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UPPER GREAT LAKES CONNECTING CHANNELS INTERLABORATORY PERFORMANCE EVALUATION STUDY QM-9: TOTAL MERCURY IN SURFACE WATER FINAL REPORT

by

R. Szawiola, W. Horn and D. Takeuchi

Research and Applications Branch
National Water Research Institute
Canada Centre for Inland Waters
Burlington, Ontario, Canada

and the Quality Management Work Group

October 1987

UPPER GREAT LAKES CONNECTING CHANNELS

INTERLABORATORY PERFORMANCE EVALUATION STUDY

QM-9: TOTAL MERCURY IN SURFACE WATER

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and

The Quality Management Work Group

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 13 interlaboratory performance evaluation studies were implemented.

This report describes the results from the ninth interlaboratory performance evaluation study, QM-9 which consisted of the analysis of total mercury in water samples. Results were received from seven Canadian and four U.S. laboratories out of twelve original participants. Overall, 60% of the data reported was satisfactory and comparable. Accuracy seemed to be more of a problem than precision. All participating laboratories have been provided with appropriate feed-back.

Dr. J. Lawrence
Director, Research and Applications Branch
National Water Research Institute

PERSPECTIVE -GESTION

Les chenaux reliant les Grands Lacs d'amont (CRGLA) ont été désignés comme des "secteurs préoccupants" par la Commission mixte internationale. Une étude binationale Canada - É-U. portant sur l'identification et l'évaluation des impacts environnementaux des substances toxiques dans ces zones a été entreprise en 1984. Un Groupe de travail sur la gestion de la qualité a été mis sur pied et 13 études interlaboratoires d'évaluation de la performance ont été faites afin d'aider les laboratoires analytiques qui fournissent des données pour l'étude des CRGLA.

Le présent document décrit les résultats de la neuvième étude interlaboratoire d'évaluation de la performance, QM-9, qui consistait à doser le mercure total des échantillons d'eau. Des douze participants originaux, sept laboratoires du Canada et quatre des Etats-Unis ont fait parvenir leurs résultats. Dans l'ensemble, 60 % des données signalées étaient satisfaisantes et comparables. L'exactitude semblait présenter plus de problèmes que la précision. Tous les laboratoires participants ont reçu une rétroaction appropriée.

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, thirteen interlaboratory performance evaluation studies were designed and conducted by the Quality Management Work Group.

This report describes the results from the ninth interlaboratory performance evaluation study, QM-9, which consisted of the analysis of mercury in surface water samples. Results were received from 11 out of 12 participating laboratories (seven Canadian, four U.S.). Data was evaluated for bias using Youden's ranking technique and results which deviated significantly from the median values were flagged. There was good agreement between the medians and the design values. Precision seemed to be less of a problem than accuracy. Included in this report is a summary of each laboratory's performance.

RÉSUMÉ

L'étude des chenaux reliant les Grands Lacs d'amont (CRGLA) reconnaît que les aspects assurance de la qualité/contrôle de la qualité (AQ/CQ) sont des éléments vitaux pour l'utilité globale des résultats de l'étude. Dans le cadre du programme AQ/CQ, treize études interlaboratoires d'évaluation de la performance ont été conçues et faites par le Groupe de travail sur la gestion de la qualité.

Le présent document décrit les résultats de la neuvième étude interlaboratoire d'évaluation de la performance, QM-9, qui consistait à doser le mercure dans des échantillons d'eau de surface. Onze des douze laboratoires participants ont présenté leurs résultats (sept du Canada et quatre des Etat-Unis). On a vérifié si les données contenaient des erreurs à l'aide de la technique de classement Youden et les résultats qui s'écartaient considérablement des valeurs médianes ont été marqués. Il y avait une bonne corrélation entre les valeurs médianes et les valeurs nominales. Le problème ne résidait pas tant du côté de la précision que de l'exactitude. Ce rapport comprend également un résumé de la performance 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, thirteen 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 the 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 ninth interlaboratory study, QM-9, was initiated on February 28, 1986. It involved the analysis of mercury in surface water. The original deadline for reporting results was set for May 15, 1986. However, since several laboratories were late in reporting, the study was not closed until September 30, 1986.

