Government of India & Government of The Netherlands

Technical Assistance
HYDROLOGY PROJECT

DHV CONSULTANTS & DELFT HYDRAULICS with HALCROW, TAHAL, CES, ORG & JPS

Findings of
Inter-Laboratory AQC Exercise

July 1999

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1 Background

Analytical Quality Control (AQC) is one of the main components of a Quality Assurance (QA) system, wherein the quality of analytical data being generated in any laboratory is controlled through minimising or controlling errors to achieve a target accuracy. A particular water quality study or any organised water quality monitoring programme involves the collection, comparison and interpretation of analytical data, which leads to a decision for the management and use of the water resource. The correctness of decision or action depends largely upon the accuracy of the analytical results. If the errors of the analytical results were high, the manpower, material and money spent on any monitoring programme or study would be futile and further lead to wrong decision and improper action plans.

The need for analytical quality control (AQC) in HP laboratories was first discussed in the 'Water Quality Standardization Workshop', December 9-10, 1996, Hyderabad. It was recommended that AQC exercises should be organized for the HP laboratories to achieve a target accuracy so that the results obtained from different laboratories are comparable. Consequently the following actions were taken:

- In May 1997, 30 HP laboratories were invited to participate in a *within*-laboratory AQC exercise covering only 4 routine parameters.
- The results of the exercise were discussed in two technical meetings, held at Bangalore and Bhopal and a report was issued in February 1998.
- A second round of the exercise covering 8 parameters was started in March 1998. The results of the second round were reported in June 1999.
- Since the *within*-laboratory AQC exercise evaluates only the precision of the laboratory, an *inter*-laboratory exercise was conducted in December 1998 to test the bias of the laboratories. The Central Pollution Control Board (CPCB) laboratory acted as the reference laboratory for this exercise.

Thirty three laboratories were invited to participate in the *inter*-laboratory AQC exercise. Out of these 25 laboratories responded by sending the required fee to the CPCB laboratory. The present report gives the result of the exercise.

The CPCB laboratory organised the exercise and did the statistical analysis of the data.

2 Objectives

The objectives of an *inter*-laboratory AQC programme are:

- to assess the status of analytical facilities and capabilities of participating laboratories.
- to identify the serious constraints (random & systematic) in the working environment of laboratories.
- to provide necessary assistance to the concerned laboratories to overcome the short comings in the analytical capabilities.
- to promote the scientific and analytical competence of the concerned laboratories to the level of excellence for better output.
- to enhance the internal and external quality control of the concerned laboratories

3 Methodology

3.1 Standard samples

The following 9 parameters were covered under the present exercise:

1. Conductivity (COND)
2. Total dissolved solids (TDS)
3. Total Hardness (TH)
4. Fluoride (F)
5. Sulphate (SO4)
6. Nitrate –N.(NO3-N)
7. Phosphate –P (PO4-P)
8. Sodium (Na)
9. Boron (B)

The above parameters were selected for the exercise because the procedures for their determination involve various analytical techniques, namely, potentiometric (COND), gravimetric (TDS), titrimetric (TH), absorption-spectrometric (F, NO3-N, PO4-P, B), nephelometric (SO4) and emission-spectrometric (Na) and common laboratory operations such as weighing, heating, filtering, etc. These tests are routinely carried out in the HP laboratories for characterisation of surface and groundwaters. Thus, capability of a laboratory to perform these tests satisfactorily would indicate its preparedness to carry out its assigned HIS functions.

Two synthetic test samples, A and B, were prepared by mixing different volumes of 7 different solutions made from high quality chemicals and distilled water. The list of solutions and their strengths and the volumes used for each sample are given in Annexe I.

The samples were distributed to all the 25 participating laboratories through Courier service to avoid any transport delay. A copy of the instructions sent with the samples is given in Annexe II.

3.2 Reference value

The strength of the samples was determined in three different ways:

- by the recommended analytical procedure in the CPCB laboratory
- from theoretical considerations assuming that the solutions were made correctly and that the purity of the chemicals used was as displayed on the bottle labels
- from the combined results of analysis of the participating laboratories.

The procedure of estimation of the value of a parameter from the combined analysis results of the participating laboratories is illustrated for the conductivity measurements of samples A and B in Annexe III. Briefly, the data were first subjectively scrutinised for removal of outliers. This was followed by calculating the mean, X, of the remaining data and the 95 % confidence limits for the mean. The data values within the 95 % confidence limits were filtered out for calculating the reference mean, X_R.

Table 1 compares the concentrations of the parameters in the test samples estimated by the three procedures. It is seen that there is a close agreement among the values calculated by the three methods. Therefore the reference mean, calculated from the combined results of analysis of the participating laboratories, was taken as the reference value.

Table 1 Determination of concentration of parameters for test samples A and B

S. No	Parameter[a]	Sample- A			Sample- B		
		Reference mean	CPCB	Theoretical	Reference mean	CPCB	Theoretical
1	Conductivity	333.4	340	335	192.4	198	190
2	TDS	189.1	183	178	114.3	110	101
3	Total Hardness	55.2	54	50	29.1	32	27
4	Fluoride	1.92	2.02	2.00	1.33	1.37	1.40
5	Sulphate	25.7	24.2	25	13.6	13.0	14.0
6	Nitrate - N	3.87	3.85	4.00	2.37	2.43	2.50
7	Phosphate-P	0.448	0.485	0.500	0.250	0.267	0.275
8	Sodium	34.43	34	32.00	20.06	20.00	18.00
9	Boron	1.215	1.260	1.500	0.691	0.670	0.750

a - mg/l, except Conductivity, which is expressed in micro mho/cm

3.3 Acceptable range for reported values

In order to determine the acceptable range for reported values, the standard deviation, S_R, of the filtered data set was multiplied by $\sqrt{2}$ to adjust the, 'Within Run Precision' to 'Between Day Precision', S_{adj}. This was done to account for the fact that the analyses were performed at different times at different locations. The acceptable range was then calculated as $X_R \pm 3S_{adj}$. The procedure is illustrated for the conductivity results in Annex III.

A laboratory was considered to qualify for the analysis of a parameter if both the reported analyses results for the two samples A and B were in the acceptable ranges.

4 Findings and discussion

Table 2 gives the reference values and the acceptable ranges for the parameters covered in the exercise. These were calculated according to the procedure described in sections 3.2 and 3.3

Table 2 Reference values and acceptable ranges for results of analyses

Parameter[a]	Sample A		Sample B	
	Reference value	Acceptable range	Reference value	Acceptable range
Conductivity	333.4	306.6 – 360.3	192.4	177.8 – 207.0
TDS	189.1	149.9 – 228.4	114.3	89.5 – 139.1
Total Hardness	55.2	47.6 – 62.8	29.1	24.4 – 33.8
Fluoride	1.92	1.54 – 2.31	1.33	1.18 – 1.49
Sulphate	25.7	20.9 – 30.4	13.6	9.98 – 17.1
Nitrate - N	3.87	2.42 – 5.31	2.37	2.03 – 2.71
Phosphate-P	0.448	0.377 – 0.518	0.250	0.208 – 0.292
Sodium	34.43	31.85 – 37.00	20.06	17.90 – 22.21
Boron	1.215	1.063 – 1.366	0.691	0.607 – 0.775

a-mg/L, except Conductivity, which is expressed in micro mho/cm

Based on these values the performance of the laboratories was evaluated. The reported analysis results for the two samples for each parameter were compared with the respective acceptable ranges. The findings are summarised in Table 3. The following observations can be made regarding the performance of the laboratories:

- Out of the 25 laboratories that participated in the AQC exercise only 6 laboratories could provide results for all the 9 parameters.

