactory and comparable. All laboratories have been provided with the appropriate feed-back.

Dr. J. Lawrence
Director
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PERSPECTIVES - GESTION

Les canaux reliant les Grands Lacs d'amont (Upper Great Lakes Connecting Channels (UGLCC)) ont été désignés "zones de préoccupation" par la Commission mixte internationale. Une étude binationale Canada-E.-U. portant sur l'identification et l'évaluation des impacts environnementaux des substances toxiques dans ces zones a été entreprise en 1984. Afin d'aider les laboratoires d'analyse qui fournissent des données pour l'étude de ces canaux, à produire des données fiables et précises au cours de l'étude, un Groupe de travail sur la gestion de la qualité a été créé et treize études interlaboratoires d'évaluation du rendement ont été entreprises. Le présent rapport décrit les résultats de la cinquième étude interlaboratoire d'évaluation du rendement, QM-5, qui a porté sur l'analyse de sept métaux à l'état de trace dans les échantillons d'eau. Des résultats ont été fournis par 11 des 14 laboratoires participants (six du Canada, cinq des É.-U.). Dans l'ensemble, la plus grande partie des données reçues des participants était satisfaisante et acceptable. Tous les laboratoires ont reçu des commentaires appropriés.

ABSTRACT

The Upper Great Lakes Connecting Channels (UGLCC) Study recognizes Quality Assurance/Quality Control (QA/QC) aspects as crucial elements to the overall utility of study results. As part of the QA/QC program, 13 interlaboratory performance evaluation studies were designed and conducted by the Quality Management Work Group.

This report describes the results from the fifth interlaboratory performance evaluation study, QM-5, which consisted of the analysis of trace metals in waters samples. Results were received from 11 out of 14 participating laboratories (six Canadian, five U.S.). Data was evaluated for bias by Youden's ranking technique and results which deviated significantly from the median were flagged. The interlaboratory comparability of trace metal data was satisfactory for all of the parameters. The agreement between the design values and the interlaboratory medians was good in all cases. Results were accurate and precise in most cases. Laboratories U096 and U075 had the highest percentage of their results flagged (48% and 36% respectively). Included in this report is a summary of each laboratory's performance.

RÉSUMÉ

L'Etude sur les canaux reliant les Grands Lacs d'amont (Upper Great Lakes Connecting Channels (UGLCC)) a reconnu que les aspects de l'assurance de la qualité et du contrôle de la qualité (AQ/CQ) étaient des éléments capitaux pour l'utilité d'un ensemble des résultats de l'étude. Dans le cadre du programme (AQ/CQ), 13 études interlaboratoires d'évaluation du rendement ont été conçues et menées par le Groupe de travail sur la gestion de la qualité.

Ce rapport décrit les résultats de la cinquième étude interlaboratoire d'évaluation du rendement, QM-5, qui a porté sur l'analyse des métaux à l'état de traces dans les échantillons d'eau. Des résultats ont été reçus de 11 des 14 laboratoires participants (six du Canada, cinq des É.-U.). Les données ont été évaluées pour la mise en évidence d'erreurs systématiques selon la technique de classification de Youden et les résultats qui présentaient des déviations significatives par rapport à la médiane ont été indiqués. La comparabilité interlaboratoire des données sur les métaux à l'état de traces était satisfaisante pour tous les paramètres. L'accord entre les valeurs de conception et les médianes interlaboratoires étaient bonnes dans tous les cas. Les résultats étaient exacts et précis dans la plupart des cas. Les laboratoires U096 et U075 avaient le plus fort pourcentage d'écarts indiqués (48 % et 36 %, respectivement). On trouvera ci-inclus un résumé des données de rendement de chaque laboratoire.

INTRODUCTION

The Upper Great Lakes Connecting Channels (UGLCC) have been designated as "Areas of Concern" by the International Joint Commission (IJC). To identify and deal with the environmental problems, a three year, binational study was initiated in 1984, involving Canadian and U.S. environmental and resource agencies, to study the St. Marys, St. Clair and Detroit Rivers, and Lake St. Clair. The study involves identifying, quantifying and determining the environmental impacts of conventional and toxic substances from various sources.

The UGLCC Study recognizes Quality Assurance/Quality Control (QA/QC) aspects as crucial elements to the overall utility of study results. As part of the QA/QC program, 13 interlaboratory performance evaluation (QC) studies were designed and conducted by the Quality Management Work Group. The goal of these QC studies is to assist analytical laboratories, which are producing data for the UGLCC study, to generate reliable, accurate data and to assess their overall performance during this study. A total of some 100 parameters (organic, inorganic and physical properties) in three types of matrices (water, sediment and biota), will be assessed.

This fifth interlaboratory study, QM-5, was intitiated on January 31, 1986. It involved the analysis of seven trace metals in surface water. The original deadline for reporting results was set for April 30, 1986. However, several laboratories were late in reporting, so the study was not closed until August 8, 1986.

STUDY PROFILE

From the returned questionnaires, the following 13 laboratories affirmed that they would participate in this study: U001, U010, U013, U014, U049, U057, U075, U077, U079, U091, U063, U078, U090. By the time the study closed, the last three laboratories had not sent back any results. Laboratory U096 was a new participant who joined the

study at a later stage and requested samples well into the study. (See the list of participants at the end of this report.)

Each laboratory was provided with four water samples, that had been preserved with nitric acid, as described in Table 1. Samples 501 and 504 were naturally occurring surface water samples spiked with trace metals and samples 502 and 503 were prepared from a 1:3 dilution of sample 501 with distilled deionized water. All samples were well characterized reference waters developed by the Quality Assurance Project team, Research and Applications Branch of the National Water Research Institute (NWRI). The design values and interlaboratory medians are given in Table 2. The design values are based on in-house and external analyses. The same water samples were used in the Federal-Provincial Interlaboratory QA Program (1). The design values for the trace metals in these samples were confirmed by the interlaboratory medians of the Federal-Provincial Studies.

Participants were asked to analyze samples 501-504 for seven trace metals (iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb)). In order to provide some indication of the precision of such analyses, these samples were sent out in blind duplicate pairs, as shown in Table 1.

RESULTS AND DISCUSSION

Analytical Methodology

All samples could be analyzed by direct aspiration, with suitable standards. However, some laboratories have employed wet digestion techniques, to obtain the same acid matrix as their calibration standards, and/or to preconcentrate the water samples by evaporation to improve detectability. Seven laboratories used flame atomic absorption spectrophotometry (AAS) for the analyses. Three laboratories used inductively coupled plasma atomic emission spectrometry (ICP-AES) and two laboratories used direct current plasma (DCP)-AES. See Table 3 for details of the methodology.

Data Evaluation

All raw data submitted by the participants are listed by parameter in the data summary (Appendix II). Individual laboratory results for QM-5 were evaluated by the Youden ranking technique (2) for the detection of bias, as well as a computerized flagging procedure (3). A laboratory's results are judged biased high or low, when its total rank is outside of a statistically allowable range. Results are flagged very low, low, high or very high, when they deviate significantly from the interlaboratory median. For a further explanation of the ranking and flagging procedure, see Appendix I. This statistical procedure, which semi-quantitatively evaluates data accuracy is widely used in other interlaboratory QC studies. A summary of the ranking and flagging of the data is given in Appendix II. The overall accuracy of trace metal results has been summarized in Table 4. In this table, the number of results reported, the sum of results flagged and a statement of biased results are presented for each laboratory.

By parameter, paired sample plots have been included as a graphical illustration of systematic vs random errors, precision and accuracy of the participants' data (see Appendix IV). The diagonal line in the plots, is a 45° line passing through the design levels of the spiked water samples. The design value is represented by the letter D and the median by the letter M. If vertical lines were drawn from the labs' points to the 45° line, the lengths of these vertical lines would be directly related to the random errors. The lines would intersect the 45° line at various distances from the design value. These distances are directly related to the systematic errors of the laboratories (4). The closer the laboratories' values are to the diagonal line, the better their precision.

General Comments

Laboratories U001, U010, U075 and U091 reported their data by the originally set deadline (April 30, 1986). All laboratories, except U013 and U096 submitted their results by the second closing date (August 8, 1986). Laboratory U096 did not become involved with this study until quite late. They requested samples on May 22, 1986, while the samples had been sent to the other participants on February 28, 1986. Since laboratory U013 submitted their results extremely late (October 17, 1986), well after the final data summary had been sent out, their results were only included in the Youden plots and not in the data summary or the ranking and flagging procedures. Their data and methodology can be found in Appendix V.

An extra set of samples was requested by laboratory U010. Computer printouts of the raw data were sent to all reporting laboratories for verification in July, 1986. All laboratories returned their results verified, except for laboratory U001, whose results were verified by telephone. Several changes occurred. Laboratory U049 had originally reported their values in the wrong units and also with different detection limits for Fe, Cu, Zn, Cd, and Pb. Laboratory U096 had reported the wrong values for Cd. In December, laboratory U013 reported a transcription error for Zn, see Appendix V.

A final data summary was sent to the participating laboratories, the Quality Management Work Group, the Work Group Chairmen, the Management Committee and Activity Integration Committee Chairmen on September 15, 1986.

The overall interlaboratory performance of trace metal analysis was satisfactory. After the rejection of outliers, the interlaboratory relative standard deviations (RSD) for all metals were within 20%. In all cases, the difference between the design values and the interlaboratory medians was less than 10%. After the rejection of laboratory U075's Fe data for sample 502, the difference between the

medians and means was less than 10% for all of the parameters. In most cases, the precision of within laboratory analysis was within a relative standard deviation (RSD) of 10%, except for five sets of samples from laboratory U013 and one set from laboratories U049, U075, U079 and U091. Detection limits reported by the laboratories ranged from 0.2 to 100 µg/l, and can be found in Appendix II in the Youden ranking and flagging section.

General Comments by Parameter

Most laboratories analyzed all seven metals, except for laboratory U057 which did not analyze Pb and laboratory U096 which did not analyze Fe or Pb.

All parameters were analyzed well by most laboratories, with a few exceptions. As can be seen from Table 4, laboratory U001 had the most accurate results with no flags or biases for both methods used. Laboratory U049 results were also accurate with no biases and only 2% of their results flagged. Laboratory U096 had the least accurate results with 48% of their results flagged and two parameters biased low. Laboratory U075 was next in line with 36% of their results flagged and three biased high parameters.

Youden plots are included as an indication of systematic vs random errors, precision and accuracy (see Appendix IV).

