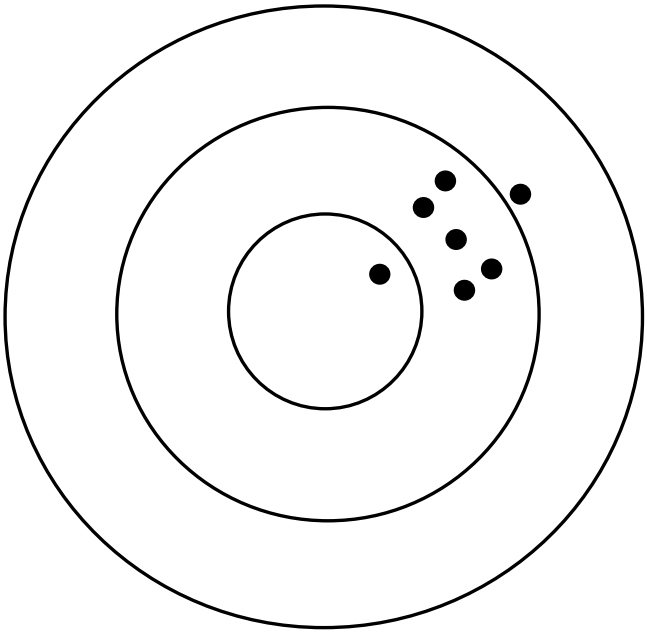

Findings of

Within-Laboratory AQC Exercise

2nd round ('98)

June 1999

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1 Introduction

The need for analytical quality control (AQC) in HP laboratories was first discussed in the 'Water Quality Standardisation Workshop', December 9-10, 1996, Hyderabad. It was recommended that AQC exercises should be organised 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.
- Since the *within*-laboratory AQC exercise evaluates only the precision of the laboratory, an *inter*-laboratory exercise was started in June 1998 to test the bias of the laboratories. The Central Pollution Control Laboratory is acting as the reference laboratory for this exercise. The result of this exercise will be communicated separately.

The present document summarises the findings of the second round of the *within*-laboratory exercise. Readers may refer to the report titled 'Within-Laboratory AQC Exercise, 2nd round', March 1998, for basic statistics concepts and other background material of the exercise.

2 Response of laboratories

The first round of the exercise covered only 4 parameters. The scope of the second round was increased to cover 8 parameters including 3 parameters covered in the first exercise. It was, however, emphasised that any laboratory, which was not equipped to perform one or more of the selected parameters, could still participate in the exercise with the parameter(s) it was able to measure.

Out of nearly 30 laboratories nominated for the exercise only 17 responded. During the first round, on the other hand, 23 laboratories had participated in the exercise. The break-up of the participating laboratories, state and agency wise is given in Table 1.

While the laboratories of Central agencies, in general, have better facilities and are in operation for a longer period of time compared to the State agencies, their response to the exercise was below expectation. Further, it is seen that while the participation of the State agencies decreased from 15 to 13 in the second round, the response of the Central agencies decreased from 8 to 4. There was no response from the State laboratories of Andhra Pradesh and Orissa in either of the two rounds.

The importance of the *within*-laboratory AQC exercises as a means to keep a control on the precision of analytical procedures and to avoid errors that might creep in need not be repeated. Such exercises are particularly required where a number of laboratories contribute to a common database such as the Hydrological Information System under HP.

Table 1. Participation of laboratories in within-laboratory AQC exercise

	Laboratory	1st round	2nd round
States	Andhra Pradesh	none	none
	Gujarat	4	3
	Karnataka	2	none
	Kerala	2	1
	Madhya Pradesh	1	1
	Maharashtra	4	6
	Orissa	none	none
	Tamilnadu	2	2
	Total of state labs.	15	13
Central	CWC	4	2
	CGWB	4	2
	Total	23	17

The number of parameters analysed by the participating Central laboratories was on an average higher compared to those determined by the State agencies. This shows the higher analytical capability of the central organisations: CGWB (6 out of 8 parameters), CWC (5.5 out of 8 parameters) and the States (3 out of 8 parameters).

In the states that actively participate, we may mention the states of Maharashtra, Gujarat (ground water) and Tamilnadu in this respect. We feel that the laboratory staff is appreciating the exercise and have gained more confidence by checking their own performance from time to time.

3 Discussion of results

3.1 Coefficient of variation

The most important parameter to evaluate the results in a *within*-laboratory exercise is the precision. The statistical term to evaluate precision is the standard deviation. The numerical value of the standard deviation depends on the average concentration (standard deviation has the same units as the average). Numerical values of standard deviations of low concentration solutions are usually smaller than solutions of higher concentrations. The precision of measurement for low concentration solutions, however, is generally lower and therefore the numerical value of standard deviation is not a universal measure for precision. The coefficient of variation (cv) or normalised standard deviation (CV = standard deviation/mean x 100) is more commonly used to evaluate precision. This is particularly useful when comparing results of analysis for samples having different concentrations.

