Commonwealth Edison
Zion Generating Station
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November 27, 1989

U. S. Nuclear Regulatory Commission
Region III
Attn: Mr. A. Bert Davis,
Regional Administrator
799 Roosevelt Road
Glen Ellyn, IL 60137

Mr. Davis,

This letter refers to Inspection Reports No. 50-295/89031 (DRSS) and No. 50-304/89027 (DRSS), specifically Open Items Nos. 50-295/89031-02 and 50-304/89027-02; which were the result of a routine inspection conducted by Dr. R. B. Holtzman of the USNRC Region III during September 13-19, 1989.

The Open Items were a concern regarding Zion Station's laboratory QC program weaknesses and the progress made to resolve these weaknesses. Zion Station has been aggressively pursuing improvements in the laboratory QC area. The following describes the actions taken to date to address this concern.

A key factor in development and implementation of the laboratory QC program is personnel. Additional personnel have been obtained, an analytical chemist and a second Laboratory Supervisor (previously titled Laboratory Foreman), with a third Laboratory Supervisor scheduled to begin in December. The analytical chemist was previously with corporate Chemistry Services and worked in the analytical chemistry area. His previous experience has resulted in immediate contributions to the analytical and QC areas of the station Chemistry Department. The second Laboratory Supervisor was previously a Chemistry Technician. These additional people all have responsibilities towards the progress and implementation of the laboratory QC program.

A station specific Laboratory QC Program is being developed. A draft of the program is attached for your information. The program will provide specific information such as review of Quality Control Charts, identification of trends, biases, and other anomalies, data analysis of Control Chart parameters, frequency of data analysis and review of Control Charts, and Intralaboratory Testing of Chemistry Technicians. This program will be fully implemented as a Chemistry Department approved program. It should be noted that most of the program either has or will be implemented in conjunction with it's development. Already as a result of the implementation of the program, a number of Control Charts limits have been reviewed and have had their control limits reduced for tighter control. A summary of these changes to the Control Chart limits is attached, and show reductions in the limits ranging from 4.0% to 49.0%. This program will be fully implemented by June 1990.

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The Technician Proficiency Testing Program (TPTP) is currently in progress. Two "rounds" are being distributed and performed concurrently. Each round consists of six unknowns, representing flouride, chloride, chromate and boron in a primary matrix, and chloride and sulfate in a secondary matrix. The acceptance criteria has been revised from a blanket ten percent, to criteria which reflect INPO's recommendations of acceptable error for each parameter in the applicable matrix. The current status of the TPTP is 70 percent complete. The two rounds of the TPTP analyses will be completed by December 31, 1989.

Any additional information or further questions will gladly be discussed by D. P. Hemmerle, Zion Station.

Sincerely,

for T. P. Joyce
Station Manager
Zion Station

TPJ/DPH/rmd

cc: w/attachment:
Dr. R. B. Holtzman (USNRC RIII)
Resident Inspection (USNRC RIII)
G. Trzyna (NLA)
W. Stone (Regulatory Assurance)
B. Schramer (Chemistry)
T. Saksefski (Regulatory Assurance)

A. Review of Quality Control Charts

1. "Walk-thru" review

1.1 While a control chart is in use, "walk thru" reviews should be done periodically dependent upon the scheduled frequency of the analysis.

Therefore, the following guidelines are applicable:

Frequency of Analysis	Frequency of Review (not to exceed . . .)
Shiftly	Every two days
Daily (includes 5 to 7 times per week)	Weekly
Three times per week	Every two weeks
Twice per week	Every three weeks
Once per week	Monthly

The "walk-thru" reviews are cursory verifications to identify control chart problems (see Control Chart Problems), to ensure corrective actions are documented, and to verify the completeness and correctness of the data on control charts (ie. ensure all data is properly plotted and the numerical value is recorded on the performance check worksheet and the instrument response data is recorded, if applicable).

2. Control Chart Problems

2.1 Out-of-Control conditions:

When two consecutive points fall outside the control limits, then these individual data points are Out-of-Control. If any samples were analyzed since the last performance check that was within the control limits, then data from these samples are invalid. The Out-of-Control points should be documented and the subsequent corrective actions should be documented, also.

2.2 Other problems that should be investigated:

The identification of systematic behavior such as trends, biases, and other anomallies in a set (or group) of data points, when no two consecutive points plot outside the control limits, should be documented.

IF both R- and $\bar{x}$ - charts exhibit non-random behavior, the reviewer should identify the assignable causes on the R- chart, first. In general, this may explain and eliminate the non-randomness of the x - chart. The following are the various indicators of non-random behavior.[1]

1 Montgomery, Douglas C., Introduction to Statistical Quality Control, John Wiley & Sons, 1985, p. 189-192.

2.2.1. Trends are seven consecutive graphed data points that have an increasing or decreasing slope. Some investigation should be initiated into the standardization, environmental conditions, methodology, and/or instrument operation.