For Fe, precision for all laboratories was within a RSD of 10% except for laboratory U075 (502 & 503 - 55%). Most of the laboratories were within ±10% of the design value except laboratory U075 was notably inaccurate for sample 502 and very high for sample 503, and results from laboratory U014 were biased high.

For Co, precision was very good with a RSD of 6% except for laboratories U079 (502 & 503 - 14%) and U013 (502 & 503 - 20%). Results were accurate in most cases, except sample 503 for laboratory U075 was very high.

For Ni, precision was also quite good with a RSD of 7%. Results were accurate, except that all Ni results from laboratory U096 were biased low and the plots indicated a systematic error.

For Cu, precision was within a RSD of 11%, except for laboratory U013, whose results were more erratic (RSD > 20%), and in two cases high. Results from both laboratories U075 and U077 were biased high.

For Zn, precision was within a RSD of 8%. Overall, the results reported were fairly accurate, except results from laboratory U075 for samples 502 and 503 were extremely high, which indicated a contamination problem in those two samples.

For Cd, precision was within a RSD of 10%. Results were accurate, except that laboratory U096 seemed to have a systematic problem, as allresults were precise but biased low.

For Pb, precision was within RSD of 11%, except for laboratory U013, where the RSD was 30% (502 & 503) and in two cases high. Results from the rest of the laboratories were accurate, except for biased high results from laboratory U010 and two very low results from laboratory U014.

Lab-Specific Comments (See Appendix III for each laboratory's appraisal)

U001 (U001A, U001B)

This laboratory provided two sets of data, one determined by AAS (U001A) and the other by ICP - AES (U001B). Both sets of results were accurate and precise with no flags or biases.

The precision between duplicate results was within a RSD of 6%.

U010

This laboratory had 13% of their results flagged. Fe results were satisfactory, except for one high flag. Results for Co, Cu and Cd

were all satisfactory with no flags or biases. For Ni, although no results were flagged, ranking indicated results were biased high. Results for Zn had two high flags and one very high flag. Pb had one very high flag and ranking indicated results were biased high. Precision between duplicate samples was within a RSD of 8%.

U014

This laboratory had 14% of their results flagged. Results for Co, Ni, Cu, Zn and Cd were all satisfactory with no flags or biases. Fe results had two very high flags and ranking indicated that the results were biased high. Pb results had two very low flags. Precision between duplicate samples was within a RSD of 10%.

U049

Overall, this laboratory's results were satisfactory. Only 2% of the results were flagged and there were no biases. Data for all parameters were satisfactory and only Pb results had one low flag. The precision between duplicate samples was within a RSD of 6% for all parameters except for Cu (501 & 504 - 11%).

U057

This laboratory had 8% of its results flagged. Pb was not analyzed. Data for Co, Cu, Zn, and Cd were all satisfactory with no flags or biases. One Fe result was flagged low and ranking indicated the results were biased low. Ni data had three low flags. Precision between duplicate samples was within a RSD of 8%.

U075

This laboratory had 36% of their results flagged either VH or H. Ni, Cd and Pb data were satisfactory with no flags or biases. Fe results had two very high flags and ranking indicated that the results were biased high. Co results had one high and very high flag. Cu results had two high flags, two very high flags, and ranking indicated that the results were biased high. Results for Zn had one high flag, three very high flags and ranking indicated that the results were also biased high. Results for samples 502 and 503 for Fe, Co, Cu and Zn had high percent recoveries ranging from 127 to 306%. The precision between duplicate samples was within a RSD of 6%, except for Fe (502 & 504 - 55%).

U077

Only seven percent of this laboratory's results were flagged. Data for Fe, Co, Zn, Cd and Pb were all satisfactory with no flags or biases. Although no results were flagged for Ni, ranking indicated that the results were biased high. Cu results had two very high flags and ranking indicated that the results were biased high. The percent recovery of the design value for Cu averaged 133%. The precision between duplicate samples was within a RSD of 5%.

U079

This laboratory also had only seven percent of its results flagged and there were no biases. Co, Ni, Cd and Pb results were all satisfactory, with no flags or biases. Fe and Cu results were both satisfactory, except for one low flag each. Zn results had one very low flag. The precision between duplicate samples was within a RSD of 10%, except for Co (502 & 503 - 14%).

U091

Laboratory U091 also had only seven percent of its results flagged, with no biases. Co, Ni, Zn and Cd results were all satisfactory. Fe and Pb results were also satisfactory, except for one flag each (Fe-high flag, Pb-low flag). Cu data had two low flags. The precision between duplicate samples was within a RSD of 9%, except for Pb (502 & 503 - 11%).

U096

This laboratory had the least accurate results with 48% of their results flagged. No results were submitted for Fe or Pb. Cu results were satisfactory, with no flags or biases. Zn results were satisfactory, except for one low flag. Both Ni and Cd results had all four samples flagged very low, and ranking indicated that the results were biased low. Co results had two low flags. Cd data had extremely low percent recoveries averaging 15%. The precision between duplicate samples was very good, since identical values were reported for all parameters, except for Cd (502 & 503 - RSD 6%).

U013

This laboratory submitted results well after the closing deadline (October 17, 1986). Their results are only included in the Youden plots. No results were submitted for Fe. Cu (502, 504) and Pb (501, 503) percent recoveries were above 125%. Zn results (502, 503) had very high recoveries (1208%). Changes to the Zn results were made in December 1986 (see Appendix V). Precision between duplicate samples was within a RSD of 5% except for Co (502, 503 - 20%), Cu (501 & 504 - 21%), (502 & 503 - 30%); Pb (501 & 504 - 11%), (502 & 503 - 30%).

COMMENTS

Overall, most laboratories provided satisfactory trace metal results for this study. However, laboratory U075 had 36% of their results flagged and laboratory U096 had 48% of their results flagged.

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LIST OF PARTICIPANTS

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Michigan Department of Natural Resources, Lansing, Michigan, U.S.A.

National Water Quality Laboratory, Burlington, Ontario, Canada

Ontario Ministry of Environment, Inorganic Trace Contaminants, Waters Unit, Rexdale, Ontario, Canada

Ontario Ministry of Environment, Thunder Bay, Ontario, Canada

Raytheon Service Corporation (U.S. Environmental Protection Agency - Large Lakes Research Station) Grosse Ile, Michigan, U.S.A.

US Geological Survey - National Water Quality Laboratory, Arvada, Colorado, U.S.A.

Wastewater Technology Centre (Conservation and Protection, Toronto), Burlington, Ontario, Canada

The following laboratories were sent samples but did not submit any results:

Mann Testing Laboratories Ltd., Mississauga, Ontario, Canada

National Water Research Institute - Environmental Contaminents Division - Inorganics Section, Burlington, Ontario, Canada

US Army Corps of Engineers - Environmental Analysis Branch, Detroit, Michigan, U.S.A.

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TABLE 1

Samples Distributed for Analysis in QM-5

Sample	Description
501	CM-TM-93 + (3% nitric acid)
502	1:3 dilution of sample 501
503	Same as 502
504	Same as 501

TABLE 2

Design Values and Interlaboratory Medians for Trace Metals
(All values are in ug/ℓ)

Parameter	Design Value	Interlab. Median		Design Value	Interlab. Median	
		Sample 501	504		Sample 502	503
Iron	499	520	510	166	170	170
Cobalt	297	296	290	99.0	100	100
Nickel	481	490	484	160	168	168
Copper	103	110	110	34.0	36.0	36.0
Zinc	108	107	100	36.0	34.0	37.0
Cadmium	98.0	97.0	96.0	33.0	32.0	33.0
Lead	485	487	491	162	164	161

TABLE 3

Analytical Methodology for Trace Metals

Lab No.	Sample Treatment	Method of Detection
U001A	direct aspiration	Flame-A.A.S
U001B	-	I.C.P.-A.E.S.
U010	direct aspiration	I.C.P.-A.E.S.
U014	HNO_3 digestion	Flame-A.A.S.
U049	direct aspiration	D.C.P.-A.E.S.
U057	direct aspiration	I.C.P.-A.E.S.
U075	preconcentration 10x with $HCl/HNO_3/H_2O_2$ digestion	Flame-A.A.S. and/or D.C.P-A.E.S
U077	direct aspiration	Flame-A.A.S.
U079	direct aspiration	Flame-A.A.S.
U091	wet acid digestion HNO_3 and HCl	Flame-A.A.S.
U096	$HNO_3/HCl/H_2O_2$ digestion	Flame-A.A.S.

TABLE 4

Summary of Trace Metal Results by Laboratory Based on the the Flagging and Youden Procedures. (See Appendix III)

Lab Code	No. of Results Reported	Elements not Analyzed	No. of Results Flagged VH	H	L	VL	% Flagged*	Comments
U001A	28	-	0	0	0	0	0%	All satisfactory
U001B	28	-	0	0	0	0	0%	All satisfactory
U010	28	-	2	3	0	0	13%	Ni & Pb - biased high
U014	28	-	2	0	0	2	14%	Fe - biased high
U049	28	-	0	0	1	0	2%	No bias
U057	24	Pb	0	0	4	0	8%	Fe - biased low
U075	28	-	8	4	0	0	36%	Fe, Cu & Zn - biased high
U077	28	-	2	0	0	0	7%	Ni & Cu - biased high
U079	28	-	0	0	2	1	7%	No bias
U091	28	-	0	1	3	0	7%	No bias
U096	20	Fe, Pb	0	0	3	8	48%	Ni & Cd - biased low

* H and L flags are counted as half of a VH and VL flag. Less than values that were flagged are included in the calculation of the % flagged.

APPENDIX I

GLOSSARY OF TERMS

APPENDIX I

Glossary of Terms

(1) Ranking

Ranking is a non-parametric statistical technique used for the detection of pronounced systematic error (bias) in interlaboratory studies. According to Youden's procedure, rank 1 is given to the laboratory that provided the lowest result, rank 2 to the next lowest. In case of a tie, the average rank is given to the tied laboratories. Results with a < sign are not ranked. For each parameter, the total rank of each laboratory is the sum of individual ranks on each sample. In the case of six test samples and ten laboratories, the 5% probability limits for ranking scores are 14 and 52. A laboratory with a score lower than 14 is identified as biased low. Similarly, a laboratory with a total rank higher than 52 is biased high. In both cases, their results are classified as outliers. In cases where a laboratory did not provide all the results, or some of the results were not ranked, the average rank instead of total rank was used for the determination of biased statements.