STUDY PROFILE

From the returned questionnaires, the following 12 laboratories confirmed their participation in this study: U001, U010, U014, U049, U057, U075, U077, U078, U079, U091, U013 and U090. By the time this study was closed (September 30, 1986), the last two laboratories had not submitted any results. Laboratory U013 submitted results well after September 30, 1986 and the data summaries had been sent. See the list of participants at the end of this report.

Since erratic in-house standards and improper digestion have been shown to be major sources of error in mercury analysis, this study was designed to evaluate the accuracy of the participants' calibration standards and digestion procedures for total mercury.

Each laboratory was provided with four preserved solutions as described in Table 1. All standard solutions and test samples were prepared by the Quality Assurance Project Team, Research and Applications Branch of the National Water Research Institute (NWRI). An organic mercury stock solution was prepared gravimetrically from primary standard grade phenyl mercuric nitrate which had been obtained from Eastman Kodak and had a purity of 97%. The working solutions were obtained after serial dilution of the stock solution with distilled deionized water to an appropriate range. The accuracy of the design values was confirmed by internal analysis on two separate dates. The design values and interlaboratory medians are presented in Table 2.

Participants were asked to analyze the four samples, which had been preserved with sulphuric acid and potassium dichromate, for total mercury using in-house procedures and standards. In order to provide some indication of analytical precision, the samples were sent out in blind duplicate pairs as shown in Table 1.

RESULTS AND DISCUSSION

Analytical Methodology

Out of eleven laboratories reporting results, ten used "strong acid" digestion (a combination of H_2SO_4, HNO_3, $K_2S_2O_8$, $KMnO_4$ and/or $K_2Cr_2O_7$), cold vapour generation (either by $SnCl_2$ or $SnSO_4$ reduction) and atomic absorption spectroscopy or mercury monitor for detection. Only one laboratory analyzed the samples by $NaBH_4$ hydride generation without digestion. See Table 3 for details of sample preparation and detection.

Data Evaluation

All raw data submitted by the participants are listed in the data summary (Appendix II) except for laboratory U013 whose results can be found in Appendix IV. The total mercury results were evaluated by the Youden ranking technique (1) for the detection of bias, as well as a computerized flagging procedure (2). 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. The overall accuracy of mercury 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 and flags are presented for each laboratory.

Paired sample plots have been included as a graphical illustration of systematic vs random errors for precision and accuracy of the participants' data (see Appendix III). The diagonal line, in the plots, is a 45° line passing through the design levels of the 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 (3). The closer the laboratories' values are to the diagonal line, the better their precision.

General Comments

Only three of the nine reporting laboratories submitted their data by the originally set deadline (U001, U014, U075) while seven laboratories made the second closing date. Laboratory U013 submitted their results on December 2, 1986 after the final data summary had been sent out. Therefore, their results were not included with the other data, but can be found in Appendix IV.

Computer printouts with the raw data were sent to all reporting laboratories for verification on October 10, 1986. All results were verified as they had been reported.

A final data summary was sent to the participating laboratories, the Quality Management Work Group, the Work Group chairmen and the MC and AIC chairmen on November 19, 1986.

The interlaboratory relative standard deviation (RSD) was poor, ranging from 27% to 57%. The difference between the design value and the median was less than 10%. The difference between the median and the mean was less than 7% for all samples, except for sample 902 (16%).

According to the Youden plots, most laboratories' results were precise, but not as accurate. Laboratory U075 results were low and laboratory U079 results were high indicating a systematic problem.

Laboratory Specific Comments

Laboratory U001 results were accurate and precise with no flags or bias. Precision was within an RSD of 3%.

Laboratory U010 had one VL flag. Precision was poor for samples 901 and 904 (RSD of 33%), while identical values were reported for samples 902 and 903.