2.2.2. Biases ('mean or average' shifts) are seven consecutive graphed data points that lie on one side of controlling mean. The probability that seven independent measurements (observations) of the performance check standard are on one side of the mean is 0.78% likely to not indicate a bias. This is represented by the equation, $1/(2)^n$, where n is the number of observations. Some investigation should be initiated into the standardization, environmental conditions, methodology, and/or instrument operation.

2.2.3. Cycles are periodic patterns in the graphed data points. Generally, cycles occur for the following reasons: particular technician's round on an instrument, reoccurring and regular power fluctuations, and other periodic environmental and analytical conditions.

2.2.4. Stratification or a tendency for the points to cluster artificially around the centerline occurs when there is a lack of natural variability in the graphed data points. The method of calculation of these control limits is one area that should be checked. Also, these data points may be from more than one lot of performance check standard. Thus, various lots may have various distributions (or various widths of bands which each particular lot may cover) which combine together to give low variability or straight-line effect in the graphed data.

2.2.5. A Mixture is indicated when the plotted points tend to fall near and/or slightly outside the both upper and lower control limits with relatively few points near the centerline; however, no two consecutive points are outside the limits. A Mixture is caused by an overlap of two or more distributions. Some investigation should be initiated into the standardization, environmental conditions, methodology, and/or instrument operation.

2.2.6. If there is a correlation between the $\bar{x}$ and R values (eg. the data points on the two charts "follow" each other), then this indicates the underlying distribution is skewed. Some investigation should be initiated into the standardization, environmental conditions, methodology, and/or instrument operation.

B. Data Analysis of Control Chart Parameters

1. Periodically, the control limits shall be recalculated and statistically compared to previous control limits. Chemistry supervision should identify shifts in calculated means (or centerlines of control charts). The frequency of this recalculation depends upon the scheduled frequency of the analysis. Therefore, the following are guidelines for the frequency of recalculation:

Frequency of Analysis	Frequency of Control Limits Recalculation (not to exceed . .)
Shiftly	Every two weeks
Daily	Every five weeks
Five times per week	Every two months
Three times per week	Every three months
Twice per week	Every four months
Once per week	Every six months

2. After calculating the mean and the standard deviation, the following statistical tests should be performed:

2.1. Outlier test as per ASTM E178-80 - This test will remove data which does not fall within the assumed normal sample population. If this data is not removed, it will skew the calculation of mean and standard deviation the data.

2.2 F-test as per ASTM D4210-89 - This test will detect a significant change in the variability between the new data and the old data. If a significant change is detected, then the data should be evaluated for a cause of the change.

2.3 Student's t-test - After demonstrating the data has no significant change in variability by the F-test, the Student's t-test will detect significant changes in the means of the old and new data sets. If no significant change in the means has occurred, then the means may be combined into a grand average.

C. Intralaboratory Testing
(Chemistry Technician Proficiency Testing in the Laboratory)

The purposes of intralaboratory testing are the following:

- To provide a measure of accuracy and precision of analytical methodology and identify weak methodology.
- To detect training needs.
- To upgrade the overall quality of the laboratory performance.
- To provide an assessment of the performance capability of individual analysts.

Intralaboratory testing provides the most information on the performance capabilities of chemistry technicians. To verify the quality of chemistry technicians' performance, blind samples shall be analyzed by each technician twice a year. The following parameters must be analyzed by each technician boron, lithium, primary anions (chloride and fluoride), and secondary anions (chloride and sulfate).[2] Also, other plant parameters may be tested (see Appendix A.) In Appendix A, there are goal values for the acceptance criteria for each analysis in particular matrices. However, the technician cannot be expected to perform better than the capabilities of a particular analysis under this laboratory's environmental conditions. Therefore, during a testing period the acceptance criteria should not be tighter than the control limits on a particular parameter. For example, if the control limits for primary system chloride are + or - 15% and goal acceptance criterion is + or - 10%, then the actual acceptance criterion that should be used is + or - 15%.

Blind (or check) samples shall be used to determine analytical capabilities of the chemistry technician, and these check samples should be prepared using the following guidelines:

1) The concentration of the check samples
   a) should be within plant parameters at various, possible operating or non-operating conditions,
   b) should simulate various concentrations in various plant systems,
   c) OR should be near action limit concentrations.
2) Also, some check samples should reflect abnormal plant conditions to familarize the chemistry technician with these analysis at these conditions.
3) Check samples should be analyzed along side actual routine samples.
4) Check samples shall be prepared by Chemistry Supervision or a qualified vendor.
5) Because most samples are low-level concentrations, these check samples should be prepared as concentrates. Then, the technician shall dilute these concentrates to the designated concentration range. The resistivity of the dilution water used to prepare concentrates and "working" check samples shall be greater than 16 megohms.

2 NRC commitment item # 50-295/86010-02; 50-304/86009-02 in the NRC Inspection Report [No. 50-295/87029(DRSS); 50-304/87030(DRSS)] November 4, 1987, p.3.

Finally, Chemistry Supervision shall compile and maintain documentation of the information on the preparation of the check samples, the analytical data of the technician, and the technician's results.