The more comparable, i.e., better, laboratories should have ranks in the middle rather than at the extreme ends. However, laboratories with middle ranks do not necessarily mean that they provide more consistent results since very high results (high ranks) and very low results (low ranks) would average out to yield a total rank close to the median. Therefore, ranking alone is not sufficient to determine the performance of a laboratory.

(2) Flagging

When the true values of constituents in test samples are unknown, individual results can be evaluated in terms of their absolute differences from the interlaboratory medians. Medians are chosen rather than means since they are not influenced by a moderate number of extreme values. By ths flagging technique, all results are graded into the

following three groups in the order of decreasing accuracy: (1) results with no flags, (2) results with H or L flags, and (3) results with VH or VL flags. Before evaluation is performed, three parameters, namely, Lower Limit for use of Basic Acceptable Error (LLBAE), Basic Acceptable Error (BAE), and Concentration Error Increment (CEI) are to be set. LLBAE is usually set at the lower end of the medians in the test samples. A 10-20% error at LLBAE is considered reasonable and thus this is used as BAE. For samples whose medians are at or below LLBAE, the results are evaluated according to the following formulae:

	Absolute difference between sample and median results	$\leq$ BAE :	acceptable
BAE <	Absolute difference between sample and median results	$\leq$ 1.5 x BAE:	H or L
	Absolute difference between sample and median results	> 1.5 x BAE:	VH or VL

For samples whose medians are above the LLBAE, the allowable BAE is augmented by adding an increment to the BAE. This increment is calculated by multiplying the CEI by the difference between the sample median and LLBAE values. In this study the CEI is set at 0.1. Sample results are again evaluated by the above three formulae except that the augmented BAE is used instead of BAE.

For further discussion on this evaluation technique, please refer to the original paper by Clark.

Bias: A set of results is said to be biased when the set exhibits a tendency to be either higher or lower than some standard - the standard which has been used in the analysis of our studies thus

far has been the performance of all other participating laboratories. The ranking procedure employed in testing for bias is described in W.J. Youden's paper, "Ranking Laboratories by Round-Robin Tests from Precision Measurement and Calibration, H.H. Ku, Editor, NBS Special Publication 300 - Volume 1, U.S. Government Printing Office, Washington, D.C., 1969. In this paper, Youden establishes the rationale for evaluating laboratories' performance by ranking results. In our use of the procedure there is about one chance in twenty of deeming a set of results biased when in fact it is not, that is, $t = 0.05$.

Codes

W: A "W" code is used with a reported result when no measurement was possible due to no response of the instrument to the sample. The "W" is preceded by the smallest determinative division that can be used in the units used in reporting.

T: The "T" code is used with values between the Criterion of Detection and the "W" value. The Criterion of Detection is commonly thought of by many as the limit of detection.

NA:	not analyzed
NRA:	not routinely analyzed
N or ND:	not detected
NAPP:	not applicable
H:	high
VH:	very high
L:	low
VL:	very low
LTV:	less than value (<)

APPENDIX II

UGLCC INTERLABORATORY PERFORMANCE EVALUATION STUDY

QM-5: TRACE METALS IN SURFACE WATERS

Data Summaries

QM5 TRACE METALS IN SURFACE WATER

PRINTOUT PREPARED: 86/10/29.

PARAMETER: IRON UG/L

SAMPLE RESULTS

LAB	501	502	503	504
U01A	519.	169.	171.	513.
U018	505.	171.	170.	506.
U010	590.	170.	170.	530.
U014	575.	190.	220.	600.
U049	520.	170.	170.	520.
U057	467.	155.	165.	442.
U075	547.	508.	222.	548.
U077	484.	164.	161.	478.
U079	500.	160.	140.	500.
U091	530.	175.	200.	500.
TOTAL LABS REPORTING	10	10	10	10
TOTAL LABS USED	10	10	10	10
MEAN	523.70000	203.20000	178.90000	513.70000
STD DEV	38.51133	107.50173	26.49717	41.87296
MEDIAN	519.50000	170.00000	170.00000	509.50000
DI[redacted] VALUE	499	166	166	499

QM5 TRACE METALS IN SURFACE WATER

PRINTOUT PREPARED: 86/10/29.

PARAMETER: COBALT UG/L

SAMPLE RESULTS

LAB	501	502	503	504
U01A	299.	102.	101.	304.
U01B	296.	100.	98.	296.
U010	310.	110.	110.	310.
U014	310.	110.	110.	290.
U049	280.	90.	90.	280.
U057	274.	91.	94.	279.
U075	297.	115.	126.	290.
U077	272.	93.	92.	270.
U079	290.	90.	110.	296.
U091	301.	90.	91.	294.
U096	259.	100.	100.	259.
TOTAL LABS REPORTING	11	11	11	11
TOTAL LABS USED	11	11	11	11
MEAN	289.81818	99.18182	102.00000	288.00000
STD DEV	16.51556	9.22841	11.03630	14.90637
MEDIAN	296.00000	100.00000	100.00000	290.00000
DESIGN VALUE	297	99	99	297

QM5 TRACE METALS IN SURFACE WATER

PRINTOUT PREPARED: 86/10/29.

PARAMETER: NICKEL UG/L

SAMPLE RESULTS

LAB	501	502	503	504
U01A	502.	171.	174.	491.
U01B	498.	168.	167.	500.
U010	510.	190.	180.	510.
U014	490.	170.	170.	483.
U049	470.	150.	150.	470.
U057	427.	139.	148.	400.
U075	500.	164.	159.	484.
U077	520.	180.	190.	500.
U079	480.	173.	168.	500.
U091	479.	156.	173.	480.
U096	335.2	121.1	121.1	335.2
TOTAL LABS REPORTING	11	11	11	11
TOTAL LABS USED	11	11	11	11
MEAN	473.74545	162.00909	163.64545	468.47273
STD DEV	52.20606	19.48284	18.68161	53.15203
MEDIAN	490.00000	168.00000	168.00000	484.00000
DESIGN VALUE	481	160	160	481

QM5 TRACE METALS IN SURFACE WATER

PRINTOUT PREPARED: 86/10/29.

PARAMETER: COPPER UG/L

SAMPLE RESULTS

LAB	501	502	503	504
U01A	115.	36.	37.	115.
U018	102.	36.	36.	101.
U010	110.	40.	40.	110.
U014	110.	30.	30.	100.
U049	102.	30.	32.	119.
U057	99.	32.	33.	98.
U075	131.	61.	62.	129.
U077	148.	44.	42.	138.
U079	92.	31.	32.	100.
U091	89.	33.	33.	91.
U096	120.	40.	40.	120.
TOTAL LABS REPORTING	11	11	11	11
TOTAL LABS USED	11	11	11	11
MEAN	110.72727	37.54545	37.90909	111.00000
STD DEV	17.37292	9.03730	8.89331	14.58081
MEDIAN	110.00000	36.00000	36.00000	110.00000
DESIGN VALUE	103	34	34	103

QM5 TRACE METALS IN SURFACE WATER

PRINTOUT PREPARED: 86/10/29.

PARAMETER: ZINC UG/L

SAMPLE RESULTS

LAB	501	502	503	504
U01A	107.	35.	36.	106.
U01B	107.	36.	37.	108.
U010	120.	40.	40.	120.
U014	100.	34.	38.	95.
U049	114.	32.	35.	105.
U057	109.	34.	38.	100.
U075	125.	69.	65.	131.
U077	101.	37.	37.	94.
U079	97.	30.	28.	100.
U091	101.	33.	34.	100.
U096	100.	30.	30.	100.
TOTAL LABS REPORTING	11	11	11	11
TOTAL LABS USED	11	11	11	11
MEAN	107.36364	37.27273	38.00000	105.36364
STD DEV	9.02522	10.92786	9.63328	11.09300
MED	107.00000	34.00000	37.00000	100.00000
DESIGN VALUE	108	36	36	108

QM5 TRACE METALS IN SURFACE WATER

PRINTOUT PREPARED: 86/10/29.

PARAMETER: CADMIUM UG/L

SAMPLE RESULTS

LAB	501	502	503	504
U01A	102.	36.	36.	102.
U01B	97.	32.	32.	98.
U010	104.	35.	35.	103.
U014	100.	35.	35.	100.
U049	87.	28.	29.	87.
U057	93.	32.	33.	88.
U075	100.	36.	35.	100.
U077	90.	30.	30.	88.
U079	106.	33.	38.	96.
U091	93.5	31.	32.	94.
U096	12.9	5.7	5.2	12.9
TOTAL LABS REPORTING	11	11	11	11
TOTAL LABS USED	11	11	11	11
MEAN	89.58182	30.33636	30.92727	88.08182
STD DEV	26.11080	8.56298	8.93634	25.59284
MEDIAN	97.00000	32.00000	33.00000	96.00000
DE[redacted] VALUE	98	33	33	98

QM5 TRACE METALS IN SURFACE WATER

PRINTOUT PREPARED: 86/10/29.

PARAMETER: LEAD UG/L

SAMPLE RESULTS

LAB	501	502	503	504
U01A	499.	171.	156.	491.
U01B	493.	165.	168.	500.
U010	520.	180.	200.	520.
U014	460.	130.	130.	460.
U049	490.	150.	140.	460.
U075	470.	164.	165.	500.
U077	448.	157.	160.	445.
U079	487.	168.	161.	500.
U091	480.	145.	170.	480.
TOTAL LABS REPORTING	9	9	9	9
TOTAL LABS USED	9	9	9	9
MEAN	483.00000	158.88889	161.11111	484.00000
STD DEV	21.56965	15.20234	19.66879	24.50000
MEDIAN	487.00000	164.00000	161.00000	491.00000
DESIGN VALUE	485	162	162	485

QM-5

Flagging and Youden's Ranking Procedures

PARAMETER [redacted]81 IRON UG/L

QUALITY ASSURANCE AN[redacted]HODS SECTION
NATIONAL WATER RES[redacted] INSTITUTE
BURLINGTON ONTARIO

QMS TRACE METALS IN SURFACE WATER

LOWER LIMIT FOR USE OF BASIC ACCEPTABLE ERROR=150.0 BASIC ACCEPTABLE ERROR=22.50 CONCENTRATION ERROR INCREMENT= .10
LABORATORIES YET TO REPORT: U063, U078, U090
LABORATORY RESULTS OMITTED ARE NONE