- The decreasing order of response for various parameters was as follows: Total Hardness, 100 %; Conductivity, 96%; Sodium, 96%; Fluoride, 88%; Sulphate, 88%; Total Dissolved Solids, 84%; Nitrate - N; 84%; Phosphate-P, 52%; Boron, 32% .

- The poor response for the parameters like PO4-P(52%) and B (32%) may be due to lack of chemicals.

Table 3 Evaluation of analysis results in comparison with the reference values

Laboratory code	Cond	TDS	TH	F	SO4	NO3-N	PO4-P	Na	B	No. in acceptable range.	Total no. reported
401	√	√	X	X	√	√	√	X	X	5	9
402	√	NR	X	X	√	√	NR	√	NR	4	6
403	√	√	X	X	X	X	X	X	√	3	9
404	X	√	X	X	X	X	NR	√	NR	2	7
405	√	X	X	X	X	X	√	X	NR	2	8
406	√	√	X	X	X	X	NR	X	NR	2	7
407	√	X	X	X	X	NR	NR	X	NR	1	6
408	X	NR	X	√	X	X	NR	X	NR	1	6
409	X	X	√	X	√	X	√	√	NR	4	8
410	√	NR	√	√	√	X	√	X	√	6	8
411	X	X	X	X	X	X	NR	√	NR	1	7
412	X	X	√	√	√	√	NR	X	NR	4	7
413	NR	√	√	X	NR	NR	NR	X	NR	2	4
414	√	X	X	X	X	X	X	X	NR	1	8
415	√	X	√	√	√	X	X	√	√	6	9
416	X	X	√	X	√	√	X	√	NR	4	8
417	√	X	X	NR	NR	NR	NR	√	NR	2	4
418	X	X	√	X	X	X	NR	X	NR	1	7
419	X	X	√	NR	NR	NR	NR	X	NR	1	4
420	√	√	√	√	X	√	X	√	X	6	9
421	X	NR	√	X	√	√	X	√	NR	4	7
422	X	√	√	NR	X	√	NR	√	NR	4	6
423	√	√	X	√	√	√	X	√	X	6	9
424	X	X	√	X	√	√	X	NR	√	4	8
425	√	√	√	√	√	√	√	√	√	9	9
No. acceptable.	13	09	13	07	11	10	05	12	5		
Total reported.	24	21	25	22	22	21	13	24	8		
√ - within acceptable range				X – not in acceptable range				NR – not reported			

- Out of the 25 laboratories, which participated, only one laboratory was found qualifying in all the 9 parameters. On the lower side, 6 laboratories were found to qualify for only one parameter and 5 laboratories for only 2 parameters.

- Percent of laboratories, which reported the stated parameter within acceptable limits, are given in Table 4.

Table 4 Percent of laboratories, which reported the stated parameter in acceptable limits

S. No	Parameter	% of labs within limits
01	Boron	63 %
02	Conductivity	54 %
03	Total Hardness	52 %
04	Sulphate	50 %
05	Sodium	50 %
06	Nitrate - N	48 %
07	TDS	43 %
08	Phosphate-P	38 %
09	Fluoride	32 %
OVER All PERFORMANCE		47.2 %

- The overall performance of the laboratories was below expectation. Only about 50% of the laboratories could perform routine tests such as conductivity, total hardness, sulphate, and sodium to produce results, which were within acceptable limits. Only 32% of the laboratories could determine fluoride, which is a critical parameter for drinking water supplies particularly from groundwater sources, satisfactorily.

An overall view of the performance of laboratories for each parameter can be obtained from Youden 2-sample plots. Figures 1 to 9 give the plots for the 9 parameters covered under this exercise. For each parameter, the plot shows the value for sample A against that for sample B reported by a laboratory. Thus there is one data point for each laboratory for the two samples.

The acceptable limits for the two samples are also drawn on the plot as two parallel horizontal lines for the sample values plotted on the Y-axis and two parallel vertical lines for the sample values plotted on the X- axis.

The centre of the rectangular block created by the two sets of parallel lines is the reference value for the parameter. Results close to this point are considered to represent a high degree of accuracy.

The figure can be divided in 4 quadrants by drawing a vertical and a horizontal line through the reference value. If only random errors influence the determinations, the points would be expected to be randomly distributed in all the four quadrants. This is rarely seen. The points tend to concentrate in the first (++) or the third (--) quadrant, indicating that the laboratories tend to get, for both the samples, either high values or low values. This points to the

dominant role of systematic error. If a point lies on a line of unit slope passing through the reference value, then the determination has only systematic error.

An estimate of the random error and systematic error components of the total error (reported value minus reference value) can be obtained by drawing a perpendicular from a data point on the line of unit slope. The ratio of random error to the systematic error is equal to the ratio of the length of the perpendicular to the distance of the foot of the perpendicular to the reference value measured along the unit slope line.

The coefficient of variation of reported results, after excluding the outliers, is given in Table 5. It is expected that as the laboratories acquire better facilities and improve their technique, the coefficient of variation would decrease.

Table 5 Coefficient of variation of reported results, after excluding outliers

Parameter[a]	Sample A		Sample B	
	Reference value	Coefficient of variation	Reference value	Coefficient of variation
Conductivity	333.4	5.98	192.4	8.54
TDS	189.1	14.87	114.3	11.02
Total Hardness	55.2	10.37	29.1	16.84
Fluoride	1.92	17.42	1.33	11.29
Sulphate	25.7	17.26	13.6	17.17
Nitrate - N	3.87	22.28	2.37	16.00
Phosphate-P	0.448	10.29	0.250	17.07
Sodium	34.43	9.03	20.06	10.68
Boron	1.215	11.48	0.691	7.14

Though the identity of laboratories is not revealed in the plots, each laboratory can easily recognise its own result. In a few plots, one or two data points, which had an extremely large deviation from the reference value, had to be omitted. Otherwise, the plots include the outliers also.

It would be befitting to identify here the ***Geochemistry laboratory, PWD, Thanjavur, Tamil Nadu,*** the only laboratory which reported correct values for all the 9 parameters.