Late results for laboratory U013 were satisfactory and precision was good for one set of samples (902, 903 - RSD 3%), but higher for the other set (901, 904 - RSD 14%).

For laboratory U014 results for samples 902 and 903 were reported as less than values. The design values for these two samples were below this laboratory's detection limits. Identical values were reported for samples 901 and 904.

Laboratory U049 had one VH and two H results. Precision was within an RSD of 3%.

Laboratory U057 had one VL and two L results and precision was not that good (901, 904 - RSD 9%; 902, 903 - RSD 23%). Improper or incomplete digestion may be the cause.

Laboratory U075 had biased low results and all four results were flagged VL. Precision was within an RSD of 8%. Digestion procedures may be satisfactory although an inaccurate standard solution may be a problem.

Laboratory U077 had accurate and precise results with no flags or bias. As identical results were reported the RSD was 0%.

Laboratory U078 had one VH flag. Precision was within an RSD of 7% for 901 and 904 and 47% for 902 and 903.

Laboratory U079 had biased high results with one H flag and three VH flags. The design values for samples 902 and 903 were close to this laboratory's detection limit. Precision was within an RSD of 9% for 901 and 904 and identical results were reported for 902 and 903.

Laboratory U091 had accurate and precise results with no flags or bias. Precision was within an RSD of 3%.

ACKNOWLEDGEMENTS

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LIST OF PARTICIPANTS

Barringer Magenta Ltd., Rexdale, Ontario

Beak Analytical Services, Mississauga, Ontario.

Detroit Wastewater Treatment Plant, Analytical Laboratory, Detroit, Michigan.

Mann Testing Laboratories Ltd., Mississauga, Ontario.

Michigan Department of Natural Resources, Lansing, Michigan.

National Water Quality Laboratory, Burlington, Ontario.

Ontario Ministry of the Environment, Inorganic Trace Contaminants, Rexdale, Ontario.

Ontario Ministry of the Environment, Thunder Bay, Ontario.

Raytheon Service Corporation (U.S. EPA - Large Lakes Research Station), Grosse Ile, Michigan.

U.S. Geological Survey - NWQL, Arvada, Colorado.

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

The following laboratory requested samples, but did not submit any results:

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

REFERENCES

1 Youden, W.M. and Steiner, E.H. Statistical Manual of ADAC, published by AOAC, P.O. Box 540, Benjamin Franklin Station, Washington, D.C. 20044 (1975).

2. Clark, J.L., Evaluation of Performance of Laboratories Determining Water Quality Constituents Through Natural Water Samples Whose True Values are Unknown. In summary of Conference Presentations, Environmetrics 81, pages 54-55, 1981. Alexandria, Virginia, April 8-10, 1981.

3. Lee, H.B. and Chau, A.S.Y. National Interlaboratory Quality control Study No. 25: PCB's in Wet Sediments. NWRI report series No. 71, page 2, 1981.

TABLE 1

Samples Distributed for Study QM-9

Sample	Description
901	0.60 ug/L mercury (as phenyl mercuric nitrate)
902	Sample 901 diluted to 40% (0.24 ug/L mercury)
903	Same as 902
904	Same as 901

TABLE 2

Design Values and Interlaboratory Medians for Total Mercury

(all values are in ug/L)

Parameter	Design Value	Interlab. Median Sample 901	Interlab. Median Sample 904	Design Value	Interlab. Median Sample 902	Interlab. Median Sample 903
Total Mercury	0.60	0.575	0.570	0.24	0.250	0.260

