

U.S. NUCLEAR REGULATORY COMMISSION
REGION I

Report Nos. 50-317/88-03
50-318/88-03

Docket Nos. 50-317
50-318

License Nos. DPR-53 Priority - Category C
DPR-69

Licensee: Baltimore Gas and Electric Company
P. O. Box 1475
Baltimore, Maryland 21203

Facility Name: Calvert Cliffs Nuclear Power Plant, Units 1 and 2

Inspection At: Lusby, Maryland

Inspection Conducted: February 29 - March 4, 1988

Inspector: Lawey Zibulsky 4-7-88
H. Zibulsky, Chemist date

Approved by: W. J. Paschak 4/11/88
W. J. Paschak, Chief, Effluents Radiation date
Protection Section, FRSCB, DRSS

Inspection Summary: Inspection on February 29 - March 4, 1988 (Combined
Inspection Report Nos. 50-317/88-03 and 50-318/88-03)

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

Results: No violations were identified.

DETAILS

1. Individuals Contacted

- *J. Lemons, Manager, Nuclear Operations Department
- *P. Crinigan, General Supervisor, Chemistry
- *S. Hutson, Supervisor, Plant Chemistry
- *E. Eshelman, Analyst
- *C. Phifer, Jr., QA Auditor
- *D. Shaw, Licensing Engineer
- R. Kreger, Chemistry Technician
- J. York, Chemistry Technician
- J. Szymkowiak, Principal Chemistry Technician

*Denotes those present at the exit interview.

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

2. Analytical Procedures Evaluation

During the inspection, standard chemical solutions were submitted by the inspector to the licensee for analysis. The standard solutions were prepared by Brookhaven National Laboratory (BNL) for the NRC, and were analyzed by the licensee using normal methods and equipment. The analysis of standards is used to verify the various plant measurement systems with respect to Technical Specification and other regulatory 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 measurements comparison indicated that six out of twenty-six comparisons were in disagreement under the criteria used for comparing results (see Attachment 1). The results of the comparisons are listed in Table 1.

The silica and hydrazine disagreements were due to poor calibration and the use of an old colorimeter. The licensee was calibrating with a multi-point calibration on an old colorimeter that wasn't able to produce repeatability on the samples. The licensee had a new spectrophotometer that had to be calibrated. When the new instrument is brought into service, the old colorimeter will be retired. The copper disagreement was due to a single point calibration (see paragraph 3). The fluoride and chloride disagreements were due to sampling. A 100 lambda and a 300 lambda aliquot of the NRC standard was diluted to one liter which may have introduced error into the final analysis.

3. Measurement Control Evaluation

Verification of the licensee's measurement capabilities on actual plant water samples is done by splitting samples with the licensee and BNL. A reactor coolant sample was taken for boron analysis, and steam generator samples were taken for anion and metal analyses. 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 and copper. The 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 50-317/88-03-01 and 50-318/88-03-01).

The inspector observed that the licensee was using two commercially bought standard solutions for calibration and control. The standard solutions, however, were from the same lot number. The licensee agreed that, for independence of the two standard solutions, different lot numbers should be used. It was also suggested by the inspector that the licensee not generate a new measurement control chart every month but to extend the duration of the chart to 3 or 4 months. This will enable the licensee to observe trending.

It was demonstrated with the NRC sodium standards that single point calibrations for the Atomic Absorption (AA) or any other measurement system is unacceptable. Also, all the calibration curves generated must be statistically fit to the data points and not graphically approximated. The NRC sodium standards were analyzed by the licensee using their procedure CP908 - Determination of Sodium by Flame Emission, calibrating with a 100 ppb standard and using the readout made on the AA and a 20 ppb calibration check point. The resulting biases on the NRC standards were -20%, -10% and -26%. Using a four point calibration curve that was statistically fit, results in biases of +4%, +8% and -8% which were well within the ± 2 sigma acceptance criteria.

4. Exit Interview

The inspector met with the licensee representatives (denoted in paragraph 1) at the conclusion of the inspection on March 4, 1988, 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 ResultsCalvert Cliffs, Units 1&2

<u>Chemical Parameter</u>	<u>Analytical Procedure</u>	<u>NRC Value</u>	<u>Lic. Value</u>	<u>Ratio (Lic./NRC)</u>	<u>Comparison</u>
<u>Results in parts per billion (ppb)</u>					
Chloride	Ion Chromato- graph (IC)	8.03±1.03	7.94±0.64	0.99±0.15	Agreement
		12.47±0.40	13.19±0.84	1.06±0.08	Agreement
		8.05±0.22	8.83±0.24	1.10±0.04	Disagreement
Fluoride	IC	7.70±0.17	6.82±0.46	0.89±0.06	Agreement
		14.50±0.63	11.82±0.12	0.82±0.04	Disagreement
		8.35±0.28	8.41±0.13	1.01±0.04	Agreement
Sulfate	IC	6.67±0.30	5.74±0.70	0.86±0.11	Agreement
		13.70±0.80	12.30±0.70	0.90±0.07	Agreement
		8.08±0.30	8.22±0.30	1.02±0.05	Agreement
Silica	Colorimetry	54.3±5.60	90.0±15.0	0.60±0.12	Disagreement
		218±14	188±4	0.86±0.06	Disagreement
		160±5	163±16	1.02±0.11	Agreement
Hydrazine	Colorimetry	22.3±1.4	20.7±1.6	0.93±0.09	Agreement
		113.8±1.4	90.0±0.0	0.79±0.01	Disagreement
Sodium	AA-Flame	4.6±0.5	4.8±0.0	1.04±0.11	Agreement
		9.2±0.8	9.9±0.0	1.08±0.10	Agreement
		14.4±0.8	13.3±1.5	0.92±0.12	Agreement
Copper	AA-Graphite	4.68±0.24	3.49±0.09	0.75±0.04	Disagreement
		19.4±0.68	20.3±0.06	1.06±0.04	Agreement
		43.5±1.8	44.5±1.4	1.02±0.05	Agreement
Iron	AA-Graphite	4.89±0.35	4.15±0.9	0.85±0.19	Agreement
		19.1±0.68	19.1±1.4	1.0	Agreement
		44.1±1.26	43.1±2.3	0.98±0.06	Agreement
<u>Results in parts per million (ppm)</u>					
Boron	Titration	1000±10	1002±4	1.0	Agreement
		3024±46	2969±9	0.98±0.02	Agreement
		4947±61	4935±8	1.0	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

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

- (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.

$$(|1 - \text{ratio}| \leq 2 \text{ uncertainty})$$

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

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

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