Figure 1. Performance of laboratories for Conductivity

Youden 2-sample plot

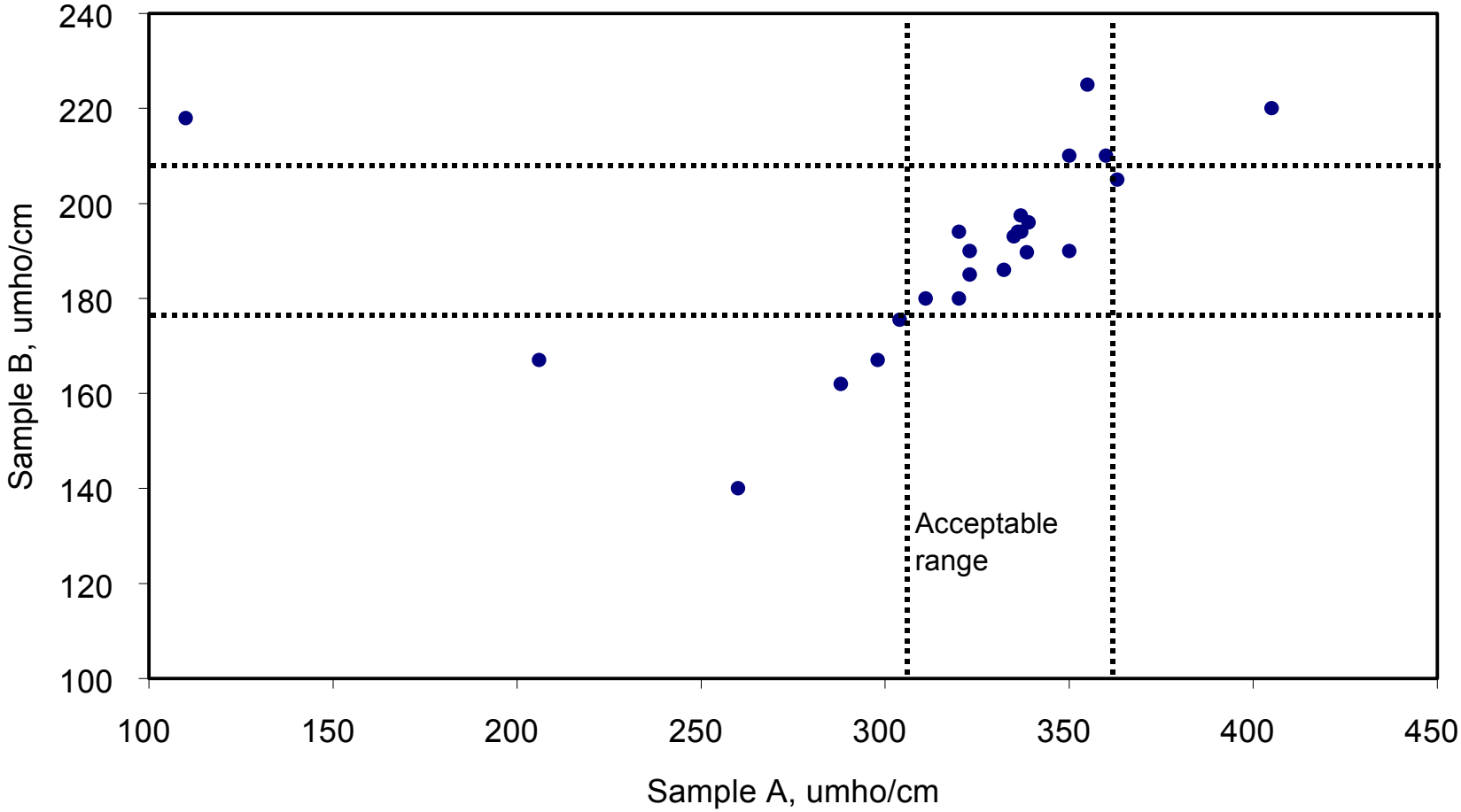


Figure 2. Performance of laboratories for Total Dissolved Solids

Youden 2-sample plot

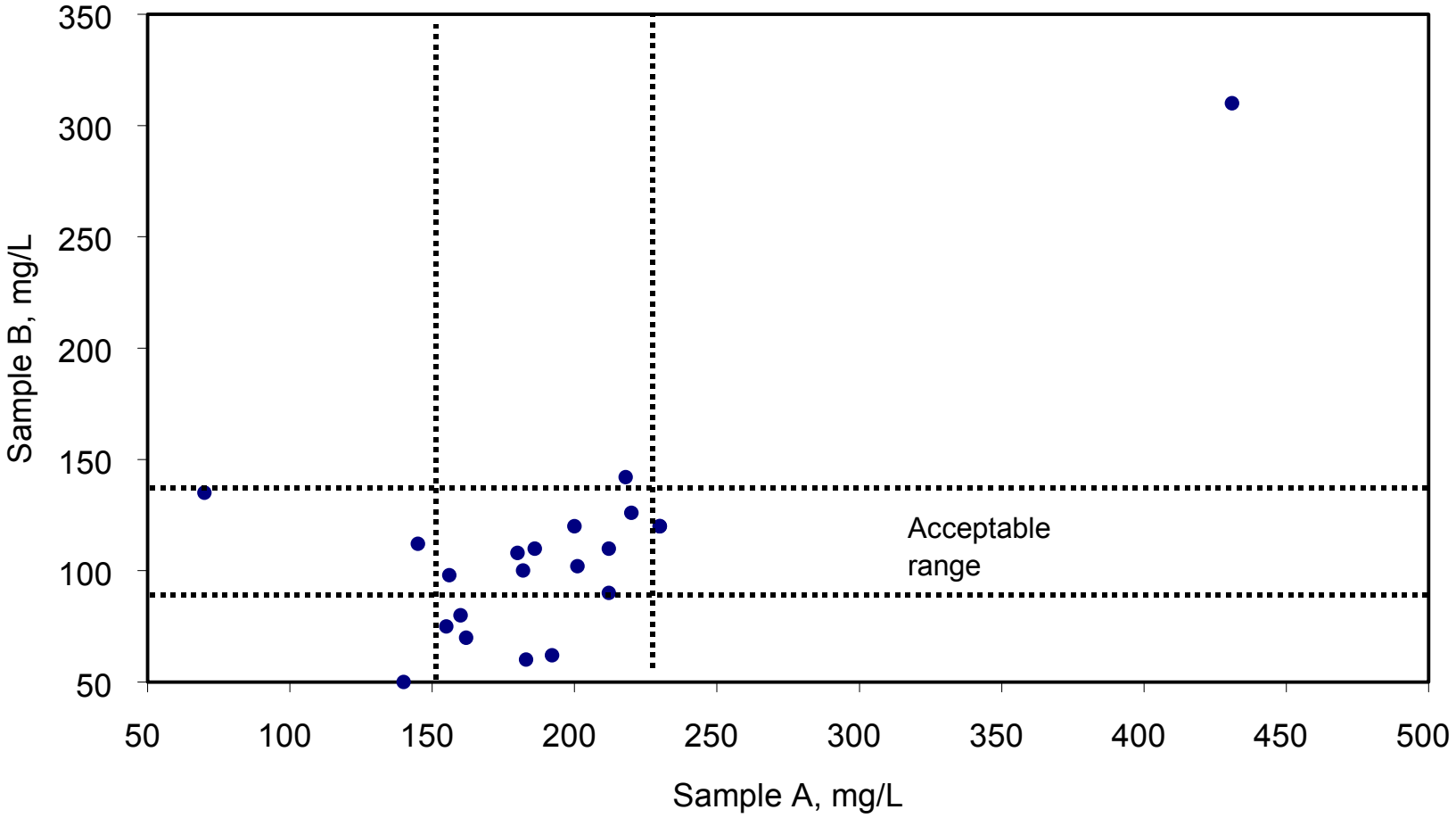


Figure 3. Performance of laboratories for Total Hardness

Youden 2-sample plot

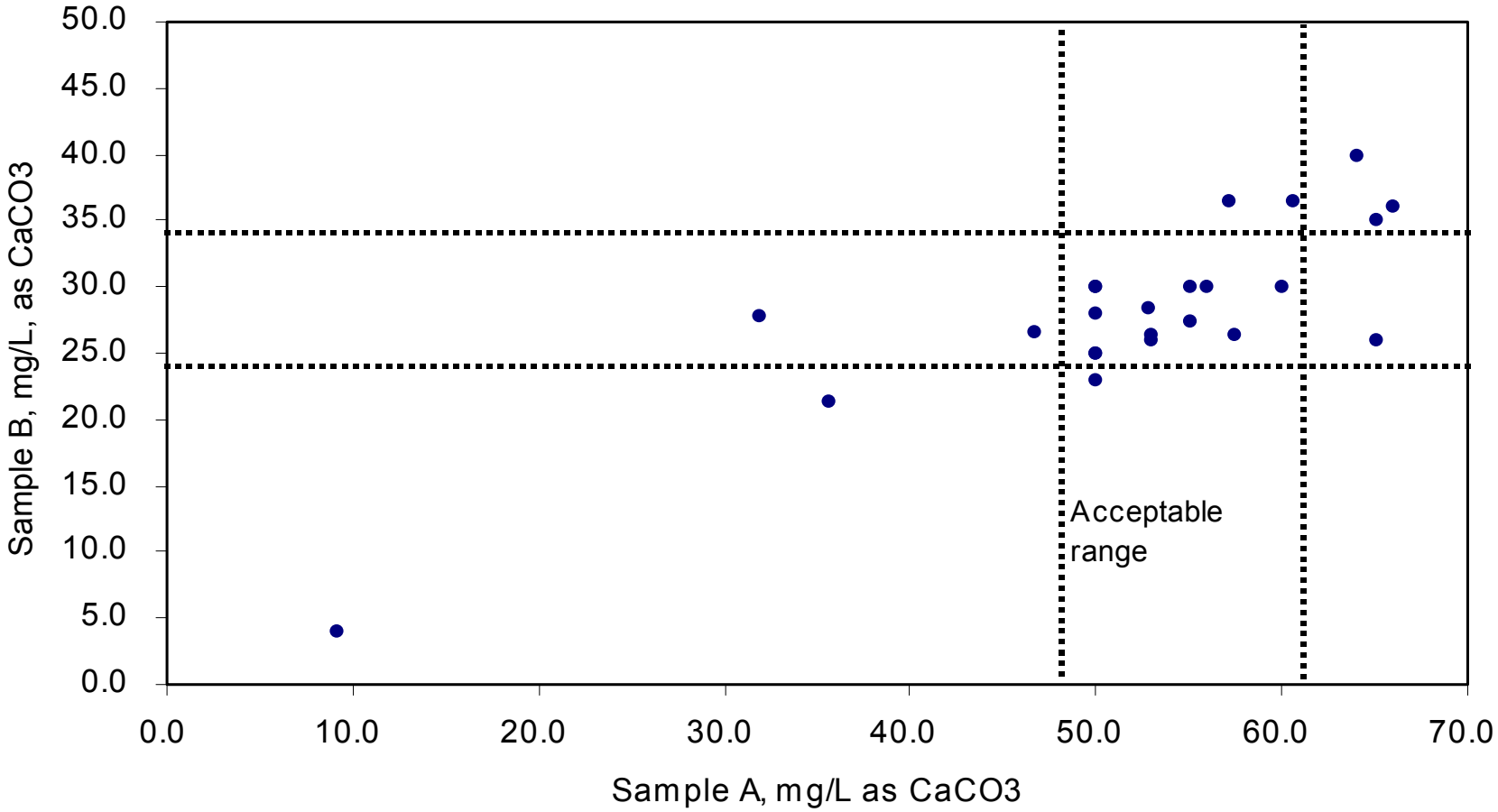


Figure 4. Performance of laboratories for Fluoride

Youden 2-sample plot

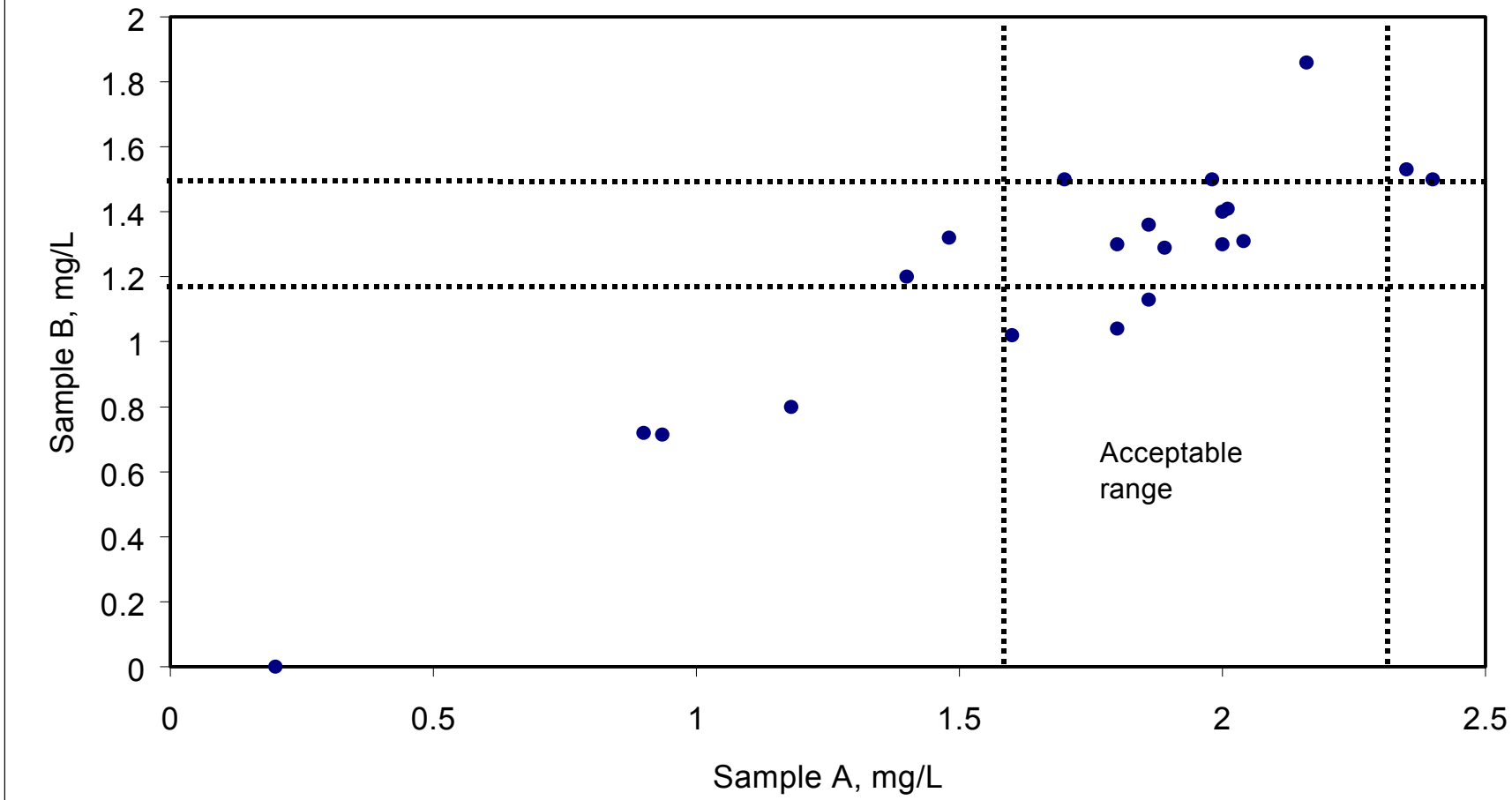