TABLE 3

Analytical Methodology for Total Mercury

Lab No.	Sample Preparation	Detection	Detection Limit (ug/L)
U001	H_2SO_4, HNO_3, $K_2S_2O_8$, $KMnO_4$ at 105°C; $(NH_2OH)_2.H_2SO_4$	$SnSO_4$ cold vapour reduction; automated A.A.S.	0.01
U010	H_2SO_4, HNO_3, $K_2S_2O_8$, $KMnO_4$	$SnSO_4$, $NH_2OH.HCl$ cold vapour reduction A.A. Hg monitor	0.01
U014	H_2SO_4, HNO_3, $KMnO_4$, $K_2S_2O_8$ @95°C; $NH_2OH.HCl$	$SnCl_2$ cold vapour reduction; Perkin Elmer MHS-20 hydride system + 306 A.A.	0.5
U049	H_2SO_4, HNO_3, $KMnO_4$, $K_2S_2O_8$ @95°C; H_2O_2	$SnSO_4$, $(NH_2OH)_2.H_2SO_4$ cold vapour reduction; Perkin Elmer 403 A.A.	0.02
U057	HNO_3, H_2SO_4, $KMnO_4$; $NH_2OH.HCl$	$SnCl_2$ cold vapour reduction; Laboratory Data Control 1205 mercury monitor	0.05

TABLE 3

Analytical Methodology for Total Mercury - (continued)

Lab No.	Sample Preparation	Detection	Detection Limit (ug/L)
U075	$K_2Cr_2O_7$, HNO_3 @90°C, $KMnO_4$	$NH_2OH.HCl$, $SnCl_2$ cold vapour reduction; Fisher Hg-3 mercury analyzer	0.03
U077	H_2SO_4, $K_2Cr_2O_7$, $K_2S_2O_8$ at 95°C; $NH_2OH.HCl$	$SnCl_2$ cold vapour reduction; automated A.A.S.	0.1
U078	not applicable	$NaBH_4$ hydride generation; Perkin Elmer A.A.S.	0.1
U079	HNO_3, H_2SO_4, $KMnO_4$, $K_2S_2O_8$ @121°C; $NH_2OH.HCl$	$SnCl_2$ cold vapour reduction; Perkin Elmer MAS-50A mercury analyzer.	0.2
U091	H_2SO_4, HNO_3, $KMnO_4$ $K_2S_2O_8$ @95°C; $NH_2OH.HCl$	$SnSO_4$ cold vapour reduction; LDC mercury monitor.	0.03

Table 4

Summary of Mercury results by laboratory based on the Flagging and Youden Procedures (see Appendix II)

Lab Code	No. of results reported	No. of results flagged VH	H	L	VL	% Flagged*	Comments
U001	4	0	0	0	0	0	Satisfactory
U010	4	0	0	0	1	25	Flagged VL on sample 904
U014	4(2"<")	0	0	0	0	0	Samples 902, 903 are unuseable ("<" values)
U049	4	1	2	0	0	50	Flagged VH on sample 901; flagged H on samples 902, 904
U057	4	0	0	2	1	50	Flagged VL on sample 902; flagged L on samples 903, 904
U075	4	0	0	0	4	100	Biased low; flagged VL on all 4 samples
U077	4	0	0	0	0	0	Satisfactory
U078	4	1	0	0	0	25	Flagged VH on sample 902
U079	4	3	1	0	0	88	Biased high; flagged H on sample 901; flagged VH on samples 902, 903, 904
U091	4	0	0	0	0	0	Satisfactory

* H and L flags are counted as half of a VH or VL flag.

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 this 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 24% error at LLBAE is considered reasonable for mercury 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 biasd 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.

H : high
VH : very high
L : low
VL : very low
LTV : less than value (<)

APPENDIX II

UGLCC Interlaboratory Performance Evaluation Study

QM-9: TOTAL MERCURY IN SURFACE WATERS

Data Summaries

QM9 MERCURY IN WATER

PRINTOUT PREPARED: 86/11/25.

