U. S. NUCLEAR REGULATORY COMMISSION
REGION I

Report No. 50-213/87-29

Docket No. 50-213

License No. DPR-61 Priority -- Category C

Licensee: Connecticut Yankee Atomic Power Company
P. O. Box 270
Hartford, Connecticut 06101

Facility Name: Haddam Neck Nuclear Power Station

Inspection At: Haddam Neck, Connecticut

Inspection Conducted: November 30-December 4, 1987

Inspectors: Harvey Zibulsky 1-4-88
H. Zibulsky, Chemist date

J. C. Jang 1-4-88
J. Jang, Senior Radiation Specialist date

date

Approved by: W. J. Pasciak 1-14-88
W. J. Pasciak, Chief, Effluents date
Radiation Protection Section

Inspection Summary: Inspection on November 30-December 4, 1987 (Report No. 50-213/87-29)

Areas Inspected: Routine, announced inspection of the nonradiological chemistry program. Areas reviewed included measurement control and analytical procedure evaluations.

Results: No violations were identified.

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DETAILS

1. Individual Contacted

G. Bouchard, Station Service Superintendent
*P. Heffernan, Assistant Chemistry Supervisor
*G. Goncarovs, Chemist
S. Matthess, Chemist
*D. Miller, Jr., Station Superintendent
M. Quinn, Chemistry Supervisor

*Denotes those present at the exit interview.

The inspector also interviewed other licensee employees including members of the chemistry staff.

2. Measurement Control Evaluation

Verification of the licensee's measurement capabilities on actual plant water samples is done by splitting samples with the licensee and Brookhaven National Laboratory (BNL). The steam generator sample was taken for anion and metal analyses and the mix tank sample was taken for boron analysis. One steam generator sample was spiked with a standard solution of fluoride, chloride, and sulfate and another steam generator sample was spiked with a standard solution of iron, copper, nickel, and chromium. These standard spike solutions were prepared by BNL for the NRC. On completion of the analyses by BNL and the licensee, an evaluation will be made (Inspector Follow-up Item 50-213/87-29-01).

3. Analytical Procedures Evaluation

Standard chemical solutions were submitted to the licensee for analysis during this inspection. The standard solutions were prepared by BNL for the NRC, and were analyzed by the licensee using normal methods and equipment. The analysis of standards is used to verify the licensee's capability to monitor chemical parameters in various plant systems with respect to Technical Specification, vendor, and fuel warranty requirements. In addition, the analysis of standards is used to evaluate the licensee's analytical procedures with respect to accuracy and precision.

The results of the standard measurement comparisons indicated that one out of thirty six measurements was in disagreement under the criteria used for comparing results (see attachment 1). The results of the comparisons are listed in Table 1.

The nickel, chromium, and iron results in Table 1 are rerun analyses. The licensee's standard solutions for the three analytes, were degraded. The licensee, therefore, prepared new standard solutions to calibrate equipment. In addition, the micro-pipet which was used to aliquot the NRC standard solutions was also calibrated.

The inspectors observed that two point calibrations were being performed for the atomic absorption analyses of the metals. Nonlinearity of the calibration curves were difficult to identify. A minimum of three data points, excluding zero, for calibrations will be incorporated into the licensee's measurement program.

The fluoride disagreement at low concentration (around 5 ppb) using the ion chromatograph was due to the equipment rather than the analytical procedure. The licensee used an ion chromatograph (Waters 1LC-1 Model) to measure fluoride concentration. The "air" peak was immediately followed by the fluoride peak (the air peak partially overlapped the fluoride peak), making it difficult to separate the two peaks. Two methods, area integration and peak-height determination, can be used to measure the fluoride concentration. The licensee used the area integration method and the results were not in agreement. During the inspection, the licensee used the peak-height determination method to determine the fluoride value and the results are listed in Table 1. The licensee is going to investigate the possibility of using a different eluant concentration to separate the air peak and the fluoride peak in the near future.

One fluoride disagreement was due to calculated statistical difference. The actual difference was 7% of BNL's value which is not considered significant.

4. Exit Interview

The inspectors met with the licensee representatives (denoted in paragraph 1) at the conclusion of the inspection on December 4, 1987, and summarized the scope and findings of the inspection. At no time during this inspection was written material provided to the licensee by the inspectors.