Figure 5. Performance of laboratories for Sulphate

Youden 2-sample plot

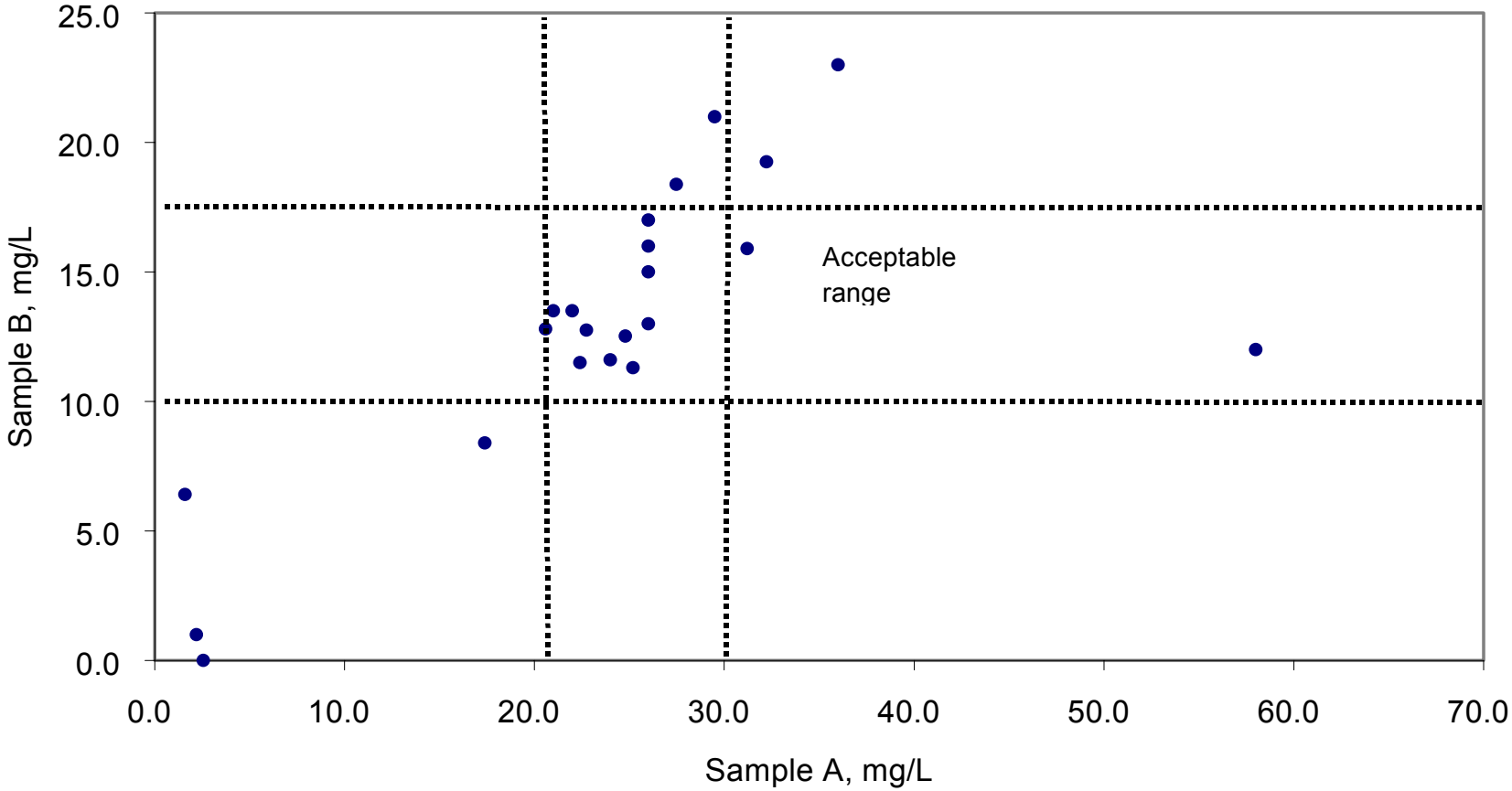


Figure 6. Performance of laboratories for Nitrate

Youden 2-sample plot

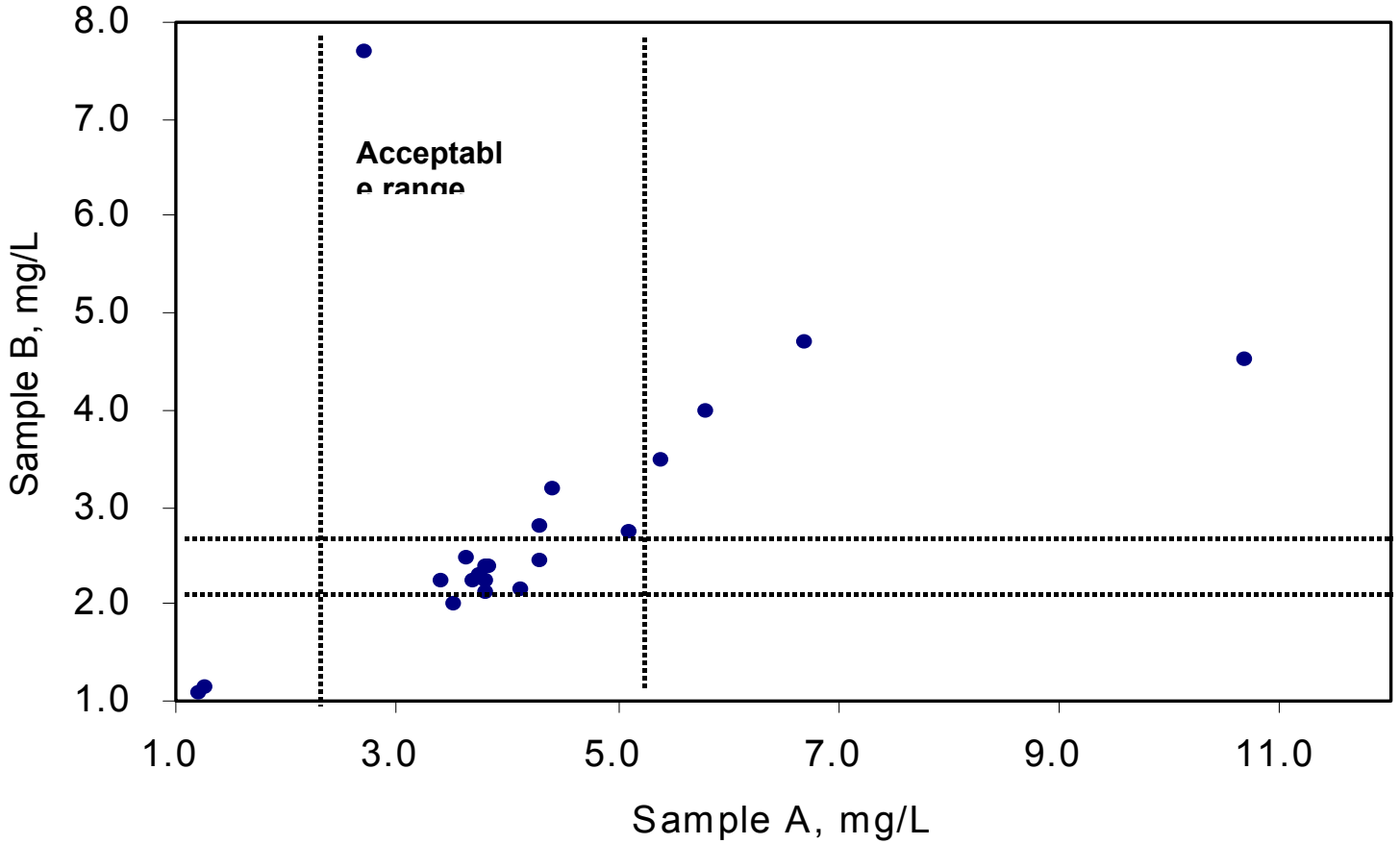


Figure 7. Performance of laboratories for Posphate

Youden 2-sample plot

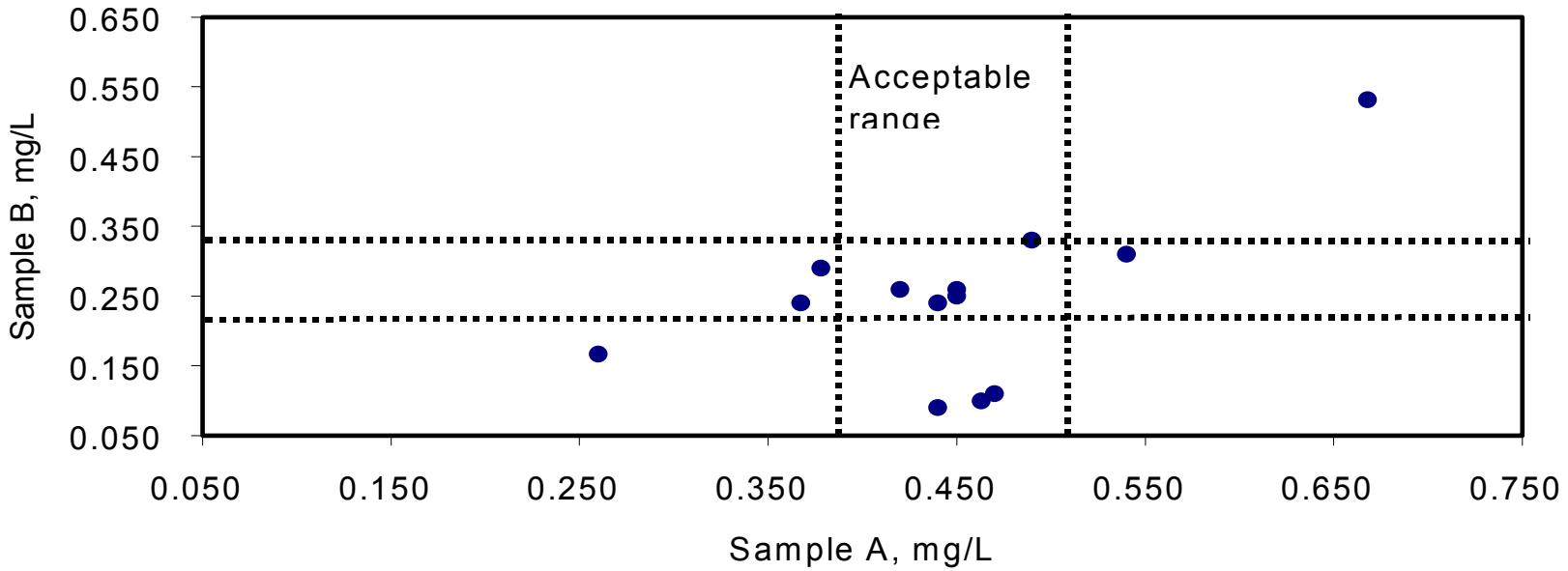


Figure 8. Performance of laboratories for Sodium

Youden 2-sample plot

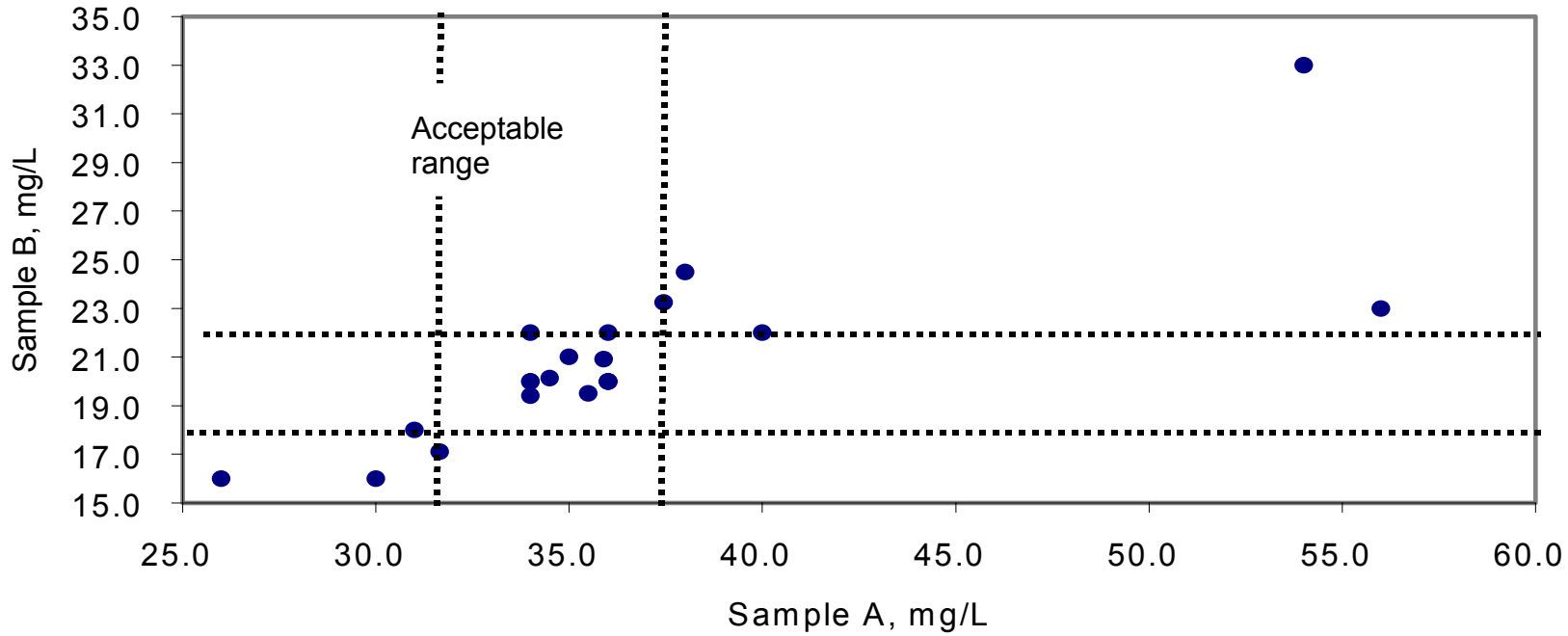