SAMPLE	501		502		503		504	
LAB NO	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK
U01A	519.	5.00	169.	4.00	171.	7.00	513.	6.00
U018	505.	4.00	171.	7.00	170.	5.00	506.	5.00
U010	590. H	10.00	170.	5.50	170.	5.00	530.	8.00
U014	575.	9.00	190.	9.00	220. VH	9.00	600. VH	10.00
U049	520.	6.00	170.	5.50	170.	5.00	520.	7.00
U057	467.	1.00	155.	1.00	165.	3.00	442. L	1.00
U075	547.	8.00	508. VH	10.00	222. VH	10.00	548.	9.00
U077	484.	2.00	164.	3.00	161.	2.00	478.	2.00
U079	500.	3.00	160.	2.00	140. L	1.00	500.	3.50
U091	530.	7.00	175.	8.00	200. H	8.00	500.	3.50
MEDIAN CONC.	519.500		170.000		170.000		509.500	

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING		DETECTION LIMIT
U01A	22.00	5.500	4			20
U018	21.00	5.250	4			
U010	28.50	7.125	4	H		40
U014	37.00	9.250	4	VHVH	BIASED HIGH	100
U049	23.50	5.875	4			30
U057	6.00	1.500	4	L	BIASED LOW	5
U075	37.00	9.250	4	VHVH	BIASED HIGH	100 I 15 S
U077	9.00	2.250	4			30
U079	9.50	2.375	4	L		40
U091	26.50	6.625	4	H		50

OVERALL AVERAGE RANK IS 5.500

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING		DETECTION LIMIT
U057	6.00	1.500	4	L	BIASED LOW	5
U077	9.00	2.250	4			30
U079	9.50	2.375	4	L		40
U018	21.00	5.250	4			
U01A	22.00	5.500	4			20
U049	23.50	5.875	4			30
U091	26.50	6.625	4	H		50
U010	28.50	7.125	4	H		40
U075	37.00	9.250	4	VHVH	BIASED HIGH	100 I 15 S
U014	37.00	9.250	4	VHVH	BIASED HIGH	100

OVERALL AVERAGE RANK IS 5.500

IRON

QUALITY ASSURANCE AND METHODS SECTION
NATIONAL WATER RESEARCH INSTITUTE
BURLINGTON ONTARIO

QMS TRACE METALS IN SURFACE WATER

LOWER LIMIT FOR USE OF BASIC ACCEPTABLE ERROR=100.0 BASIC ACCEPTABLE ERROR=10.00 CONCENTRATION ERROR INCREMENT= .10
LABORATORIES YET TO REPORT: U063, U078, U090
LABORATORY RESULTS OMITTED ARE NONE

SAMPLE LAB NO	501 REPORTED VALUE	501 RANK	502 REPORTED VALUE	502 RANK	503 REPORTED VALUE	503 RANK	504 REPORTED VALUE	504 RANK
U01A	299.	8.00	102.	8.00	101.	7.00	304.	10.00
U018	296.	6.00	100.	6.50	98.	5.00	296.	8.50
U010	310.	10.50	110.	9.50	110.	9.00	310.	11.00
U014	310.	10.50	110.	9.50	110.	9.00	290.	5.50
U049	280.	4.00	90.	2.00	90.	1.00	280.	4.00
U057	274.	3.00	91.	4.00	94.	4.00	279.	3.00
U075	297.	7.00	115. H	11.00	126. VH	11.00	290.	5.50
U077	272.	2.00	93.	5.00	92.	3.00	270.	2.00
U079	290.	5.00	90.	2.00	110.	9.00	296.	8.50
U091	301.	9.00	90.	2.00	91.	2.00	294.	7.00
U096	259. L	1.00	100.	6.50	100.	6.00	259. L	1.00
MEDIAN CONC.	296.000		100.000		100.000		290.000	

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	DETECTION LIMIT
U01A	33.00	8.250	4		10
U018	26.00	6.500	4		
U010	40.00	10.000	4		20
U014	34.50	8.625	4		50
U049	11.00	2.750	4		10
U057	14.00	3.500	4		5
U075	34.50	8.625	4	HVH	100 I 15 S
U077	12.00	3.000	4		3.0
U079	24.50	6.125	4		50
U091	20.00	5.000	4		10
U096	14.50	3.625	4	LL	.102MG/L @ 4 MG/L
OVERALL AVERAGE RANK IS		6.000			

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	DETECTION LIMIT
U049	11.00	2.750	4		10
U077	12.00	3.000	4		3.0
U057	14.00	3.500	4		5
U096	14.50	3.625	4	LL	.102MG/L @ 4 MG/L
U091	20.00	5.000	4		10
U079	24.50	6.125	4		50
U018	26.00	6.500	4		
U01A	33.00	8.250	4		10
U014	34.50	8.625	4		50
U075	34.50	8.625	4	HVH	100 I 15 S
U010	40.00	10.000	4		20
OVERALL AVERAGE RANK IS		6.000			

COBALT

PARAMETE[redacted]8081 NICKEL UG/L

QUALITY ASSURANCE AND METHODS SECTION
NATIONAL WATER RESEARCH INSTITUTE
BURLINGTON ONTARIO

QM5 TRACE METALS IN SURFACE WATER

LOWER LIMIT FOR USE OF BASIC ACCEPTABLE ERROR=160.0 BASIC ACCEPTABLE ERROR=24.00 CONCENTRATION ERROR INCREMENT= .10
LABORATORIES YET TO REPORT: U063, U078, U090
LABORATORY RESULTS OMITTED ARE NONE

SAMPLE LAB NO	501 REPORTED VALUE	501 RANK	502 REPORTED VALUE	502 RANK	503 REPORTED VALUE	503 RANK	504 REPORTED VALUE	504 RANK
U01A	502.	9.00	171.	8.00	174.	9.00	491.	7.00
U01B	498.	7.00	168.	6.00	167.	5.00	500.	9.00
U010	510.	10.00	190.	11.00	180.	10.00	510.	11.00
U014	490.	6.00	170.	7.00	170.	7.00	483.	5.00
U049	470.	3.00	150.	3.00	150.	3.00	470.	3.00
U057	427. L	2.00	139. L	2.00	140.	2.00	400. L	2.00
U075	500.	8.00	164.	5.00	159.	4.00	484.	6.00
U077	520.	11.00	180.	10.00	190.	11.00	500.	9.00
U079	480.	5.00	173.	9.00	168.	6.00	500.	9.00
U091	479.	4.00	156.	4.00	173.	8.00	480.	4.00
U096	335.2 VL	1.00	121.1 VL	1.00	121.1 VL	1.00	335.2 VL	1.00
MEDIAN CONC.	490.000		168.000		168.000		484.000	

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING		DETECTION LIMIT
U01A	33.00	8.250	4			30
U01B	27.00	6.750	4			
U010	42.00	10.500	4		BIASED HIGH	20
U014	25.00	6.250	4			5
U049	12.00	3.000	4			
U057	8.00	2.000	4	LLL		10
U075	23.00	5.750	4			5
U077	41.00	10.250	4		BIASED HIGH	100 I 15 S
U079	29.00	7.250	4			100
U091	20.00	5.000	4			60
U096	4.00	1.000	4	VLVLVLVL	BIASED LOW	10
OVERALL AVERAGE RANK IS		6.000				.074MG/L @ 3 MG/L

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING		DETECTION LIMIT
U096	4.00	1.000	4	VLVLVLVL	BIASED LOW	.074MG/L @ 3 MG/L
U057	8.00	2.000	4	LLL		5
U049	12.00	3.000	4			10
U091	20.00	5.000	4			10
U075	23.00	5.750	4			100 I 15 S
U014	25.00	6.250	4			5
U01B	27.00	6.750	4			
U079	29.00	7.250	4			60
U01A	33.00	8.250	4			30
U077	41.00	10.250	4		BIASED HIGH	100
U010	42.00	10.500	4		BIASED HIGH	20
OVERALL AVERAGE RANK IS		6.000				

NICKEL

QUALITY ASSURANCE AND METHODS SECTION
NATIONAL WATER RESEARCH INSTITUTE
BURLINGTON ONTARIO

QM5 TRACE METALS IN SURFACE WATER

LOWER LIMIT FOR USE OF BASIC ACCEPTABLE ERROR=40.00 BASIC ACCEPTABLE ERROR= 8.00 CONCENTRATION ERROR INCREMENT= .10
LABORATORIES YET TO REPORT: U063, U078, U030
LABORATORY RESULTS OMITTED ARE NONE

SAMPLE LAB NO	501 REPORTED VALUE	501 RANK	502 REPORTED VALUE	502 RANK	503 REPORTED VALUE	503 RANK	504 REPORTED VALUE	504 RANK
U01A	115.	8.00	36.	6.50	37.	7.00	115.	7.00
U01B	102.	4.50	36.	6.50	36.	6.00	101.	5.00
U010	110.	6.50	40.	8.50	40.	8.50	110.	6.00
U014	110.	6.50	30.	1.50	30.	1.00	100.	3.50
U049	102.	4.50	30.	1.50	32.	2.50	119.	8.00
U057	99.	3.00	32.	4.00	33.	4.50	98.	2.00
U075	131. H	10.00	61. VH	11.00	62. VH	11.00	129. H	10.00
U077	148. VH	11.00	44.	10.00	42.	10.00	138. VH	11.00
U079	92. L	2.00	31.	3.00	32.	2.50	100.	3.50
U091	89. L	1.00	33.	5.00	33.	4.50	91. L	1.00
U096	120.	9.00	40.	8.50	40.	8.50	120.	9.00
MEDIAN CONC.	110.000		36.000		36.000		110.000	

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING		DETECTION LIMIT
U01A	28.50	7.125	4			10
U01B	22.00	5.500	4			
U010	29.50	7.375	4			20
U014	12.50	3.125	4			20
U049	16.50	4.125	4			10
U057	13.50	3.375	4			1
U075	42.00	10.500	4	HVHVHH	BIASED HIGH	10 I 1 S
U077	42.00	10.500	4	VHVH	BIASED HIGH	10
U079	11.00	2.750	4	L		30
U091	11.50	2.875	4	LL		5
U096	35.00	8.750	4			.044MG/L@ 2 MG/L
OVERALL AVERAGE RANK IS		6.000				

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING		DETECTION LIMIT
U079	11.00	2.750	4	L		30
U091	11.50	2.875	4	LL		5
U014	12.50	3.125	4			20
U057	13.50	3.375	4			1
U049	16.50	4.125	4			10
U01B	22.00	5.500	4			
U01A	28.50	7.125	4			10
U010	29.50	7.375	4			20
U096	35.00	8.750	4			.044MG/L@ 2 MG/L
U077	42.00	10.500	4	VHVH	BIASED HIGH	10
U075	42.00	10.500	4	HVHVHH	BIASED HIGH	10 I 1 S
OVERALL AVERAGE RANK IS		6.000				