PARAMETER: MERCURY UG/L

SAMPLE RESULTS

LAB	901		902		903	904
U001	.61		.27		.28	.59
U010	.55		.24		.24	.34
U014	.5	<	.5	<	.5	.5
U049	.73		.32		.31	.70
U057	.52		.13		.18	.46
U075	.19		.09		.08	.17
U077	.6		.2		.2	.6
U078	.50		.60		.30	.55
U079	.7		.5		.5	.8
U091	.60		.25		.26	.62
TOTAL LABS REPORTING	10		10		10	10
TOTAL LABS USED	10		9		9	10
MEAN	.55000		.28889		.26111	.53300
STD DEV	.14870		.16556		.11450	.17957
MEDIAN	.57500		.25000		.26000	.57000
IGN VALUE	.60		.24		.24	.60

QM-9

Flagging and Youden's Ranking Procedures

PARAMETER: [redacted] MERCURY UG/L

QH9 MERCURY IN WATER

QUALITY ASSURANCE AND M[redacted]S SECTION
NATIONAL WATER RESEARCH INSTITUTE
BURLINGTON ONTARIO

LOWER LIMIT FOR USE OF BASIC ACCEPTABLE ERROR= .25 BASIC ACCEPTABLE ERROR= .06 CONCENTRATION ERROR INCREMENT= .10
LABORATORIES YET TO REPORT: U090, U092
LABORATORY RESULTS OMITTED ARE NONE

SAMPLE	901		902		903		904	
LAB NO	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK
U001	.61	8.00	.27	6.00	.28	6.00	.59	6.00
U010	.55	5.00	.24	4.00	.24	4.00	.34 VL	2.00
U014	.5	2.50	<.5	0.00	<.5	0.00	.5	4.00
U049	.73 VH	10.00	.32 H	7.00	.31	8.00	.70 H	9.00
U057	.52	4.00	.13 VL	2.00	.18 L	2.00	.46 L	3.00
U075	.19 VL	1.00	.09 VL	1.00	.08 VL	1.00	.17 VL	1.00
U077	.6	6.50	.2	3.00	.2	3.00	.6	7.00
U078	.50	2.50	.60 VH	9.00	.30	7.00	.55	5.00
U079	.7 H	9.00	.5 VH	8.00	.5 VH	9.00	.8 VH	10.00
U091	.60	6.50	.25	5.00	.26	5.00	.62	8.00
MEDIAN CONC.	.575		.250		.260		.570	

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	
U001	26.00	6.500	4		
U010	15.00	3.750	4	VL	
U014	6.50	3.250	2		
U049	34.00	8.500	4	VHHH	
U057	11.00	2.750	4	VLLL	
U075	4.00	1.000	4	VLVLVLVL	BIASED LOW
U077	19.50	4.875	4		
U078	23.50	5.875	4	VH	
U079	36.00	9.000	4	HVHVHVH	BIASED HIGH
U091	24.50	6.125	4		

OVERALL AVERAGE RANK IS 5.263

DETECTION LIMIT

.01
0.01
0.5
0.02
0.05
0.03
0.1
0.1
0.2
.03

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	
U075	4.00	1.000	4	VLVLVLVL	BIASED LOW
U057	11.00	2.750	4	VLLL	
U014	6.50	3.250	2		
U010	15.00	3.750	4	VL	
U077	19.50	4.875	4		
U078	23.50	5.875	4	VH	
U091	24.50	6.125	4		
U001	26.00	6.500	4		
U049	34.00	8.500	4	VHHH	
U079	36.00	9.000	4	HVHVHVH	BIASED HIGH