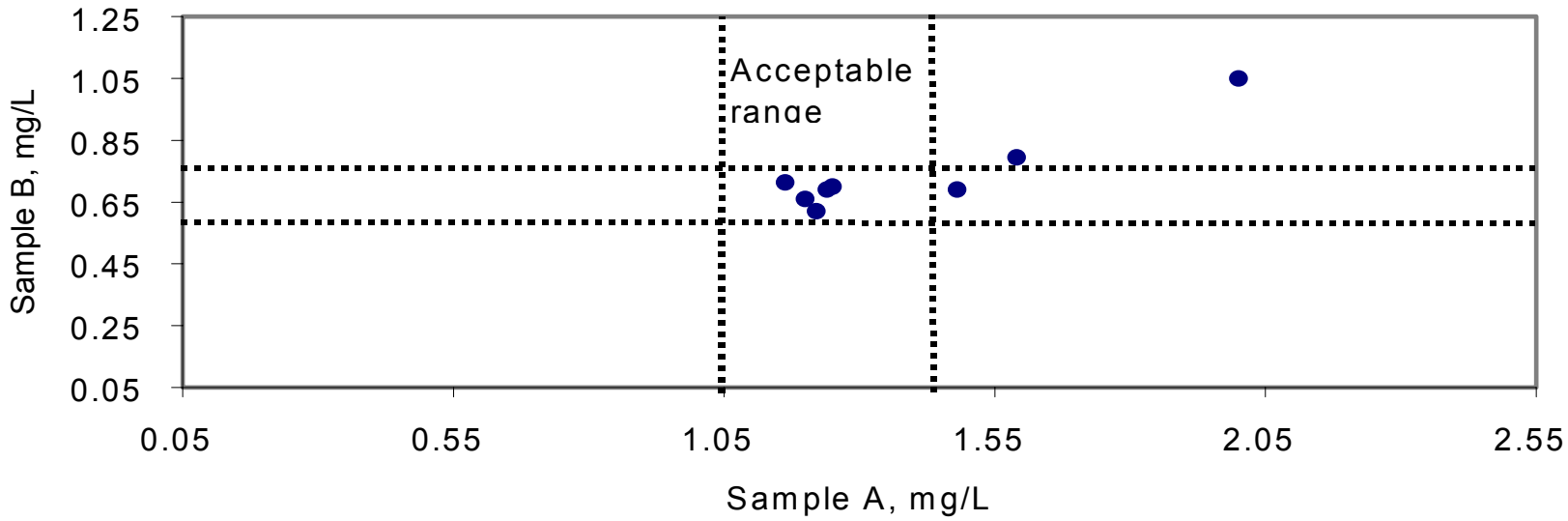


Figure 9. Performance of laboratories for Boron

Youden 2-sample plot



5 Conclusions & recommendations

- The overall results of the AQC exercise reveal that a majority of the laboratories could not report correct results for most of the parameters covered under the exercise. Further, urgent attention must be paid to the determination of critical parameters like nitrate, phosphate and fluoride.

- It is recommended that the laboratories, which have not qualified for a parameter, should give attention to identifying and rectifying the problems associated with the analysis for the concerned parameter.

- Other than upgradation of laboratories under the Hydrology Project, improvement in the performance of laboratories can also be brought about by selection of better grade chemicals, glassware and distilled water. Careful washing of glassware is often neglected.

- All laboratories should follow standard analytical procedures. It is most important to institute preventive maintenance procedures for the instruments, and calibrate and standardise them periodically to generate accurate analytical results.

- *Within*-laboratory AQC exercises should be introduced in all laboratories on regular basis, particularly for critical parameters noted above.

- It is recommended that laboratories should participate regularly in *inter*-laboratory AQC exercises.