COPPER

QUALITY ASSURANCE AND METHODS SECTION
NATIONAL WATER RESEARCH INSTITUTE
BURLINGTON ONTARIO

QMS TRACE METALS IN SURFACE WATER

LOWER LIMIT FOR USE OF BASIC ACCEPTABLE ERROR=35.00 BASIC ACCEPTABLE ERROR= 5.25 CONCENTRATION ERROR INCREMENT= .10
LABORATORIES YET TO REPORT: U063, U078, U090
LABORATORY RESULTS OMITTED ARE NONE

SAMPLE LAB NO	501 REPORTED VALUE	501 RANK	502 REPORTED VALUE	502 RANK	503 REPORTED VALUE	503 RANK	504 REPORTED VALUE	504 RANK
U01A	107.	6.50	35.	7.00	36.	5.00	106.	8.00
U01B	107.	6.50	36.	8.00	37.	6.50	108.	9.00
U010	120. H	10.00	40. H	10.00	40.	10.00	120. VH	10.00
U014	100.	2.50	34.	5.50	38.	8.50	95.	2.00
U049	114.	9.00	32.	3.00	35.	4.00	105.	7.00
U057	109.	8.00	34.	5.50	38.	8.50	100.	4.50
U075	125. H	11.00	69. VH	11.00	65. VH	11.00	131. VH	11.00
U077	101.	4.50	37.	9.00	37.	6.50	94.	1.00
U079	97.	1.00	30.	1.50	28. VL	1.00	100.	4.50
U091	101.	4.50	33.	4.00	34.	3.00	100.	4.50
U096	100.	2.50	30.	1.50	30. L	2.00	100.	4.50
MEDIAN CONC.	107.000		34.000		37.000		100.000	

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING
U01A	26.50	6.625	4	
U01B	30.00	7.500	4	
U010	40.00	10.000	4	HHVH
U014	10.50	4.625	4	
U049	23.00	5.750	4	
U057	26.50	6.625	4	
U075	44.00	11.000	4	HVHVHVH
U077	21.00	5.250	4	
U079	8.00	2.000	4	VL
U091	16.00	4.000	4	
U096	10.50	2.625	4	L

OVERALL AVERAGE RANK IS 6.000

BIASED HIGH

DETECTION LIMIT
10
20
5
20
5
10 I 1 S
10
8
5
.010MG/L @ .5 MG/L

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING
U079	8.00	2.000	4	VL
U096	10.50	2.625	4	L
U091	16.00	4.000	4	
U014	10.50	4.625	4	
U077	21.00	5.250	4	
U049	23.00	5.750	4	
U01A	26.50	6.625	4	
U057	26.50	6.625	4	
U01B	30.00	7.500	4	
U010	40.00	10.000	4	HHVH
U075	44.00	11.000	4	HVHVHVH

OVERALL AVERAGE RANK IS 6.000

BIASED HIGH

DETECTION LIMIT
8
.010MG/L @ .5 MG/L
2
5
10
20
10
5
20
10 I 1 S

ZINC

PARAMETE[redacted]8081 CADMIUM UG/L

QUALITY ASSURANCE AND METHODS SECTION
NATIONAL WATER RESEARCH INSTITUTE
BURLINGTON ONTARIO

QM5 TRACE METALS IN SURFACE WATER

LOWER LIMIT FOR USE OF BASIC ACCEPTABLE ERROR=35.00 BASIC ACCEPTABLE ERROR= 5.25 CONCENTRATION ERROR INCREMENT= .10
LABORATORIES YET TO REPORT: U063, U078, U090
LABORATORY RESULTS OMITTED ARE NONE

SAMPLE LAB NO	501 REPORTED VALUE	501 RANK	502 REPORTED VALUE	502 RANK	503 REPORTED VALUE	503 RANK	504 REPORTED VALUE	504 RANK
U01A	102.	9.00	36.	10.50	36.	10.00	102.	10.00
U01B	97.	6.00	32.	5.50	32.	4.50	98.	7.00
U010	104.	10.00	35.	8.50	35.	8.00	103.	11.00
U014	100.	7.50	35.	8.50	35.	8.00	100.	8.50
U049	87.	2.00	28.	2.00	29.	2.00	87.	2.00
U057	93.	4.00	32.	5.50	33.	6.00	88.	3.50
U075	100.	7.50	36.	10.50	35.	8.00	100.	8.50
U077	90.	3.00	30.	3.00	30.	3.00	88.	3.50
U079	106.	11.00	33.	7.00	38.	11.00	96.	6.00
U091	93.5	5.00	31.	4.00	32.	4.50	94.	5.00
U096	12.9 VL	1.00	5.7 VL	1.00	5.2 VL	1.00	12.9 VL	1.00
MEDIAN CONC.	97.000		32.000		33.000		96.000	

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	
U01A	39.50	9.875	4		
U01B	23.00	5.750	4		
U010	37.50	9.375	4		
U014	32.50	8.125	4		
U049	8.00	2.000	4		
U057	19.00	4.750	4		
U075	34.50	8.625	4		
U077	12.50	3.125	4		
U079	35.00	8.750	4		
U091	18.50	4.625	4		
U096	4.00	1.000	4	VLVLVLVL	BIASED LOW

OVERALL AVERAGE RANK IS 6.000

DETECTION LIMIT
10
4
0.2
10
1
10 I 1 S
1.0
10
3
.020MG/L@ .75 MG/L

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	
U096	4.00	1.000	4	VLVLVLVL	BIASED LOW
U049	8.00	2.000	4		
U077	12.50	3.125	4		
U091	18.50	4.625	4		
U057	19.00	4.750	4		
U01B	23.00	5.750	4		
U014	32.50	8.125	4		
U075	34.50	8.625	4		
U079	35.00	8.750	4		
U010	37.50	9.375	4		
U01A	39.50	9.875	4		

OVERALL AVERAGE RANK IS 6.000

DETECTION LIMIT
.020MG/L@ .75 MG/L
10
1.0
3
1
0.2
10 I 1 S
10
4
10

CADMIUM

PARAMETE 2081 LEAD UG/L

QUALITY ASSURANCE AND METHODS SECTION
NATIONAL WATER RESEARCH INSTITUTE
BURLINGTON ONTARIO

QM5 TRACE METALS IN SURFACE WATER

LOWER LIMIT FOR USE OF BASIC ACCEPTABLE ERROR=160.0 BASIC ACCEPTABLE ERROR=16.00 CONCENTRATION ERROR INCREMENT= .10
LABORATORIES YET TO REPORT: U063, U078, U090
LABORATORY RESULTS OMITTED ARE NONE

SAMPLE LAB NO	501 REPORTED VALUE	501 RANK	502 REPORTED VALUE	502 RANK	503 REPORTED VALUE	503 RANK	504 REPORTED VALUE	504 RANK
U01A	499.	8.00	171.	8.00	156.	3.00	491.	5.00
U01B	493.	7.00	165.	6.00	168.	7.00	500.	7.00
U010	520.	9.00	180.	9.00	200. VH	9.00	520.	9.00
U014	460.	2.00	130. VL	1.00	130. VL	1.00	460.	2.50
U049	490.	6.00	150.	3.00	140. L	2.00	460.	2.50
U075	470.	3.00	164.	5.00	165.	6.00	500.	7.00
U077	448.	1.00	157.	4.00	160.	4.00	445.	1.00
U079	487.	5.00	168.	7.00	161.	5.00	500.	7.00
U091	480.	4.00	145. L	2.00	170.	8.00	480.	4.00
MEDIAN CONC.	487.000		164.000		161.000		491.000	

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING		DETECTION LIMIT
U01A	24.00	6.000	4			50
U01B	27.00	6.750	4			
U010	36.00	9.000	4	VH	BIASED HIGH	60
U014	6.50	1.625	4	VLVL		50
U049	13.50	3.375	4	L		50
U075	21.00	5.250	4			100 I 15 S
U077	10.00	2.500	4			10
U079	24.00	6.000	4			100
U091	18.00	4.500	4	L		15

OVERALL AVERAGE RANK IS 5.000

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING		DETECTION LIMIT
U014	6.50	1.625	4	VLVL		50
U077	10.00	2.500	4			10
U049	13.50	3.375	4	L		50
U091	18.00	4.500	4	L		15
U075	21.00	5.250	4			100 I 15 S
U079	24.00	6.000	4			100
U01A	24.00	6.000	4			50
U01B	27.00	6.750	4			
U010	36.00	9.000	4	VH	BIASED HIGH	60

OVERALL AVERAGE RANK IS 5.000

LEAD

APPENDIX III

UGLCC INTERLABORATORY PERFORMANCE EVALUATION STUDY

QM-5: TRACE METALS IN SURFACE WATER

Laboratory Appraisals

CRITERIA USED TO PREPARE STATEMENTS FOR THE LABORATORY APPRAISALS

Note: Please refer to the "Glossary of Terms" and associated references for an explanation of
a) How the non-parametric process of ranking is able to discern bias in a laboratory data set and
b) The calculation and conditions that warrants a reported result to be flagged L, H, VL or VH.

Status of Data (Refer to Appendix II - Date Files)	Statement Produced in Appraisal (Appendix III)
1a) No flags, no bias in the data set.	1a) Satisfactory
b) No bias, only 1 minor flag (H or L).	b) Satisfactory except for low/high flag on sample _____.
2. No data or results reported by laboratory.	2. No results reported.
3. Data reported on less than half of the samples, no results flagged.	3. Insufficient data to assess bias.
4. Same as Item 3, but some results are flagged.	4. Flagged ___ on sample ___,___ and flagged ___ on sample. Insufficient data to assess bias.
5. No results are flagged but data set identified as biased high or low	5. Although no results are flagged ranking indicates results are biased high/low.
6. Some results are flagged, the data set is discerned as biased.	6. Flagged ___ on sample ___,___; Flagged ___ on sample ___,___. Ranking indicates results are biased.
7. Some results are flagged.	7. Flagged ___ on sample ___,___ and flagged ___ on samples ___.
8. No bias statement but two or three results are flagged. One is very high, the other is very low.	8. Flagged very high on sample ___ and very low on sample ___. These results are slightly erratic.
9. No bias statement but two or more results are flagged very high and two or more results are flagged very low.	9. Flagged very high on samples ___,___ and flagged very low on samples ___,___,___. These results are erratic.
10. Results are ranked, the data set is not biased but one result is flagged very high or very low.	10. Flagged ___ on sample ___. This extreme result suggests the measurement process is out of control.
11. Less than values	11. Unuseable values.

