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QUALITY ASSURANCE PLAN FOR MIXED OXIDE FUEL FOR LMFBR

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ABSTRACT

An evaluation of the adequacy of the methods of analysis is presented for chemical specifications of LMFBR/FFTF mixed uranium-plutonium oxide fuel. This evaluation is based on statistical analyses of the results obtained by seven laboratories on a distributed batch of FFTF fuel pellets and distributed special blends of certain impurities and a high purity uranium-plutonium oxide matrix. Based upon the results of this evaluation a quality assurance program will be discussed which will ensure the continuing existence of quality data for the chemical characterization of LMFBR/FFTF mixed oxide fuels.

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INTRODUCTION

Early in 1968 a joint project was undertaken by the Los Alamos Scientific Laboratory (LASL) and the Pacific Northwest Laboratories (PNL) for the Fuels and Materials Branch, Division of Reactor Development and Technology, USAEC. This project had, and still has, as its major objective the production of quality data for the characterization of LMFBR/FFTF fuel. The desired analyses to be made on this fuel are as follows:

a. Pu and U assay
b. Isotopic (Pu and U)
c. Oxygen/metal ratio
d. Spectrographic for impurities
e. Total gas content
f. Halogen content
g. Carbon and Nitrogen
h. Density
i. H_2O
j. Homogeneity and solid solution

In order to implement this project, LASL assumed the responsibility of planning the analytical program, evaluating the data and furnishing guidance to fuel producers. A close working relationship was established between LASL and PNL in order to get this project underway. Early in the program certain goals and objectives were formulated as being necessary for this program.

A major factor in the production of high-quality, well-characterized LMFBR/FFTF fuel is technical competence of a high degree for doing the required chemical analyses and other measurements as required by LMFBR/FFTF fuel specifications. To ensure this caliber of competence, the analytical and quality assurance program will have the following objectives:

1. To evaluate the capabilities of potential fuel producers for making the analytical measurements on LMFBR/FFTF fuel which are necessary to ensure the uniformly high quality fuel required by the LMFBR/FFTF Program.

2. To provide technical guidance, as may be required, to ensure that these capabilities are established at the level required by LMFBR/FFTF fuel specifications.

3. To establish and conduct a quality assurance program that will ensure contin-

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DISCLAIMER

uing competence of fuel producers for the analysis of LMFBR/FFTF fuel at the level required by fuel specifications.

Objective No. 1, as stated above, was considered the short-term goal of this program. In order to implement this program, material consisting of sintered pellets, whose composition was approximately 80% UO_2 and 20% PuO_2 was distributed to eight participating organizations for analyses. This program was intended to establish the extent of the analytical capabilities of potential fuel suppliers for making the measurements as outlined in the introduction.

EVALUATION OF OBJECTIVE No. 1

Lack of extensively-characterized materials suitable for all of the analyses and measurements requested, and lack of common standards against which some of the analytical methods could be calibrated, limited the amount of information that was obtained from the work done. Nevertheless, it was possible to obtain a picture of the capabilities and limitations of existing methods, and to some extent the capabilities of participating laboratories to use them. Problem areas were clearly indicated with respect to the needs for,

(1) common standards with which to calibrate certain existing methods

(2) standardization of certain methods

(3) modifying existing methods, or developing new methods, for some measurements

(4) certain laboratories to expand their facilities

(5) certain laboratories to change some of their methods.

A trip was made to each of the participating organizations to discuss the results on the analyses of the above material. One of the things that came out as a result of these discussions was that no well-defined quality control programs were in evidence for continual calibration of methods. As a follow-up of this first evaluation, a designed "round robin" was constructed with definite recommendations regarding: (a) sample preparation where special care is to be exercised, (b) specific methods where needed for better precision, and (c) modifications in some methods where improvements would obviously result. Also, the "round robin" was designed to make the data amenable to statistical analysis. As an example, the following instructions were supplied to each of the analytical laboratories for the Uranium Assay: "Five sintered pellets are to be dissolved as received, each in a separate solution. One measurement for uranium is to be made on each of four aliquots from each of these five solutions. Report each measurement made unless you have valid reasons for not doing so. Standardizations of solutions and/or calibrations of equipment must be made using NBS Primary U_3O_8 Standard No. 950. If a controlled potential coulometric method is used, which is highly recommended, do not use an electrical calibration." Similar instructions were used for the other items to be measured. This set of data was termed Phase II of the project.