Annex: I

Composition of standard samples

CENTRAL POLLUTION CONTROL BOARD-DELHI 32

LABORATORY DIVISION – WATER LABORATORY

ANALYTICAL QUALITY CONTOL, (AQC/WATER) EXERCISE – DEC.,'98

FOR THE

LABORATORIES OF SURFACE AND GROUND WATER DEPARTMENTS

OF

CENTRAL AND STATE LABORATORIES UNDER

"HYDROLOGY PROJECT"

INGREDIENT OF SOLUTIONS, Hydrology Project, December 1998

S.No.	Name of Chemical	Weight in gm.	Final Volume	Concentration
1.	MAGNESIUM SULPHATE ($MgSO_4$, $7H_2O$)	16.4	2 litres	800 ppm Mg and 3200 ppm SO_4
2.	CALCIUM CHLORIDE ($CaCl_2$, $2H_2O$)	14.7	2 litres	2000 ppm Ca 3500 ppm Cl
3.	SODIUM FLUORIDE (NaF)	2.21	1 litre	1000 ppm F
4.	POTASSIUM NITRATE ($KNO_{3)}$	7.214	1 litre	1000 ppm NO_3-N
5.	BORIC ACID (HBO_3)	5.716	1 litre	1000 ppm Boron
6.	SODIUM CHLORIDE (NaCl)	12.717	1 litre	5000 ppm Na
7.	POTASSIUM DIGYDROGEN PHOSPHATE (KH_2PO_4)	12.717	1 litre	5000 ppm Na

PREPARATION OF SAMPLE – A

300 ml $MgSO_4$.$7H_2O$ + 200 ml $CaCl_2$.$2H_2O$ + 80 ml NaF + 160 ml KNO_3 + 60 ml H_3BO_3 + 200 ml KH_2PO_4 + 240 ml NaCl ⟶ Final Vol. 40 ltrs

PREPARATION OF SAMPLE - B

165 ml $MgSO_4$.$7H_2O$ + 100 ml $CaCl_2$.$2H_2O$ + 56 ml NaF + 100 ml KNO_3 + 30 ml H_3BO_3 + 120 ml KH_2PO_4 + 140 ml NaCl ⟶ Final Vol. 40 ltrs

Annex II

Communication with the despatch of samples

CENTRAL POLLUTION CONTROL BOARD-DELHI 32

LABORATORY DIVISION – WATER LABORATORY

ANALYTICAL QUALITY CONTOL, (AQC/WATER) EXERCISE – DEC.,'98

FOR THE

LABORATORIES OF SURFACE AND GROUND WATER DEPARTMENTS

OF

CENTRAL AND STATE LABORATORIES UNDER

"HYDROLOGY PROJECT"

GENERAL INSTRUCTIONS

Note: Please read the following instructions carefully before starting analysis of samples

Two nos. of synthetic water samples (A & B) of one lit. each labeled with lab code are provided for analysing Conductivity, Total solids, Total Hardness, Sodium, Fluoride, Sulphate, Nitrate-N, Phosphate-P and Boron.

Both samples (A & B) are to be analysed separately for all 9 parameters as shown below.

S.No.	Parameter	Unit
01	Conductivity at 25°C	μ mhos/cm
02	Total Solids	mg/l
03	Total hardness as ca CO_3	mg/l
04	Sodium	mg/l
05	Fluoride as F	mg/l
06	Sulphate as SO_4	mg/l
07	Nitrate – N	mg/l
08	Phosphate – P	mg/l
09	Boron	mg/l

Note: Choose appropriate sample volume for each parameter for single run so that analysis can be done within the provided sample volume.

ANALYTICAL METHODS:

1. You may choose any relevant method being followed in your laboratory for various parameters. However, the method is to be mentioned into the data format.

2. In case of colourometric method the standard graph and the factor used for calculation is to be submitted along with the data sheet.

3. Brief outline of the procedures for each analytical parameter is to be provided as annexure along with the data sheets.

Please note the following points:

- All the samples are to be analysed most preferably during 07th to 11th December' 98 for better comparison purpose of data obtained from various laboratories.

- **Report the analysis result in the enclosed Data Format Sheet only. Kindly avoid using separate typed data sheet.**

- Be sure that Lab code & sample code numbers are mentioned in the Data format sheet while sending the report.

- Be sure that all the units of various parameters are properly taken care while reporting data.

- Analysis report should be sent directly to the following address positively latest **by 25th December 1998, without fail.**

Dr. S. D. Makhijani
Additional Director Labs
Central Pollution Control Board
Parivesh Bhavan
East Arjun Nagar
Delhi-110032

Fax (011) 222 0844

or (011) 221 7079

CENTRAL POLLUTION CONTROL BOARD-DELHI 32

I AQC/WATER	DEC. 1998

LAB CODE	

I ANALYTICAL QUALITY CONTROL (AQC/WATER) EXERCISE – DEC.'98 FOR THE LABORATORY OF SURFACE AND GROUND WATER DEPARTMENTS OF CENTRAL AND STATE UNDER "HYDROLOGY PROJECT"

01	Name of the organisation	
02	Address of the Laboratory with PIN code, Phone & Fax	PIN:
		Phone: Fax:
03	Samples analysed by: (Name & designation)	1. 2.
04	Date of receipt of samples	

RESULT

S. No.	Parameter	Sample Code		Method Adopted	Instrument Used	Calibration graph attached Yes/No	Date of Analysis
		A	B				
01	Conductivity at 25°(μ mhos/cm)					--	
02	Total Solids (mg/l)					--	
03	Total Hardness as $CaCo_3$ (mg/l)					--	
04	Sodium (mg/l)						
05	Fluoride as F (mg/l)						
06	Sulphate (mg/l)						
07	Nitrate – N (mg/l)						
08	Phosphate – P (mg/l)						
09	Boron (mg/l)						

Note: A copy of the standard Calibration graph wherever applicable as to be attached in annexure

Dated: Signature of Lab incharge

Estimation of reference value and acceptable range for conductivity measurement for samples A and B

CENTRAL POLLUTION CONTROL BOARD-DELHI 32

	COND-A0	COND-A1	COND-A2	COND-B0	COND-B1	COND-B2
	110.000			140.000		
	206.000			162.000	162.000	
	260.000			167.000	167.000	
	288.000	288.000		167.000	167.000	
	298.000	298.000		175.500	175.500	
	304.000	304.000		180.000	180.000	
	311.000	311.000		180.000	180.000	
	320.000	320.000		185.000	185.000	
	320.000	320.000		186.000	186.000	186.000
	323.000	323.000	323.000	189.700	189.700	189.700
	323.000	323.000	323.000	190.000	190.000	190.000
	332.300	332.300	332.300	190.000	190.000	190.000
	335.000	335.000	335.000	193.000	193.000	193.000
	336.000	336.000	336.000	194.000	194.000	194.000
	336.900	336.900	336.900	194.000	194.000	194.000
	337.000	337.000	337.000	194.000	194.000	194.000
	338.500	338.500	338.500	196.000	196.000	196.000
	339.000	339.000	339.000	197.400	197.400	197.400
	350.000	350.000		205.000	205.000	
	350.000	350.000		210.000	210.000	
	355.000	355.000		210.000	210.000	
	360.000	360.000		218.000	218.000	
	363.000	363.000		220.000	220.000	
	405.000			225.000	225.000	
Mean, X	316.696	330.985		190.358	192.548	
Mean, X_R			**333.411**			**192.410**
Std Dev, SD	56.974	19.791		19.227	16.453	
X+1.96SD/√N		339.658			199.272	
X –1.96SD/√N		322.311			185.823	
SD_R			6.333			3.449
$SD_{adj} = \sqrt{2}SD_R$			8.955			4.878
Lower limit = $X_R - 3SD_{adj}$			**306.545**			**177.777**
Upper limit = $X_R + 3SD_{adj}$			**360.277**			**207.043**