* Taken from LRTAP Intercomparison Study L-12 (5)

LABORATORY APPRAISAL FOR UGLCC STUDY QM-5

Your Laboratory Code is: U001A

Parameter	Comments
Iron	Satisfactory
Cobalt	Satisfactory
Nickel	Satisfactory
Copper	Satisfactory
Zinc	Satisfactory
Cadmium	Satisfactory
Lead	Satisfactory

LABORATORY APPRAISAL FOR UGLCC STUDY QM-5

Your Laboratory Code is: U001B

Parameter	Comments
Iron	Satisfactory
Cobalt	Satisfactory
Nickel	Satisfactory
Copper	Satisfactory
Zinc	Satisfactory
Cadmium	Satisfactory
Lead	Satisfactory

LABORATORY APPRAISAL FOR UGLCC STUDY QM-5

Your Laboratory Code is: U010

Parameter	Comments
Iron	Satisfactory, except for H flag on sample 501.
Cobalt	Satisfactory
Nickel	Although no results are flagged, ranking indicates results are biased high.
Copper	Satisfactory
Zinc	Flagged H on samples 501 and 502, and flagged VH on sample 504.
Cadmium	Satisfactory
Lead	Flagged VH on sample 503. Ranking indicates results are biased high.

LABORATORY APPRAISAL FOR UGLCC STUDY QM-5

Your Laboratory Code is: U014

Parameter	Comments
Iron	Flagged VH on samples 503 and 504. Ranking indicates results are biased high.
Cobalt	Satisfactory
Nickel	Satisfactory
Copper	Satisfactory
Zinc	Satisfactory
Cadmium	Satisfactory
Lead	Flagged VL on samples 502 and 503.

LABORATORY APPRAISAL FOR UGLCC STUDY QM-5

Your Laboratory Code is: U049

Parameter	Comments
Iron	Satisfactory
Cobalt	Satisfactory
Nickel	Satisfactory
Copper	Satisfactory
Zinc	Satisfactory
Cadmium	Satisfactory
Lead	Satisfactory, except for L flag on sample 503.

LABORATORY APPRAISAL FOR UGLCC STUDY QM-5

Your Laboratory Code is: U057

Parameter	Comments
Iron	Flagged L on sample 504. Ranking indicates results are biased low.
Cobalt	Satisfactory
Nickel	Flagged L on samples 501, 502 and 504.
Copper	Satisfactory
Zinc	Satisfactory
Cadmium	Satisfactory
Lead	No results reported

LABORATORY APPRAISAL FOR UGLCC STUDY QM-5

Your Laboratory Code is: U075

Parameter	Comments
Iron	Flagged VH on samples 502 and 503. Ranking indicates results are biased high.
Cobalt	Flagged H on sample 502, and flagged VH on sample 503.
Nickel	Satisfactory
Copper	Flagged H on samples 501 and 504, flagged VH on samples 502 and 503. Ranking indicates results are biased high.
Zinc	Flagged H on sample 501, and flagged VH on samples 502, 503 and 504. Ranking indicates results are biased high.
Cadmium	Satisfactory
Lead	Satisfactory

LABORATORY APPRAISAL FOR UGLCC STUDY QM-5

Your Laboratory Code is: U077

Parameter	Comments
Iron	Satisfactory
Cobalt	Satisfactory
Nickel	Although no results are flagged, ranking indicates results are biased high.
Copper	Flagged VH on samples 501 and 504. Ranking indicates results are biased high.
Zinc	Satisfactory
Cadmium	Satisfactory
Lead	Satisfactory

LABORATORY APPRAISAL FOR UGLCC STUDY QM-5

Your Laboratory Code is: U079

Parameter	Comments
Iron	Satisfactory except for L flag on sample 503.
Cobalt	Satisfactory
Nickel	Satisfactory
Copper	Satisfactory, except for L flag on sample 501.
Zinc	Flagged VL on sample 503.
Cadmium	Satisfactory
Lead	Satisfactory

LABORATORY APPRAISAL FOR UGLCC STUDY QM-5

Your Laboratory Code is: U091

Parameter	Comments
Iron	Satisfactory, except for H flag on sample 503.
Cobalt	Satisfactory
Nickel	Satisfactory
Copper	Flagged L on samples 501 and 504.
Zinc	Satisfactory
Cadmium	Satisfactory
Lead	Satisfactory, except for L flag on sample 502.

LABORATORY APPRAISAL FOR UGLCC STUDY QM-5

Your Laboratory Code is: U096

Parameter	Comments
Iron	No results reported.
Cobalt	Flagged L on samples 501 and 504.
Nickel	Flagged VL on samples 501, 502, 503 and 504. Ranking indicates results are biased low.
Copper	Satisfactory
Zinc	Satisfactory, except for L flag on sample 503.
Cadmium	Flagged VL on samples 501, 502, 503 and 504. Ranking indicates results are biased low.
Lead	No results reported.