Before evaluating the results one should answer the question ‘what is the desired precision for an analysis?’ In fact this question should be answered by the so called ‘data users’. The use of the data determines the required precision, e.g. detection of trends may require more precise results (in order to actually detect small changes in the course of time) than checking

water for a use (a rough comparison with a standard). Laboratory staff should always ask for the purpose for which they are performing the requested test.

As a minimum goal for precision, however, the precision that can be obtained by correctly and adequately following the prescribed methods of analyses for various water quality parameters covered in this exercise is given in Table 2. The table shows ranges of cv values when the results of determinations by different laboratories were analysed by Standard Methods (1995) and CPCB (1992-97) and the proposed goal for HP laboratories for the parameters covered in the second round.

Table 2 Target coefficient of variation for parameters covered in the second round of *within*-laboratory AQC exercise.

Parameter	Coefficient of variation (%)		
	CPCB	Standard Methods	Proposed
TS	2.8 - 8.5	0.76-33	**7**
EC	1.5-2.6	1-2	**2**
TH	0.9-8.4	2.9	**3**
SO_4	-	1.7	**2.5**
Na	-	4.0	**4**
o-PO_4	4.3 -13.3	6.2	**5**
B	-	22.8	**10**
F	-	8.0	**8**

Results of the second round of the within-laboratory AQC exercise are shown in Table 3. The first column gives the laboratory identification numbers. Identification numbers given to the laboratories in the first round were retained in the second round also. In addition, ID numbers 26 to 28 were allotted to laboratories that did not participate in the first round but participated in the second round. The grey colour rows indicate the laboratories, which participated in the first round but did not participate in the second round.

It is seen from the table that the cv criteria for TS, EC, TH, PO_4^{3-} and F^- was met by nearly all the participating laboratories. However, for Na^+, 64%, for B, 50% and for SO_4^{2-}, 33% of the laboratories could meet the criteria.

Table 3 Summary and analysis of results of the second round of within-laboratory AQC exercise.

Lab	TS			EC			TH			SO4			Na			oPO4			B			F		
	avg	sd	cv	avg	sd	cv	avg	sd	cv	avg	sd	cv	avg	sd	cv	avg	sd	cv	avg	sd	cv	avg	sd	cv
1																								
2																								
3	150	0.89	0.6 √	303	9.66	3.2 ×	99.8	0.56	0.6 √				9.96	0.48	4.8 ×									
4																								
5																								
6																								
7																								
8	148	3.2	2.2 √	298	2.11	0.7 √	100	0.47	0.5 √	19.9	0.72	3.6 ×	10.2	0.4	3.9 √									
9	146	4.94	3.4 √				99.4	0.88	0.9 √				9.65	0.07	0.7 √							2.04	0.05	2.4 √
10	156	6.2	4.0 √	282	4.1	1.5 √	103	1.07	1.0 √	19.6	0.3	1.5 √	9.4	0.1	1.1 √	10.4	0.09	0.8 √				2.05	0.03	1.5 √
11				303	2.29	0.8 √													1.17	0.28	23.8 ×	2.19	0.35	15.8 ×
12																								
13	149	4.77	3.2 √	283	2.33	0.8 √	98.7	3.55	3.6 ×	20	0.03	0.2 √	9.57	0.08	0.9 √	10.1	0.21	2.1 √	1	0.02	1.8 √	2.03	0.05	2.4 √
14	147	3.1	2.1 √	296	0.95	0.3 √	99.6	0.5	0.5 √	19.9	0.7	3.5 ×				1.0	0.003	0.3 √	1.01	0.01	1.0 √	2.01	0.02	1.0 √
15	149	4.75	3.2 √	295	2.1	0.7 √	100	1.75	1.7 √				9.54	0.36	3.8 √									
16	145	2.87	2.0 √	295	1.97	0.7 √	96.2	1.49	1.5 √				9.97	0.16	1.6 √									
17	151	5.5	3.6 √				101	2.61	2.6 √	21.3	0.7	3.3 ×	9.95	0.5	5.0 ×							2.11	0.13	6.2 √
18	149	2.94	2.0 √	296	3.89	1.3 √	99.7	1.42	1.4 √	20.9	1.15	5.5 ×	10.1	1.38	13.7 ×							0.79	0.03	3.8 √
19																								
20																								
21				282	1.6	0.6 √	106	2.47	2.3 √	16.3	0.74	4.6 ×	9.99	0.31	3.1 √							1.54	0.11	7.2 √
22																								
23																								
24																								
25	148	2.7	1.8 √	292	4.3	1.5 √	101	1.7	1.7 √	19.6	1.42	7.3 ×	9.13	0.52	5.7 ×	10	0.12	1.2 √	0.98	0.16	15.8 ×	1.99	0.04	2.2 √
26				300	5	1.7 √	100	0.82	0.8 √				9.99	0.37	3.7 √							0.98	0.15	15.1 ×
27	151	1.45	1.0 √	298	1.33	0.4 √	99.8	0.63	0.6 √				9.61	0.14	1.5 √							2.06	0.1	4.9 √
28				1428	18.1	1.3 √	100	0	0.0 √	20.8	0.51	2.5 √	9.6	0.42	4.4 ×							1.51	0.04	2.8 √
avg			2.4			1.1			1.3			3.5			3.9			1.1			10.6			5.4
n			12			14			11			9			14			4			4			12