EVALUATION OF PHASE II DATA

The two major objectives of the statistical evaluation of the Phase II data were (1) to obtain estimates of the precisions of the methods of analyses used by each participating laboratory and (2) to determine how closely the results of the laboratories agreed with each other. From this information, those analytical methods or laboratories needing further improvement could be ascertained. The data was analyzed using the following model:

$$y_{ijk} = \mu + \zeta_i + \lambda_{j(i)} + e_{ijk} \quad ,$$

where

y_{ijk} is the result on the k-th replicate measurement on the j-th sample in the i-th laboratory,

μ is assumed to be constant which is the true value of the component being measured.

ζ_i, i = 1, 2, ..., k represents the effects associated with the i-th laboratory,

$\lambda_{j(i)}$, j = 1, 2, ..., r_i is the effect due to samples within laboratories and r_i is the number of samples analyzed by the i-th laboratory,

e_{ijk}, k = 1, ..., $s_{j(i)}$ is assumed to be a random variable with mean zero and variance σ^2 and $s_{j(i)}$ is the number of measurements made on the j-th sample within the i-th laboratory. This model is usually referred to as the nested analysis of variance model.

TABLE I

GENERAL ANALYSIS OF VARIANCE (AOV)
TWO NESTED CLASSIFICATIONS WITH REPLICATIONS

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Expected Value of Mean Square
Between Laboratories	$S_i = sr\sum_i (\bar{y}_i - \bar{y})^2$	p - 1	$MS_1 = \frac{S_i}{p-1}$	$\sigma^2 + s\sigma_\lambda^2 + sr\sigma_\zeta^2$
Between Pellets Within Laboratories	$S_{j(i)} = r\sum_{ij}(\bar{y}_{ij} - \bar{y}_i)^2$	p(r - 1)	$MS_2 = \frac{S_{j(i)}}{p(r-1)}$	$\sigma^2 + s\sigma_\lambda^2$
Within Pellets (Analytical Method Measurement Variability)	$S_{k(ij)} = \sum_{ijk}(y_{ijk} - \bar{y}_{ij})^2$	pr(s - 1)	$MS_3 = \frac{S_{k(ij)}}{pr(s-1)}$	σ^2

TABLE II RAW DATA RESULTS FOR PLUTONIUM ASSAY

Lab.	Weight Percent Plutonium in Pellets					Lab.	Weight Percent Plutonium in Pellets				
A	22.13	22.16	22.08	22.22	22.21	R	22.06	22.17	22.09	22.16	22.01
	22.15	22.20	22.08	22.22	22.17		22.08	22.18	22.08	22.08	22.02
	22.16	22.17	22.12	22.20	22.17		22.06	22.15	22.05	22.15	21.97
	22.16	22.17	22.08	22.24	22.18		22.03	22.23	22.01	22.11	22.04
B	22.11	22.16	22.17	22.14	22.17	X	22.18	22.10	21.96	22.10	22.02
	22.13	22.15	22.14	22.13	22.12		22.25	22.15	22.04	22.12	22.01
	22.12	22.15	22.14	22.13	22.13		22.24	22.21	22.08	22.12	22.05
	22.12	22.16	22.12	22.14	22.12		22.26	22.18	22.09	22.09	22.07
C	21.97	22.12	22.35	22.25	22.20	Y	22.01	21.93	21.92	22.04	22.03
	21.95	22.12	22.28	22.36	22.13		22.04	22.04	21.91	22.02	22.06
	21.94	22.11	22.35	22.30	22.19		22.03	22.06	22.03	22.02	22.05
	21.89	22.17	22.28	22.19	[a]		22.11	22.03	21.94	22.04	22.03
K	22.08	22.14	22.10	22.11	22.03						
	22.08	22.16	22.10	22.11	22.03						
	22.04	22.08	22.03	22.08	22.06						
	22.04	22.08	22.03	22.08	22.06						

[a] Only three results reported

TABLE III STATISTICAL SUMMARY OF RESULTS FOR PLUTONIUM ASSAY

Laboratory	Avg Wt % Pu in Pellets	Analytical Measurement Standard Deviation, Abs %	Between Pellet Standard Deviation, Abs%
A	22.163	0.017	0.047
B	22.138	0.015	0.010
C	22.166	0.046	0.150
K	22.076	0.030	0.024
R	22.087	0.032	0.066
X	22.116	0.040	0.080
Y	22.016	0.042	0.032
Pooled Data[a]	22.124	0.032	0.077

[a]The data from laboratory Y were excluded in calculating the pooled values.