OVERALL AVERAGE RANK IS 5.263

METHOD CODING

0.03
0.05
0.5
0.01
0.1
0.1
.03
.01
0.02
0.2

MERCURY

APPENDIX III

YOUDEN'S TWO SAMPLE PLOTS

Legend for Youden Plots

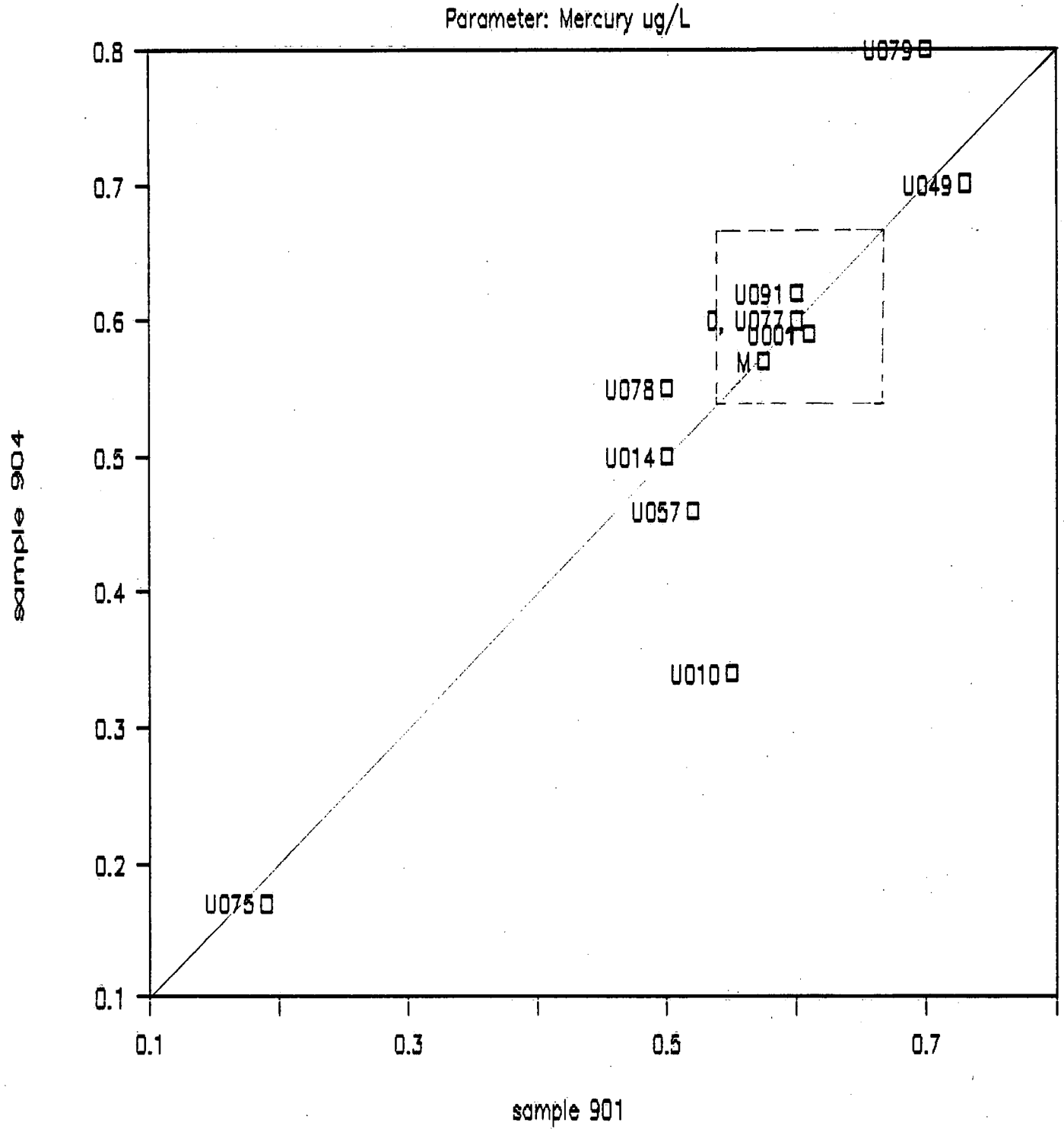
 Laboratories

D Design value

M Interlaboratory median

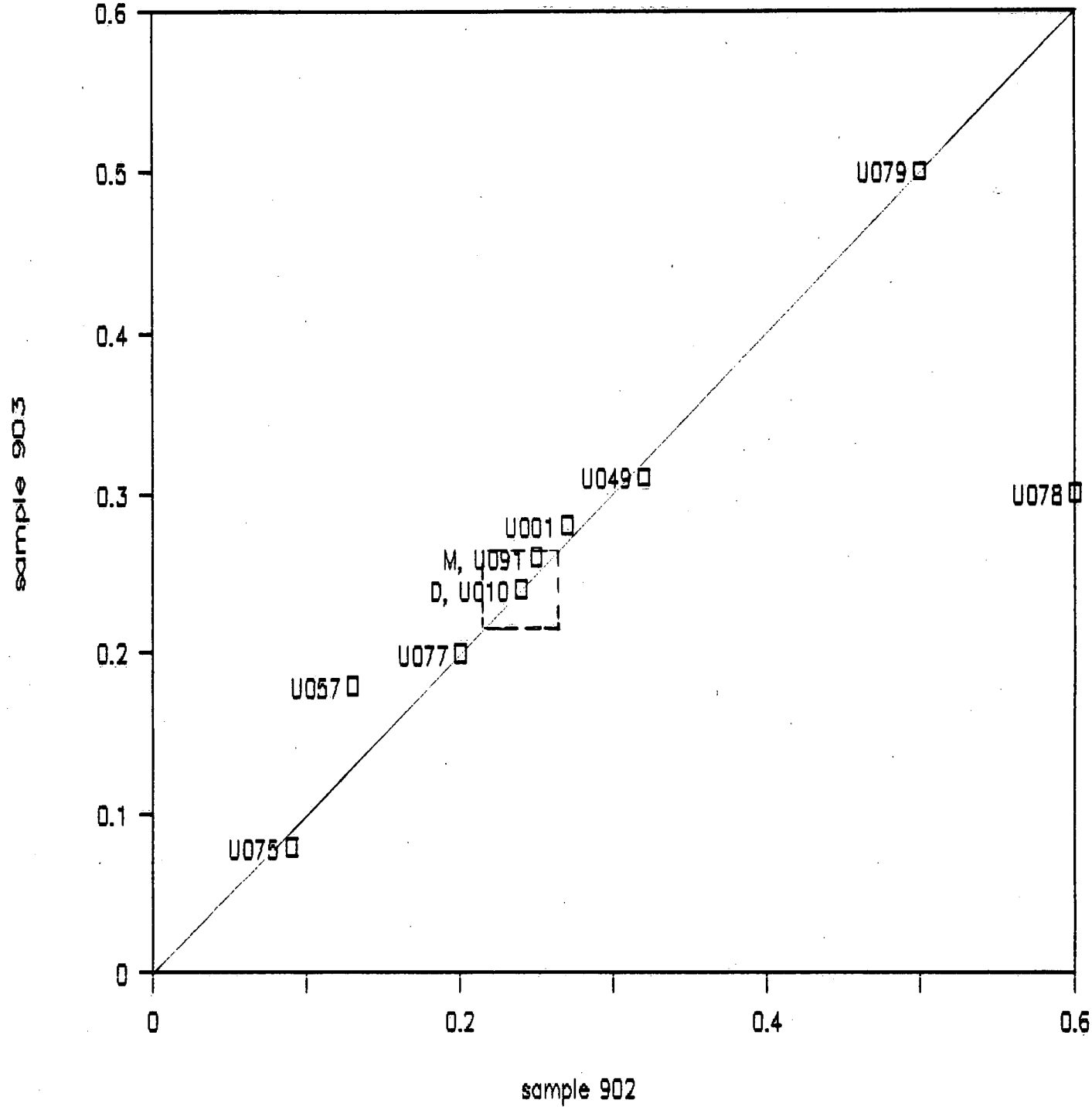
 ±10% of the design value

Paired Sample Plot - Samples 901 & 904



Paired Sample Plot - Samples 902 & 903

Parameter: Mercury ug/L



APPENDIX IV

LATE DATA SUBMITTED FOR
UGLCC INTERLABORATORY STUDY
QM-9

APPENDIX IV

Late Data Submitted by Laboratory U013

(Received on December 2, 1986)

	Detection Limit	901	902	903	904
Hg ug/L	0.003	0.61	0.25	0.24	0.50

Methodology

Sample preparation:

$KMnO_4$, HNO_3, $K_2S_2O_8$, H_2SO_4 @80°C for 1.5 hrs.; $NH_2OH.HCl$

Detection:

$SnCl_2$ reduction, Perkin Elmer 603AAS + MHS-20 analyzer