√ = meeting the precision goal × = not meeting the precision goal

avg =average value, sd=standard deviation, cv=coefficient of variation (sd/avg*100)

Control solutions: TH=100 mg/L; EC= 296 umho/cm at 25C; TS=149 mg/L; SO4=20 mg/L; Na=9.58 mg/L; oPO4=10 mg/L; B=1 mg/L and F=2 mg/L

3.2 Statistical control of analytical procedure

To keep a check on the day to day operation of a laboratory, Shewhart control charts are maintained for each parameter being analysed by the laboratory. Briefly, the charts show warning and control limits for the result of analysis of a standard sample prepared by the laboratory. The laboratory arrives at the limits by repeated analysis of the standard. Subsequently, during the routine work of the laboratory the analysis of the standard is repeated at fixed intervals and the result is plotted on the chart. It is compared with the previous results and against the limits. A set of criteria is used to evaluate if the results are within permissible limits.

Table 4 shows a summary of the analysis of the Shewhart control charts. Laboratories at ID nos. 21 and 28 analysed replicates to construct the Shewhart charts, but did not analyse further replicates to test if they were maintaining statistical control.

It is seen that among all the parameters EC measurement went out of statistical control in the largest number of laboratories, i.e., 4 laboratories out of 11 or 36% of the laboratories. A similar observation was made in the first round when 55% of the laboratories showed results out of statistical control. It may be noted that most of the agencies report the TDS values in water samples on the basis of the EC of the sample.

Fluoride is another determination which needs attention. It is a critical parameter in assessing the quality of water for domestic water supply. The table shows that in 30% of the laboratories the procedure was out of statistical control during the period of the exercise.

The above observations emphasise the value of *within*-laboratory AQC exercise in maintaining precision of a determination and warning the analyst when the procedure tends to go out of statistical control.

Table 4 Results of interpretation of Shewhart control charts for statistical control

Lab	TS	EC	TH	SO4	Na	o-PO4	B	F
1								
2								
3	√	A	√	-	A	-	-	-
4								
5								
6								
7								
8	√	√	√	√	√	-	-	-
9	√	-	√	-	√	-	-	√
10	W	C	A	√	√	√	-	√
11	√	T	A,T, W	√	A	√	-	A
12								
13	√	√	√	√	√	√	√	W
14	√	√	√	√	-	√	√	T
15	√	√	√	-	√	-	-	-
16	T	A,T	A,T	-	-	-	-	-
17	√	-	√	√	√	-	-	√
18	√	√	√	√	√	-	-	√
19								
20								
21	-	-	-	-	-	-	-	-
22								
23								
24								
25	√	√	√	√	√	√	√	√
26	-	-	S	-	√	-	-	√
27	√	√	√	-	√			√
28	-	-	-	-	-	-	-	-
Number of lab out of control /all laboratories	2/13 = 15%	4/11 = 36%	4/12 = 33%	0/8	2/12 = 16%	0/5	0/3	3/10 = 30%
Labs failing more than one criterion /all failing labs		1/4 = 25%	2/4 = 50%					

√ = under statistical control
C = 2 successive points out of Control (Action)l Limit
W = 3 out of 4 successive points out of Warning Limit
S = 5 out of 6 successive points out of standard deviation limit
T = 5 out of 6 successive points having the same trend
A = 7 successive points on one side of the average
\- = parameter not reported or insufficient repetitions for statistical evaluation

4 Conclusion and future actions

Analysis of the results of the two rounds of within-laboratory exercises has demonstrated its use in maintaining the precision of the determinations in a laboratory. Even simple and easy to measure parameters, such as EC, need careful laboratory control. Further, the value of maintaining precision for critical water quality parameters need not be emphasised.

With the above in view, it is suggested that the laboratories carry out *within*-laboratory AQC exercise on a continuing basis for the following parameters:

S No	Parameter	Laboratory level	Remarks
1	EC	II+ & II	Laboratories in general show lack of precision
2	F^-	II+ & II	Critical for domestic water supply, particularly from groundwater sources
3	$NO_2^- + NO_3^-$	II+ & II	Eutrophication in surface waters, groundwater contamination from sewage
4	Total solids	II+ & II	To check precision of analytical balance in the laboratory
5	Heavy metals	II+	At least three metals, Cd, Hg & Zn

For the measurement of parameters 1 to 4, the laboratories may use analytical methods described in 'Guidelines on Standard Analytical Procedures for water Analysis', or any other procedure followed regularly in the laboratory. For the measurement of parameter 5, heavy metals, Atomic Absorption Spectrophotometer would be used.