MARTIN MARIETTA

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STATISTICAL ANALYSIS OF FLUORIMETER OPERATION

By

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MASTER

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SUMMARY

Acceptance criteria for uranium check standards used to verify fluorimeter calibration have been developed. This work was done in response to Tiger Team finding QA/BMP-5, item 4. Data used as input to these calculations is retained in the Tiger Team closeout file, located in the Technical Service Division managers office.

INTRODUCTION

Tiger Team finding QA/BMP-5, item 4 stated "Inadequate radiological measurement QA/QC practices" were being applied in reference to the fluorimeter being used by the Environmental and Industrial Hygiene Analysis Department. This instrument is used to measure uranium fluorescence in urine, water, soil/sediment, waste, air and biota samples either directly or after ion exchange separation or solvent extraction separation. The fluorimeter is a high sensitivity, reflection type instrument under which a dried sample solution residue is fused in a flux. The material is solidified in a platinum fusion dish and fluorescence due to uranium activity is measured under ultraviolet light.

The Tiger Team concern was primarily directed at implementation of QA/QC practices to verify that the fluorimeter is statistically "in control" and that interpolation between standard points does not introduce unnecessary errors; i.e., the system operates in a linear manner. Control charts have been developed for each of the uranium standards and each method of sample preparation. In addition to verification of data within control limits, calculation of correlation coefficients will be required to determine if the fluorimeter meets accepted statistical standards for linearity.

DISCUSSION

X-bar and range charts have been developed for water, urine and extraction standard samples and are presented as Appendix A. These charts show that the fluorimeter is statistically in control, however, there does appear to be a bias in each case on the high end of the operating range. Based on the calculations made for the charts, the following control limits have been established for extractions, urine and water.

Table 1
Control Limits for Extraction

Standard (ngU)	Control Limits		Calculated
	Lower	Upper	Mean
1.0	0.746	1.24	0.993
2.0	1.65	2.24	1.94
100	87.7	114	101
200	182	227	205
400	369	423	396
800	695	828	761

Table 2
Control Limits for Urine

Standard (ngU)	Control Limits		Calculated
	Lower	Upper	Mean
0.5	0.262	0.631	0.447
1.0	0.712	1.28	0.997
2.0	1.58	2.30	1.94
4.0	3.40	4.53	3.96
8.0	7.08	8.52	7.80

Table 3
Control Limits for Water

Standard (ngU)	Control Limits		Calculated
	Lower	Upper	Mean
0.5	0.290	0.661	0.476
40	35.1	45.8	40.4
200	167	226	197
800	716	931	823

A minimum statistically adequate sample size of 30 randomly sampled data pairs has been used in each case with the exception of the 400 ngU and 800 ngU standards in the extraction data.

Until enough data has been gathered to develop the control charts for these cases, control limits of $\pm 20\%$ of the standard value should be used. These charts have been developed using a 99% confidence interval. As a result, only one measurement of a sample standard may fall outside the control limits. A second measurement outside of the control limits is indicative of instrument malfunction.

Following verification of fluorimeter control, a regression analysis is required to verify instrument linearity. The minimum

required correlation coefficient (also at a 99% confidence level) can be determined from the following table.^{1,2}

Table 4
Minimum Correlation Coefficients

<u>Number of Points</u>	<u>Constituents</u>	<u>Correlation Coefficient</u>
8	3 Standards and Blank	0.798
10	4 Standards and Blank	0.735
12	5 Standards and Blank	0.684
14	6 Standards and Blank	0.641

The control limits which have been established require that duplicate analyses be made on all standards and blanks.

CONCLUSIONS

X-bar and range charts have been developed for fluorimeter operation. These charts show that the instrument is statistically "in control". An apparent bias in high end operation has been detected in each mode of operation.

Not enough data is available to develop statistically meaningful control charts for the 400 ngU and 800 ngU extractions.

RECOMMENDATIONS

1. The control limits which have been established in this document should be used to determine the functionality of the fluorimeter.
2. Only one analysis on a standard sample may fall outside the established control limits. If a second sample is beyond the limits, it is indicative of instrument malfunction.
3. A regression analysis should be made each time new standard samples are analyzed. The minimum acceptable correlation coefficient (as a function of the number of standards) is presented in Table 4.
4. New control charts should be developed for 400 ngU and 800 ngU extractions when enough data is available. Until that time, the control limit should be assumed to be +/- 20% of the standard sample value.

REFERENCES

1. Snedecor, George W., *Statistical Methods*, The Iowa State College Press, Ames, Iowa, 1946.
2. Fisher, Ronald A., *Statistical Methods for Research Workers*, Hafner Publishing Company Inc., New York, 1950.
3. Holscher, Harry H., *Simplified Statistical Analysis*, Cahnerns Books, Boston, Massachusetts, 1971.

APPENDIX A
CONTROL CHARTS FOR EXTRACTIONS, URINE AND WATER

**X-Bar Chart for Fluorimeter
Extraction - 1 ngU Standard**

**Range Chart for Fluorimeter
Extraction - 1 ngU Standard**

**X-Bar Chart for Fluorimeter
Extraction - 2 ngU Standard**

**Range Chart for Fluorimeter
Extraction - 2 ngU Standard**

**X-Bar Chart for Fluorimeter
Extraction - 100 ngU Standard**

**Range Chart for Fluorimeter
Extraction - 100 ngU Standard**

**X-Bar Chart for Fluorimeter
Extraction - 200 ngU Standard**

**Range Chart for Fluorimeter
Extraction - 200 ngU Standard**

**X-Bar Chart for Fluorimeter
Extraction - 400 ngU Standard**

**Range Chart for Fluorimeter
Extraction - 400 ngU Standard**

**X-Bar Chart for Fluorimeter
Extraction - 800 ngU Standard**

**Range Chart for Fluorimeter
Extraction - 800 ngU Standard**

**X-Bar Chart for Fluorimeter
Urine -- 0.5 ngU Standard**

**Range Chart for Fluorimeter
Urine -- 0.5 ngU Standard**

**X-Bar Chart for Fluorimeter
Urine -- 1 ngU Standard**

**Range Chart for Fluorimeter
Urine -- 1 ngU Standard**

**X-Bar Chart for Fluorimeter
Urine -- 2 ngU Standard**

**Range Chart for Fluorimeter
Urine -- 2 ngU Standard**

**X-Bar Chart for Fluorimeter
Urine -- 4 ngU Standard**

**Range Chart for Fluorimeter
Urine -- 4 ngU Standard**

**X-Bar Chart for Fluorimeter
Urine -- 8 ngU Standard**

**Range Chart for Fluorimeter
Urine -- 8 ngU Standard**

**X-Bar Chart for Fluorimeter
Water -- 0.5 ngU Standard**

**Range Chart for Fluorimeter
Water -- 0.5 ngU Standard**

**X-Bar Chart for Fluorimeter
Water -- 40 ngU Standard**

**Range Chart for Fluorimeter
Water -- 40 ngU Standard**

**X-Bar Chart for Fluorimeter
Water -- 200 ngU Standard**

**Range Chart for Fluorimeter
Water -- 200 ngU Standard**

**X-Bar Chart for Fluorimeter
Water -- 800 ngU Standard**

**Range Chart for Fluorimeter
Water -- 800 ngU Standard**

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