APPENDIX A

Verification of Chemistry Technician Performance Accuracy (at 95% confidence) in the Chemistry Laboratory - Parameters, Concentration Ranges, and Acceptance Criteria.[3]

Table A-1
Primary System: Borated Water Matrix

Parameter	Concentration Range	Units	*Acceptance Criteria
Boron	0 - 3000	ppm	5 ppm or 1.0%
Lithium	0.1 - 3.0	ppm	0.01 ppm or 5%
Chloride	1 - 200	ppb	0.5 ppb or 10%
Fluoride	2 - 200	ppb	1.0 ppb or 15%
Sulfate	10 - 100	ppb	1.0 ppb or 10%
Chromate	10 - 400	ppb	1.0 ppb or 15%
Oil & Greas	1 - 30	mg/L	based on vendor

Table A-2
Secondary System: Ammonia Matrix

Parameter	Concentration Range	Units	*Acceptance Criteria
Ammonia	0.05 - 6.0	ppm	10%
Hydrazine	10 - 200	ppb	15%
Chloride	1 - 50	ppb	0.5 ppb or 10%
Fluoride	2 - 50	ppb	0.5 ppb or 10%
Sulfate	2 - 50	ppb	0.5 ppb or 10%
Silica	10 - 300	ppb	10%
Copper	1 - 100	ppb	0.5 ppb or 15%
Iron	1 - 100	ppb	0.5 ppb or 15%
Magnesium	5 - 50	ppb	20%
Sodium	1 - 100	ppb	0.5 ppb or 15%
Total Organic Carbon	0.01 - 3.0	ppb	0.01 ppm or 10%

* Use the greater of two values.

3 "Chemistry Quality Control Program", INPO 83-01(CY-701), Revision 02, August 1989. (NOTE: These tables are modified to reflect Commonwealth Edison's standards and Zion Station's operating conditions and parameters.)

Table A-3
Auxilary Systems: Water Matrix

Parameter	Concentration Range	Units	*Acceptance Criteria
Chloride	2 - 50	ppb	0.5 ppb or 10%
Fluoride	2 - 50	ppb	0.5 ppb or 10%
Sulfate	2 - 50	ppb	0.5 ppb or 10%
Silica	10 - 300	ppb	10%
Nitrate	1 - 20	ppm	10%
Nitrite	1 - 20	ppm	0.5 ppb or 15%
Copper	1 - 100	ppb	0.5 ppb or 15%
Chromate	50 - 300	ppm	10%
Iron	1 - 100	ppb	0.5 ppb or 15%
Iron (in nitrite matrix)	0.1 - 2.0	ppm	15%
Sodium	1 - 100	ppb	0.5 ppb or 15%
Total Organic Carbon	10 - 3000	ppb	10 ppb or 10%

Summary of Control Chart Information Effective 11-15-89

	Parameter (Analysis)	True Value	Mean $\bar{X}$	Units	Std. Dev. s	% RSD	lower limit $\bar{X} - 2s$	upper limit $\bar{X} - 2s$	Old Std. Dev.	% Change in Std. Dev.
1.	Chloride (ISE)	100	97.4	ppb	4.5	4.6%	88.4 -	106.4	6.9	-34.8%
2.	Fluoride (ISE)	50	49.3	ppb	2.5	5.1%	44.3 -	54.3	3.4	-26.5%
3.	Boron (auto-titration)	1000	999.8	ppm	3.96	0.4%	991.9 -	1007.7	5	-20.8%
4.	Chloride (I.C.)	10	10.2	ppb	0.9	8.8%	8.4 -	12.0	1.3	-30.8%
5.	Sulfate (I.C.)	20	19.6	ppb	1.1	5.5%	17.5 -	21.8	1.6	-32.5%
6.	Chromate (Flame AA)	100	104.5	ppm	4.1	3.9%	96.3 -	112.7	5	-18.0%
7.	Iron (Flame AA)	1.00	1.08	ppm	0.087	8.1%	0.90 -	1.25	0.11	-24.3%
8.	Lithium (Flame AA)	0.50	0.517	ppm	0.018	3.5%	0.48 -	0.55	0.01	-5.3%
9.	Sodium (Flame AA)	50	53.1	ppb	2.5	4.7%	48.1 -	58.1	3.75	-33.3%
10.	Ammonia (colorimeter)	2.00	2.01	ppm	0.07	3.5%	1.87 -	2.15	0.11	-36.4%
11.	Hydrazine (colorimeter)	20	19.2	ppb	1.0	5.3%	190.3 -	223.7	2	-49.5%
12.	Silica (colorimeter)	200	207.0	ppb	8.4	4.1%	190.3 -	223.7	8.75	- 4.0%
13.	Chromate (Furnace AA)	100	98.8	ppb	5	5.1%	88.8 -	108.8	5.5	- 9.1%
14.	Hydrogen (G.C.)	0.51	0.534	%	0.013	2.4%	0.508 -	0.560	0.02	-49.0%