Table 1

Capability Test Results
Haddam Neck Nuclear Power Station

Chemical Parameter	Analytical Procedure	NRC Value	Lic. Value	Ratio(Lic./NRC)	Comparison
		Results in Part Per Million (ppm)			
°Boron	Auto. Titration	1000±10	1000±1	1.0	Agreement
		3024±46	2998±2	0.99±0.02	Agreement
		4947±61	4978±3	1.01±0.01	Agreement
°Ammonia	Spectrophotometry	1.75±0.11	1.94±0.001	1.11±0.07	Agreement
		3.14±0.26	2.97±0.006	0.94±0.08	Agreement
		1.88±0.17	1.98±0.009	1.05±0.10	Agreement
		Results in parts per billion (ppb)			
°Sodium	AA-Flame	10.2±0.6	8.7±0.6	0.85±0.08	Agreement
		18.8±0.6	21.3±2.1	1.13±0.12	Agreement
		28.8±1.6	26.3±0.6	0.91±0.05	Agreement
°Copper	AA-Flame	46.8±2.8	54.0±4.0	1.15±0.11	Agreement
		96.6±4.9	97.3±1.5	1.01±0.05	Agreement
		145.0±6.0	146.7±1.2	1.01±0.07	Agreement
°Iron (Rerun)	AA-Flame	48.9±3.5	53.7±3.2	1.10±0.10	Agreement
		95.5±3.4	93.0±3.6	0.97±0.05	Agreement
		147.0±4.2	144.7±3.2	0.98±0.04	Agreement
°Nickel (Rerun)	Graphite Furnace	50.9±2.6	55.0±1.0	1.08±0.06	Agreement
		102.0±3.0	107.7±1.2	1.06±0.03	Agreement
		153.0±4.0	162.0±1.0	1.06±0.03	Agreement

°Chromium (Rerun)	Graphite Furnace	50.9±2.6	53.0±1.7	1.04±0.06	Agreement
		94.1±3.0	102.0±1.7	1.08±0.04	Agreement
		143.0±8.0	151.7±2.1	1.06±0.06	Agreement
°Hydrazine	Spectrophotometry	89.2±5.6	81.0±1.0	0.91±0.06	Agreement
		28.5±0.4	27.8±0	0.98±0.02	Agreement
		52.0±0.5	51.0±0	0.98±0.01	Agreement
°Silica	Spectrophotometry	108.6±11.2	102.7±1.2	0.95±0.10	Agreement
		218.0±14.0	211.0±1.0	0.97±0.06	Agreement
		320.0±10.0	311.0±2.0	0.97±0.03	Agreement
°Fluoride (Rerun)	Ion Chromatograph	5.8±0.1	4.9±0.2	0.84±0.04	Disagreement
		10.9±0.5	10.6±0.3	0.97±0.05	Agreement
		20.9±0.6	22.3±0.1	1.07±0.03	Statistical Disagreement
°Chloride	Ion Chromatograph	6.0±0.8	5.4±0.1	0.90±0.12	Agreement
		9.4±0.8	10.4±0.06	1.11±0.09	Agreement
		20.1±0.6	21.2±0.6	1.05±0.04	Agreement
°Sulfate	Ion Chromatograph	10.0±0.5	10.1±0.9	1.01±0.10	Agreement
		20.5±1.5	19.7±0.2	0.96±0.06	Agreement
		40.4±1.5	39.0±1.3	0.97±0.05	Agreement

ATTACHMENT 1

CRITERIA FOR COMPARING ANALYTICAL MEASUREMENTS

This attachment provides criteria for comparing results of capability tests. In these criteria the judgement limits are based on the uncertainty of the ratio of the licensee's value to the NRC value. The following steps are performed:

(1) the ratio of the licensee's value to the NRC value is computed

$$\left(\text{ratio} = \frac{\text{Licensee Value}}{\text{NRC Value}}\right);$$

(2) the uncertainty of the ratio is propagated.[1]

If the absolute value of one minus the ratio is less than or equal to twice the ratio uncertainty, the results are in agreement.

(|1-ratio| ≤ 2 uncertainty)

[1] $Z = \frac{x}{y}$, then $\frac{S_z^2}{Z^2} = \frac{S_x^2}{x^2} + \frac{S_y^2}{y^2}$

[1](From: Bevington, P. R., Data Reduction and Error Analysis for the Physical Sciences, McGraw-Hill, New York, 1969)