APPENDIX IV

YOUDEN'S TWO SAMPLE PLOTS

Legend for Youden Plots

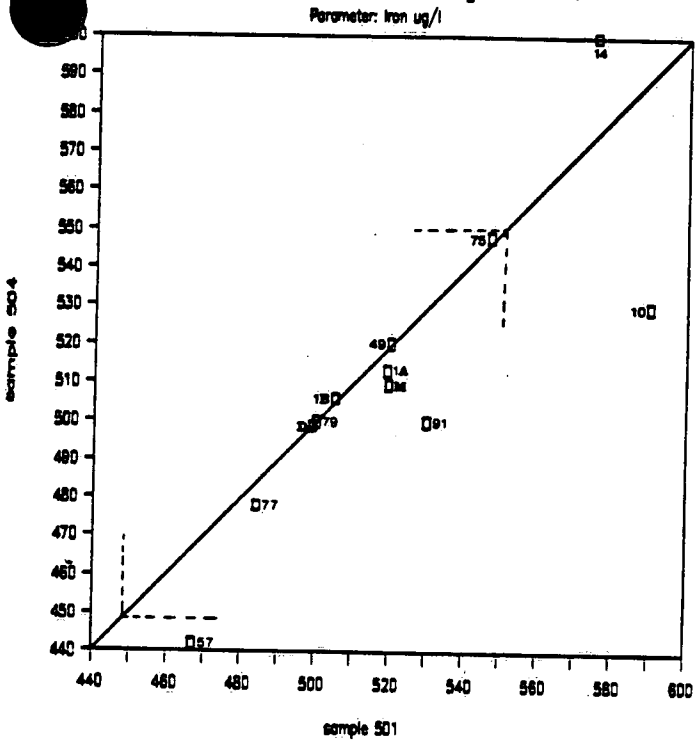

Laboratories

Design value

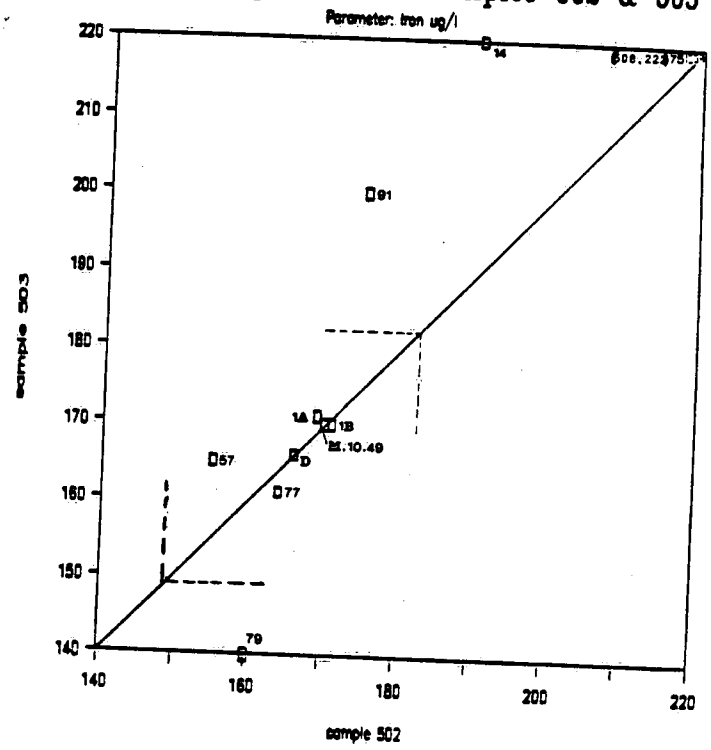
Interlaboratory median


±10% of the design value

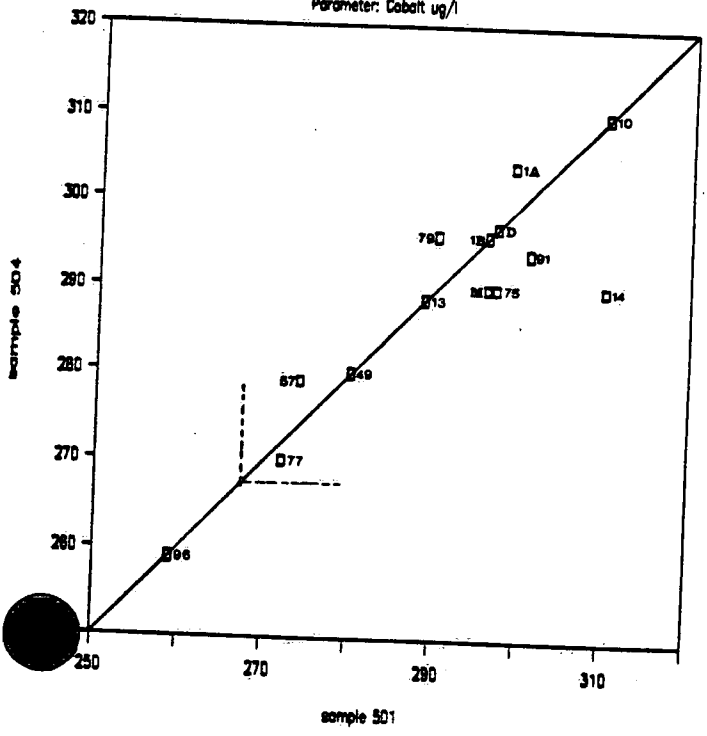
Paired Sample Plot - Samples 501 & 504



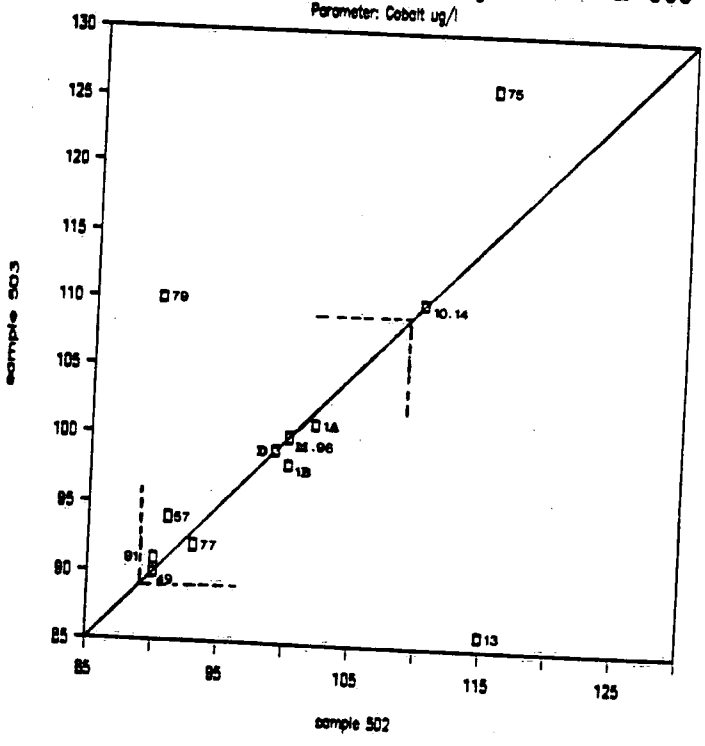
Paired Sample Plot - Samples 502 & 503



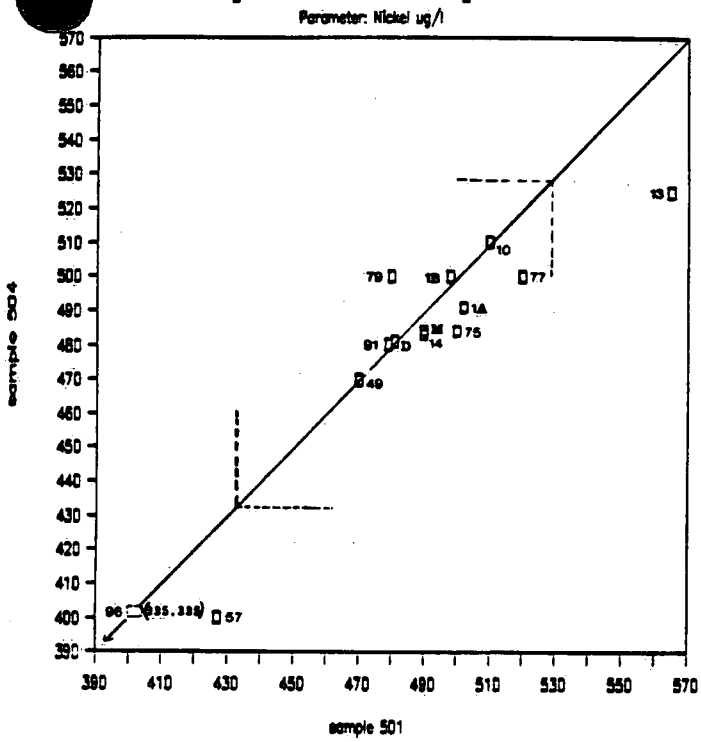
Paired Sample Plot - Samples 501 & 504



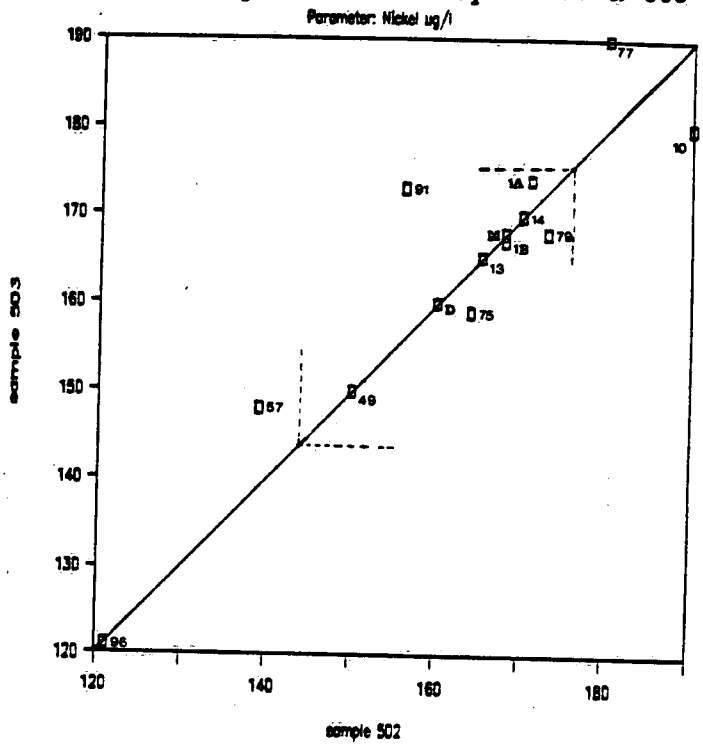
Paired Sample Plot - Samples 502 & 503



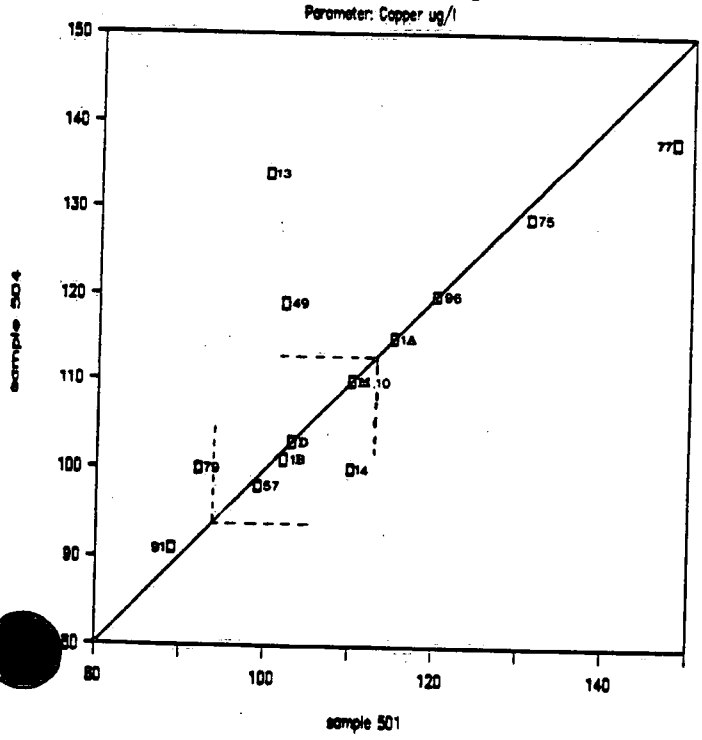
ired Sample Plot - Samples 501 & 504



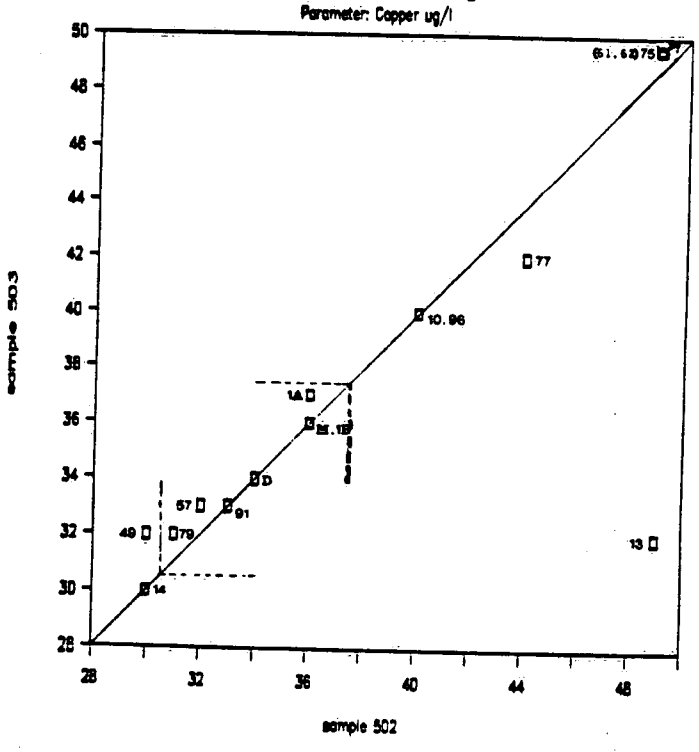
Paired Sample Plot - Samples 502 & 503



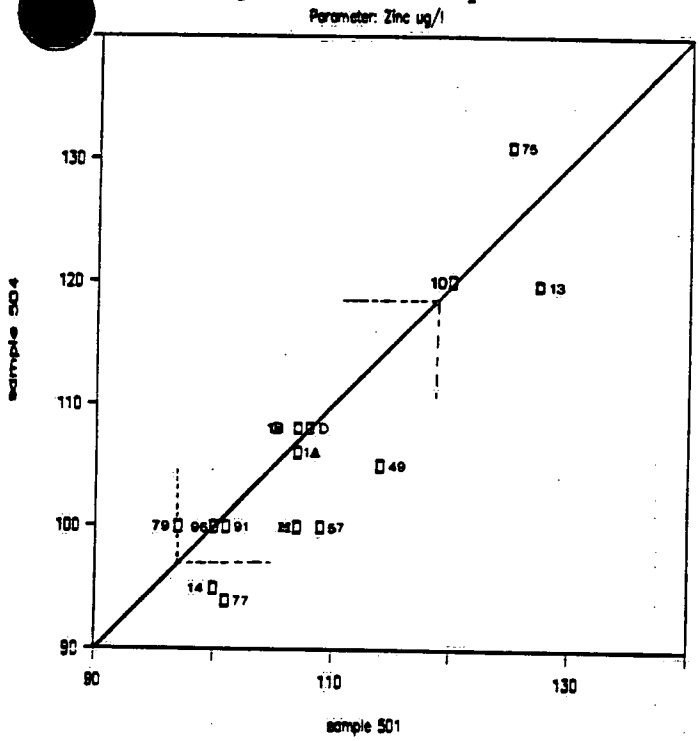
Paired Sample Plot - Samples 501 & 504



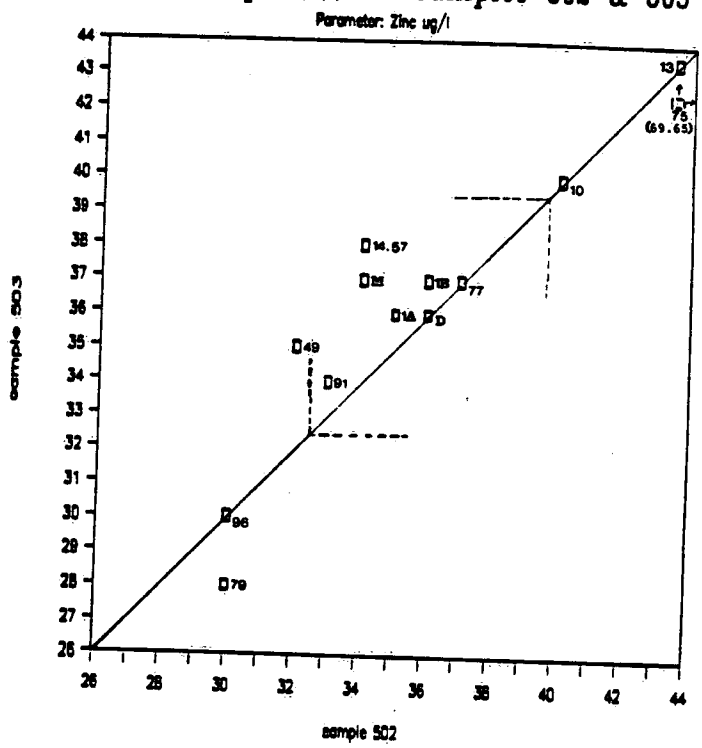
Paired Sample Plot - Samples 502 & 503



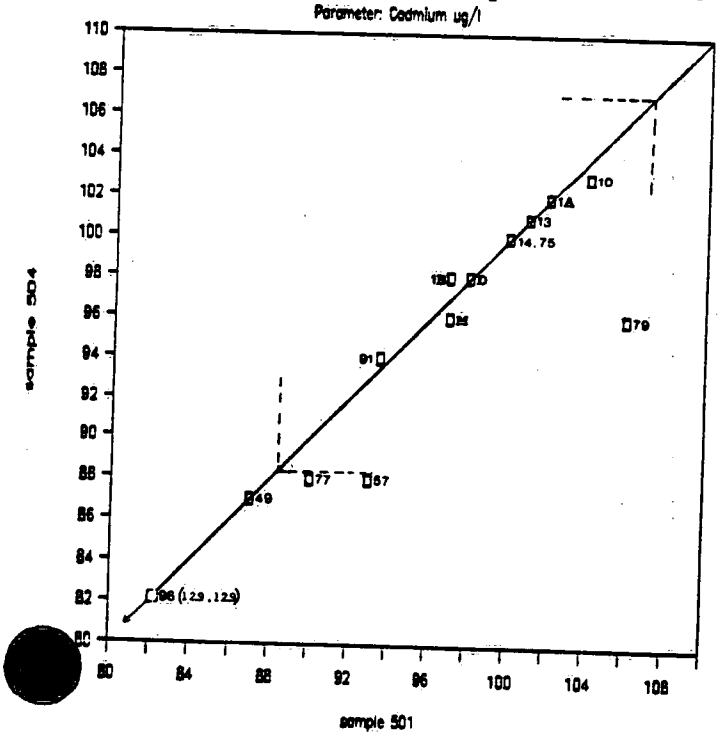
Paired Sample Plot - Samples 501 & 504



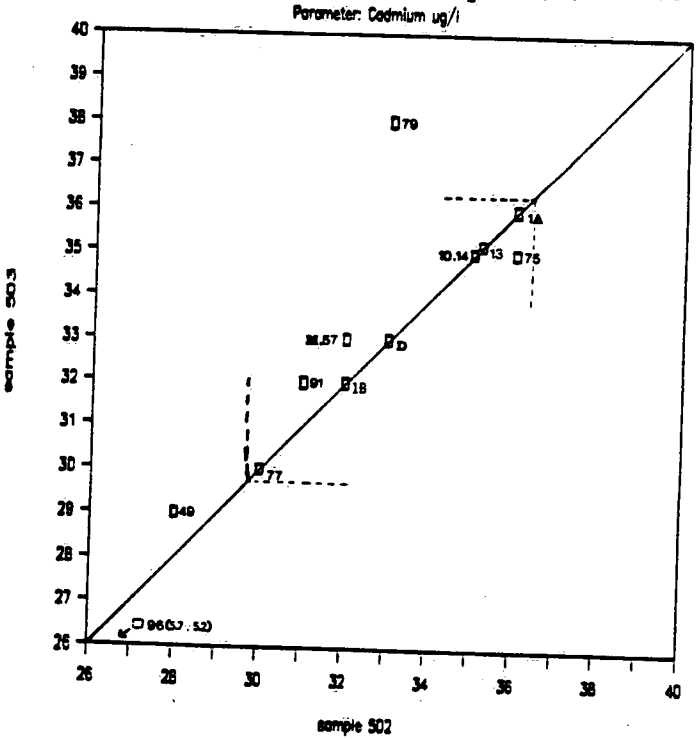
Paired Sample Plot - Samples 502 & 503



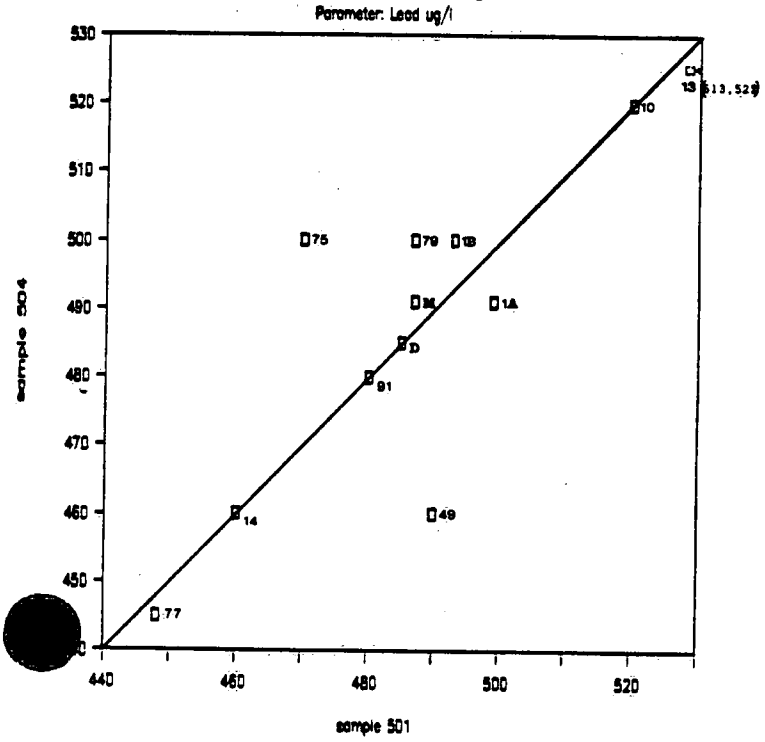