TABLE IV AOV FOR PLUTONIUM ASSAY RESULTS

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Expected Value of Mean Square
Between Laboratories	0.34273	6	0.05712	$\sigma^2 + 3.9773\ \sigma_\lambda^2 + 19.856\ \sigma_\zeta^2$
Between Pellets Within Laboratories	0.60842	28	0.02173	$\sigma^2 + 3.9699\ \sigma_\lambda^2$
Within Pellets Analytical Method Measurement Variability	0.11617	104	0.00112	σ^2

The ratio MS_1/MS_2 (.05712/.02173) is 2.62. This is greater than the tabulated value of 2.46 for 6 and 28 degrees of freedom at the .05 significance level. Fisher's least significant difference (LSD) test was then used to determine if there was a grouping of the laboratories. The results of this test are as follows:

Laboratory	C	A	B	X	R	K	V
Pu Assay Average	22.166	22.163	22.138	22.116	22.087	22.076	22.016

For the Pu assay we see that we have good agreement among the laboratories. This was not true for all measurements as demonstrated by the following set of data.

TABLE V RESULTS FOR CHLORINE AND FLUORINE ON LASL BLENDED MATERIAL

Laboratory	PPM Chlorine				PPM Fluorine			
A		24	25	24	7.2	7.8	7.0	
B		9	10	12	13	14	15	
C		19	11	11	6	4	7	
K		141	119	154	< 10	< 10	< 10	
R		8	8	10	13	13	12	
X	11.7	11.2	14.9	13.9	13.7	15.3	15.4	16.2
Y		219	599	200	13	19	13	

TABLE VI STATISTICAL SUMMARY OF RESULTS FOR CHLORINE AND FLUORINE ON LASL BLENDED MATERIAL

	PPM Chlorine		PPM Fluorine	
Laboratory	Average	Standard Deviation	Average	Standard Deviation
A	24.3	0.58	7.3	0.42
B	10.8	1.53	14.0	1.00
C	13.7	4.61	5.7	1.53
K	138	17.6	< 10	[b]
R	8.7	1.16	12.7	0.58
X	12.9	1.76	15.1	1.05
Y	339	225	15.0	3.46
Pooled Data[a]	14.1	2.40	11.6	1.68

[a] The data from laboratories K and Y were excluded when calculating the pooled data for chlorine and the data from laboratory K were excluded when calculating the pooled data for fluorine.

[b] Not statistically estimable.

The results for all the measurements of Phase II are given in reference (1). The conclusions from the evaluation of the Phase II data are as follows: (1) It provided an understanding of the capabilities and limitations of the analytical methods used by the participating laboratories for the chemical characterization of LMFBR-type fuels as required by the specification. (2) It provided an improved evaluation of the qualifications and capabilities of potential fuel producers to maintain adequate specification control by competent chemical analysis. (3) It provided useful estimates of the analytical measurement errors and the between-pellet variabilities that can be expected for most of the chemical specifications for mixed oxide fuels. (4) It showed that close control will be required of the sampling and analytical methods used by the fuel producers in order to ensure complete and adequate characterization of the high quality fuel necessary for the LMFBR program.

Based upon the results of this evaluation, recommendations were made for the qualification and control of analytical laboratories for mixed oxide fuel analysis.