Paired Sample Plot - Samples 501 & 504



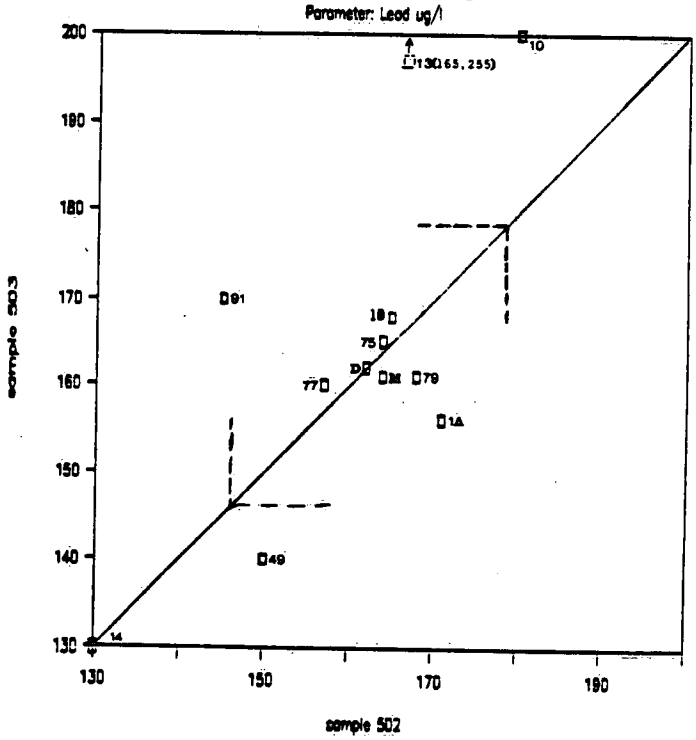
Paired Sample Plot - Samples 502 & 503



Paired Sample Plot - Samples 501 & 504



Paired Sample Plot - Samples 502 & 503



APPENDIX V

LATE DATA SUBMITTED FOR

UGLCC INTERLABORATORY STUDY

QM-5

LATE DATA SUBMITTED BY LABORATORY U013

(Received on October 17, 1986)

	Sample (ug/l)				Detection Limit
	501	502	503	504	
iron	Nd *	Nd *	Nd *	Nd *	Nd *
cobalt	288.6	115.0	86.09	288.6	Nd *
nickel	564.9	165.2	165.2	524.9	2.04
copper	99.9	49.0	32.0	133.9	3.95
zinc	127.4	434.8	434.8	119.7	16.47
cadmium	101.0	35.19	35.19	101.0	2.07
lead	612.8	165.4	254.9	523.3	5.57

* Nd - not determined

Methodology

50 ml sample acidified with 5 ml concentrated nitric acid.

Reduced to ≈ 3 ml on water bath and diluted to 50 ml with distilled deionized water.

Extracts were analyzed by an Atomic Absorption Spectrophotometer - flame.

CHANGES TO DATA SUBMITTED BY LABORATORY U013

(Received on December 2, 1986)

	Sample (µg/l)				Detection Limit
	501	502	503	504	
Zinc	127.4	43.5	43.5	119.7	16.47