QUALIFICATION AND CONTROL OF ANALYTICAL CHEMISTRY LABORATORIES

An essential part of a fuel production process is an overall quality assurance program that is designed to ensure that the fuel meets all specifications. Analytical laboratories need to establish their technical competence to do the chemical analyses required for the characterization of fuel. Also a quality control program for the continual evaluation of analytical data obtained during periods of fuel production needed to be established. In order to ensure that quality data would be obtained, certain minimum standards were recommended for the analytical laboratories involved in fuel production:

(1) Laboratory Qualification Program. The qualification of an analytical laboratory shall be based on its demonstrated competence to do the specifications analyses of the uranium dioxide powder or uranylnitrate, uranium dioxide pellets, plutonium dioxide or plutonium nitrate, and mixed oxide powder and pellets. This competence shall consist of:

(a) The satisfactory use of approved methods which have accuracies and precisions adequate for the specification requirements. Methods which have been demonstrated to have adequate precisions and accuracies may be obtained from the purchaser. If other

methods are proposed for use, the descriptions of such methods must include sufficient information to demonstrate that their accuracies and precisions are equal to or better than those recommended by the purchasee.

(b) The use of specified materials for the calibration of methods. When available, NBS Standard Reference Materials are to be used. For all other cases, calibration materials prepared by an independent laboratory and available from the purchaser are to be used.

(c) The satisfactory analysis of test standards for all chemical specifications prior to the start of fuel analysis and after any period of 90 days or more during which purchaser-provided quality control standards are not analyzed.

(2) Quality Control Program. This program provides the information required for the continual evaluation of the reliability of the analytical measurements of those laboratories involved in the fuel production. Calibration materials and quality control standards shall be provided to the supplier laboratory via the purchaser. The analytical data resulting from the analysis of quality control standards shall be provided to the purchaser on a continuing basis. Quality control standards shall be analyzed at a rate of one standard per 8-hour working shift for each analysis set up during the shift. Any variation from this rate is stated in the particular section that describes the specification analysis. If the analytical result for a quality control standard should indicate that a method is not in control, a second standard shall be analyzed. If the result for this second standard again indicates that the method is not in control, the laboratory shall take measures to bring the method back in control. No material shall be accepted while the method is out of control. Proof that adequate control of the method has been re-established shall be based on satisfactory analyses of additional quality control standards.

Provisions for reduced use of quality control standards have been made. Also, numbers of samples to be analyzed for qualification purposes, individual specification analysis, etc., were all considered in detail. Neither time nor space permits including these in this paper.

ACCEPTANCE SAMPLING

In the preceding discussion we have emphasized the controls that will be used to assure the purchaser that quality data is being generated to support the characterization of the fuel elements. To be reasonably certain that the specifications are being met on the final product, acceptance sampling plans will be used. It is anticipated that variable sampling plans as given in MIL-STD-414 will be the main plans used. The tables of Variable Sampling Plans [4] give the criterion for an acceptable lot as $\bar{x} + ks \leq U$ where $\bar{x}$ is the measured mean concentration found in the fuel elements selected at random from a lot, s is the measured standard deviation, k is a constant dependent upon the sample size and U is the upper specification limit. The following table illustrates the varying sample size the supplier would need to take, depending upon the mean concentration and the precision and accuracy of the measurement method, in order that a high percentage of his product would be accepted.

TABLE VII VARIABLE SAMPLING PLAN FOR CHLORIDE*

Specification	Lot conc.	product std. dev.	analytical std. dev.	std. dev. product + analytical	% in Lot meeting spec.	k	sample size
≤ 20	10	4	4.8	6.3	94.42	1.419	180
	10	4	2.4	4.7	98.35	1.665	29
	6	8	2.4	8.4	95.20	1.452	120
	6	4	4.8	6.3	98.72	1.712	24
	6	4	2.4	4.7	99.86	2.066	10

*LTPD = .10

It is obvious from the above table that a knowledge of the precision, accuracy, and mean concentration will be a big factor in determining the sample size which in turn will determine the cost of the sampling plan. These are factors that the supplier will need to take into consideration in determining where effort should be allocated to reduce the production costs.

SUMMARY

Currently the quality assurance and quality control programs as outlined above are in effect at the plants involved in the production of LMFBR/FFTF fuels. Calibration materials and quality control standards have been distributed. For a few measurements, such as the oxygen/metal ratio determination, no standards or calibration materials are readily available. For this determination a well defined procedure for making this measurement is being used. The personnel who have been instrumental in initiating this program feel very confident that if this plan is adhered to, that quality data will be produced for the LMFBR/FFTF fuel program.

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